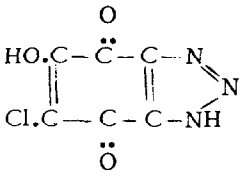
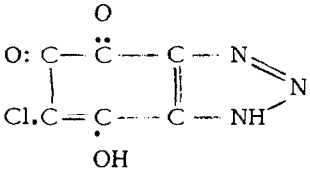
-quinone; or 6(or 5)-Chloro-7(or 4)-hydroxy -benzotriazole-4,5(or 6,7)-quinone,



or



mw 203.56, N 20.64%; yel, lustrous rhmb crysts, contg AcOH(from AcOH), mp detonates at 230 -31°; sol in w, alc, AcOH & acet; sl sol in eth, benz or benzine; was prepd by heating 6-chloro -5-hydroxy-benzotriazolo-4,7-quinone-7-aniline with alc HCl and treating the resulting product with boiling water (Ref 1, p 272; Ref 2, p 305)

This compd also forms salts & addn compds which are, themselves, unstable on heating. Other expl derivs prepd by Zincke et al(Ref 2) include:

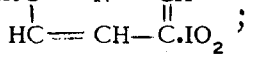
6,7-(or 4,5)-Dichloro-benzotriazole-4,5, (or 6,7)-quinone, $C_6HCl_2N_3O_2$, red ndls (from AcOH), mp blackens when heated & detonating above 260° (Ref 1,p 234; Ref 2, p 300); and

6,6,7 (or 4,5,5)-Trichloro-4,5 (or 6,7)-dioxo -4,5,6,7-tetrahydro-benzotriazole; or 6,6,7 (or 4,5,5)-Trichloro-4 (or 7)-hydroxy-5 (or 6) -oxo-5,6-dihydro-benzotriazole, $C_6H_2Cl_3N_3O_2$ $+H_2O$, col pltlts (from eth + benz), mp begins to decomp at 130° and explodes above 260° (Ref 1, p 234; Ref 2, p 296)

Refs: 1)Beil **26,** 234 & 272 2)T.Zincke et al, Ann **311,** 296, 300 & 305(1900); JCS **78** I, 524-25(1900)

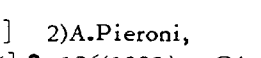
2-Chloro-3-hydroxy-1-methyl 4-isopropyl-benzene -6-diazoniumchloride, $HO.C_6H.Cl(CH_3)[CH-(CH_3)_2].N(\dot{:}N).Cl$; mw 249.12, N 10.99%; col ndls (from eth-alc), mp explodes on heating; was prepd by treating a cold alc soln of 2-chloro-6 -amino-3-hydroxy-1-methyl-4-isopropylbenzene with nitrous acid(Refs 1 & 2)

Refs: 1)Beil **16,** 533 2)M.Andresen, JPrakt-Chem **23,** 180(1881)

6-Chloro-3-iodoxy-pyridine(called 6-Chlor-3 -*jodo-pyridin* in Ger),  ;

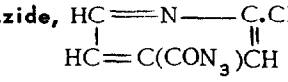
mw 281.43, N 4.98%; col crysts, mp explodes at 205°; was obtd by treating 6-chloro-pyridyl-3-iododichloride with pyridine & water (Refs 1 & 2)

Refs: 1)Beil **20,** [154] 2)A.Pieroni, AttiAccadLinceiRend [6] **2,** 126(1925) & CA **20,** 764(1926)

6-Chloro-3-iodoso-pyridine(called 6-Chlor-3 -jodoso-pyridin in Ger),  ;

mw 265.43, N 5.28%. Its Chloride salt, $ClNC_5H_3.ICl_2$, called *6-Chloro-pyridyl-3 -iodochloride,* yel crysts, mp 104-6°(dec) (Ref 3) & 115°(dec)(Ref 2); was prepd by reacting Cl with 6-Chloro-3-iodopyridine in chlf(Ref 1)

Refs: 1)Beil **20,** [154] 2)C.Rath, GerP 468302(1924) & CA **23,** 612(1929) 3)A. Pieroni, AttiAccadLinceiRend [6] **2,** 126(1925) & CA **20,** 764(1926)

2-Chloro-isonicotinoyl Azide, 

mw 182.57, N 30.69%; wh ndls, mp 46-7°; sublimes in vacuo at 40°; sol in ether; was prepd by treating 2-chloro-isonicotinoyl hydrazide with Na nitrite in w, as described in Ref 2. Its expl props were not detd

Refs: 1)Beil - not found 2)J.Bäumler et al, Helv **34,** 497 & 500(1951); CA **45,** 7572 (1951)

Note: See also 4-Chloro-picolinyl Azide

Chloromethane and Derivatives

Chloromethane or Methyl Chloride(called Chlormethan or Methylchlorid in Ger), $CH_3.Cl$; mw 50.49; col gas, fr p -97.7°, bp -23.7, flash p below 32°, d 0.918 at 20°; vap d 1.78; MAC 100ppm or 209 mg/m³ of air; explosive range 8.1-17.2%. It has very sl irritant props and may be inhaled without discomfort. Its narcotic action is somewhat weaker than that of chloroform (qv)(Refs 1,2 &3). Other props & methods of prepn are given in Refs 1 & 2

Refs: 1)Beil **1,** 59, (8), [11] & {36}

2)Kirk & Othmer **3**(1949), 738 3)Sax(1957), 887

Nitrosochloromethane, ON.CH_2.Cl; mw 79.49, N 17.62%; lt yel crysts(bimolecular in soln, monomolecular when melted), possessing a sharp lacrimatory & irritating smell, mp ca 62°(with blue coloration) & decomp vigorously at 65-66°; sol in org solvs; insol in w or cold NaOH; can be prepd from trimolecular formaldoxime, $(H_2C{:}NOH)_3$, but better from formaldehydeoxime-hydrochloride by reaction with nitrosyl chloride in ether under cooling (Refs 1 & 2)

Refs: 1)Beil **1**, [39] 2)H.Rheinboldt & M.Dewald, Ann **451**, 275(1927) & CA **21**, 1107(1927)

Mononitrochloromethane, $O_2N.CH_2Cl$; mw mw 95.49, N 14.67%.oil, bp 122-23°, d 1.4766 at 15°; sol in 20ps w; mod sol in KOH; can be prepd from Na salt of nitromethane and chlorine water(Ref 2), or by other methods(Ref 1)

Refs: 1)Beil **1**, 76, [41] & {112} 2)J.Tscherniak, Ber **8**, 608(1875)

Dinitrochloromethane, $(O_2N)_2CH.Cl$; mw 140.49, N 19.94%. This compd is known only in the form of its salts & other derivs, some of which are expl:

Potassium Salt, $(O_2N)_2C.K(Cl)$; mw 178.58, N 15.69%; lt yel prisms (from w), mp explodes 83-85°; readily sol in warm w; sl sol in cold w or alc; was prepd by action of alc KOH on dinitrodichloromethane(Ref 1,p [44]; Ref 3)

Silver Salt, $(O_2N)_2C.Ag(Cl)$; mw 247.35, N 11.33%; yel ndls, mp explods 80-81°; insol in w; was prepd by mixing the K salt with $AgNO_3$(Ref 1,p [44]; Ref 3)

Dinitrochlorobromomethane, $(O_2N)_2C.Br(Cl)$; mw 219.39, N 12.77%; col to yel pungent oil, fr p 9.2-9.3°, bp 75-76° at 15 mm, dec on heating at atm pressure, d 2.0394 at 20°, n_D 1.4739 at 20°; mod sol in alc; was prepd by passing chlorine thru an aq soln of K dinitrobromomethane(Ref 1,p 78; Ref 2); or by passing chlorine into equal wts of K dinitrobromomethane & Na acetate(Ref 1,p [44]; Ref 3); or by passing chlorine into an ice-cold aq soln of Amm dinitrobromomethane(Ref 1,p {115}; Ref 4). Alcoholic KOH reacts with dinitrochlorobromomethane to form a yel salt which, when crystd from w, exploded at 147°. This salt possessed a K content intermediate between those of K chloro- & K bromo-dinitromethanes(Refs 2 & 4)

Dinitrochloroiodomethane, $(O_2N)_2C.I(Cl)$; mw 2.66.38, N 10.52%; col oil, having characteristic odor of halogenonitroparaffins, slowly becomes reddish-brn on standing, dec on heating, d 2.1424 at 12°; was prepd by passing chlorine into an ice-cold aq soln of dinitroiodomethane & Na acetate. Alcoholic KOH converts this compd into a mixt of expl salts, K chloro- & K iododinitromethane(Ref 1,p [45]; Ref 3)

Refs: 1)Beil **1**, 78, [44 & 45] & {115} 2)S.N.Losanitsch, Ber **17**, 848(1884) & JCS **46** II, 1107(1884) 3)R.Gotts & L. Hunter, JCS **125**, 447(1924) & CA **18**, 1270(1924) 4)F.C.Schmidt et al, JOC **9**, 421(1944) & CA **39**, 275(1945)

Trinitrochloromethane, $(O_2N)_3C.Cl$; mw 185.49, N 22.66%; yel liq, fr p 4.0-4.5°, bp 51.5 - 52.0 at 30mm, explodes on heating at atm pressure, d 1.6616 at 19°, n_D 1.4560 at 14.9°; v sol in w; sol in most org solvents; can be prepd by several methods such as by treating K trinitromethane with chlorine in ice-cold ether(Ref 1) or in w (Ref 3) or by adding acetone to a mixt of fuming nitric acid and NaCl(Ref 4)

Refs: 1)Beil **1**, [46] & {116} 2)E.Schmidt et al, Ber **54**, 1483(1921) 3)A.K.Macbeth & D.D.Pratt, JCS **119**, 354-55(1921) 4)W.J. Boyd, JCSI **44**, 222T(1925)

Note: See also Chloroform and Derivatives

Chloromethoxy-picric Acid. See Trinitrochlorohydroxyanisole under Chlorohydroxyanisole

Chloromethylacetylene or 1-Chloro-1-propyne, $CH_3C{:}C.Cl$. It was obtd in small quantity, mixed with ethyl bromide, by interaction of p-toluenesulfonyl chloride with methylacetylene -magnesium bromide in dibutyl ether. It was not purified. The pure compd, bp 32.8-33°, n_D 1.4131 at 20°, was prepd by dehydrohalogenation of cis -1,2-dichloro-1-propene or by chlorination of 1 -propyne (Ref 3)

Refs: 1)Beil **1**, {922} 2)F.F.Cleveland & M.J.Murray, JChemPhys **11**, 451-52(1943)

3) A. T. Morse & L. C. Leitch, Can J Chem **32**, 503 (1954)

21) P.E. Stewart & W.A. Bonner, AnalChem **22**, 793 (1950) 22) L. Médard, MP **33**, 132 (1951) & CA **47**, 5683g (1953) 23) T.L. Cottrell et al, TrFaradSoc **47**, 584 (1951) 24) S.C. Johansson, USP 2532407 & CA **45**, 1006a (1951) 25) L.D. Horsley, "Tables of Azeotropes and Nonazeotropes" in "Azeotropic Data", Advances in Chemistry Series No 6, ACS (1952) 26) J. Decompe, BullFr **1953**, 1038 & CA **48**, 2568b (1954) 27) S.M. Kaye & S.N. Chinai, "The Development of a Method of Determination of the HMX Content of RDX by Differential Refractometry", PATR **2016** (March 1954) 28) F. Klages & J. Dasch, Ber **88**, 379 (1955) 29) G.C. Petukhov, SbornikStatei-ObshchKhim **2**, 989 (1953) & CA **49**, 6858g (1955) 30) H. Maisner, USP 2712989 & CA **49**, 2736 (1955) 31) G. Nahmani & Y. Manheimer, JChemPhys **24**, 1074 (1956) 32) E.E. Toops, JPhChem **60**, 304 (1956) 33) A. Makovy & L. Lenji, ChemRev **58**, 638 (1958) 34) ICC Doc 3666, ExParte MC 13 (Sept 10, 1958) 35) J.G. Tschinkel & C.R. Morrison, JChemEngData **3**, 350 (1958) 36) W.R. Tomlinson & O.E. Sheffield, "Properties of Explosives of Military Interest", PATR **1740** Rev 1 (1 April 1958), p 265 37) I.R. Cohen & A.P. Altshuller, AnalChem **31**, 1638 (1959) 38) A. Wehrli & E. Kovàts, Helv **42**, 2709 (1959) & CA **54**, 12722f (1959) 39) E.S. Starkman, IEC **51**, 1477 (1959) 40) Houben **1/2** (1959), p 845 41) A. Balasubramanian & C.N.R. Rao, Chem&Ind **1960**, 1025 & CA **55**, 1413c (1961) 42) J.R. Cavanaugh & B.P. Dailey, JChemPhys **34**, 1099 (1961) 43) H. Feuer & R. Harmetz, JOC **26**, 388 (1961) 44) J. d'Ans & H. Gold, GerP 1099537 & CA **55**, 27005b (1961) 45) C. Caldo, ChimeInd(Milan) **44**, 258 (1962) & CA **60**, 11893b (1964) 46) H. Feuer, ed, "Nitroparaffins", ProcSymposium, 25-6 May 1961; Publ as Tetrahedron **19**, suppl 1 (1963) 47) Sax (1963), p 970 48) Urbański **1** (1964), p 581 49) V.G. Subbotin, GigSanit **32**, 9 (1967) & CA **67**, 120062b (1967) 50) Merck (1968), pp 740 & 1193 51) Houben **10/1** (1971) 52) "Combustible Solids, Dusts, & Explosives", National Fire Codes, Vol **3** (NFPA 1971–2), pp 49–167 53) G.C. Cox & T.N. Liggett, USP 3671515 (1972) & CA **77**, 64228c (1972) 54) F. Helm et al, "The Development and Manufacture of a Gelled Nitromethane Explosive for Project ESSEX", **UCRL-51536**, Contr IACRO EERL-E-85-72-7006 (10 Oct 1974) 55) M. Heusinkveld et al, "Controlled Blasting Calculations with the TENSOR74 Code", **UCRL-51740** (24 Feb 1975)

NITRO HALOGEN DERIVATIVES OF METHANE

Fluoronitromethane. FCH_2NO_2, mw 79.04, N 17.73%; OB to CO_2 −20.24%; a colorl liq, bp at 125–30mm, 57–62°; CA Registry No 21824-09-9. It has been prepd by the hydrolysis of diethyl fluoronitromalonate, followed by decarboxylation, yield 5–32%, yields are erratic. IR peaks are at 6.27, 7.27, 7.37 and 8.8μ. It is stable only at 0–5°

Refs: 1) Beil – not found 2) J.P. Lorand et al, JOC **34**, 4176 (1969)

Difluoronitromethane. F_2CHNO_2, mw 97.03, N 14.44%; OB to CO_2 −8.24%; a volatile liq, bp 43–3.5°; d at 20°, 1.4600g/cc; RI at 20°, 1.3175 (Ref 5); CA Registry No 1493-05-6

It has been prepd by the reaction of Ag nitrite with difluoroiodomethane (Ref 2); by the decarboxylation of difluoronitroacetic acid with anhyd K fluoride (Ref 3), or anhyd K carbonate, yield 46% (Ref 5); or by heating 1,1-difluoro-4-methyl-1-nitro-2-trifluoromethyl-4-penten-2-ol to 100° with a trace of K hydroxide, yield 82% (Ref 4)

Refs: 1) Beil **1**, {112} 2) O. Ruff, Ber **69**, 299 (1936) 3) Yu.L. Kruglyak et al, USSRP 159821 (1964) & CA **60**, 11897b (1964); 4) N.P. Gambaryan et al, IzvestAkadNSerKhim **1965**, 1466 & CA **63**, 6202h (1965) 5) A.V. Fokin et al, ZhObshchKhim **36**, 540 (1966) & CA **65**, 613b (1966)

Trifluoronitromethane. (Fluoropicrin) F_3CNO_2, mw 115.02, N 12.18%; a colorl gas, bp −21° (Ref 3); CA Registry No 335-02-4

It was first prepd in low yield by the action of Cl trifluoride on bromodifluoronitrosomethane and by the oxidn of trifluoronitrosomethane with Pb dioxide (Ref 2). The Pb dioxide oxidn of the nitroso compd was repeated by Hazeldine who obtd a 37% yield (Ref 3). This oxidn has also been carried out using dimanganese heptoxide (Ref 3), 30% hydrogen peroxide in a sealed tube (Ref 4), and activated C (apparently contg adsorbed O_2) in a sealed tube at 150° for 1

hour, yield 7% (Ref 5). It has also been prepd by the action of Sb trifluorodichloride on chlorodifluoronitromethane (Ref 3)
Spectra. The IR spectrum and band assignments are given in Ref 6; in the UV there is a $n \rightarrow \pi^*$ transition at 35842^{-1} (Ref 7)
Use: A mixt of 0.151 to 1 part of ammonia is claimed as a liq rocket monoprop, Isp 218 lb-sec/lb (Ref 8)
Refs: 1) Beil **1**, ⟨105⟩ 2) W. Hückel, Nach-AkadWissGöttingen, Math-PhysikKlasse **1946**, 36 & CA **43**, 6793d (1949) 3) R.N. Hazeldine, JCS **1953**, 2075 4) J. Banus, JCS **1953**, 3755 5) J. Jander & R.N. Hazeldine, JCS **1954**, 919 6) J. Mason & J. Dunderdale, JCS **1956**, 769 7) A. Balasubramian & C.N.R. Rao, Chem&Ind **1960**, 1026 & CA **55**, 1412c (1961) 8) H.W. Bost & R.C. Doss, USP 3127736 & CA **61**, 5445a (1964)
Chloronitromethane. This article supplements the material in Vol **3**, C258-Rff under Chloromethane and Derivatives. Bp at 60mm 58–60°, d at 20° 1.472g/cc, RI at 20°, 1.4450 (Ref 3); CA Registry No 1794-84-9

It is prepd by the action of w on 2,3-dichloro-3,3-difluoro-2-nitropropionyl chloride at 45–50° for 4 hours, yield 61% (Ref 3). It undergoes the ter Meer reaction with Na nitrite to give dinitromethane (Ref 2). The IR and Raman spectral peaks are assigned in Ref 6. The pK_a at 25° was found to be 7.20 (Ref 4). In polarographic analysis it gives two breaks in the curve, indicating a two electron reduction probably by the eqn $ClCH_2NO_2 + 2e^- = CH_2NO_2^- + Cl^-$ (Ref 5)
Refs: 1) Beil **1**, ⟨106⟩ 2) H. Feuer, "Recent Advances in the Chemistry of Polynitro Compounds" in T. Urbański, Ed, "Nitro Compounds", ProcInternSymp, Warsaw **1963**, Tetrahedron **20**, Supp 1, 103 3) I.V. Martynov & Yu.L. Krugylak, ZhObshchKhim **35**, 248 (1965) & CA **62**, 14490b (1965) 4) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966) 5) J. Armand, BullFr **1966**, 546 & CA **64**, 17040e (1966) 6) P. Gluzinski & Z. Eckstein, SpectrochimActa **24A**, 1777 (1968)
Chlorofluoronitromethane. $ClCHFNO_2$, mw 113.49, N 12.34%; OB to CO_2 −7.05%; bp 79–81°; d at 20°, 1.532g/cc. RI at 20° 1.3840 (Ref 2). It is prepd by the decarboxylation of chlorofluoronitroacetic acid with hot w (Ref 3), or anhyd K fluoride (Ref 2). Its pK_a in w is given as 10.14 in Ref 4
Refs: 1) Beil – not found 2) I.V. Martynov et al, ZhObshchKhim **33**, 3384 (1963) & CA **60**, 4000a (1964) 3) Yu.L. Krugylak et al, USSRPat 159821 & CA **60**, 11897b (1964) 4) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966)
Chlorodifluoronitromethane. $ClCF_2NO_2$, mw 131.48, N 10.66%; bp 24–25° (Ref 2). It is prepd by the oxidn of the nitroso compd with dimanganese heptoxide, yield 15% (Ref 2), or by the interaction of difluorodiazirine with nitryl chloride, yield 15% (Ref 3)
Refs: 1) Beil **1**, ⟨106⟩ 2) R.N. Hazeldine, JCS **1953**, 2075 3) R.A. Mitch, JHeterocyclicChem **1**, 233 (1964)
Dichloronitromethane. This article supplements the material in Vol **5**, D1213-R under Dichloromethane and Derivatives. In polarographic analysis it shows a complex curve indicating two 2-electron reductions giving finally NMe and two Cl^- ions (Ref 1). Its pK_a at 25° was found to be 5.99 (Ref 2)
Refs: 1) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966) 2) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966)
Trichloronitromethane. This article supplements the material in Vol **3**, C256-R under Chloroform and Derivatives; CA Registry No 76-06-2. The IR spectrum and assignment of peaks are given in Ref 2; and in the UV there is a $n \rightarrow \pi^*$ transition at $35907cm^{-1}$ (Ref 3). A procedure is described in Ref 5 for its spectrophotometric detn in w. The thermodynamic props are calcd in Ref 4
Refs: 1) Beil **1**, ⟨106⟩ 2) J. Mason et al, JCS **1959**, 2014 3) A. Balasubramanian & C.N.R. Rao, Chem&Ind **1960**, 1025 & CA **55**, 1413c (1961) 4) A.H. Castelli & F. Pristera, "The Thermodynamic Properties of Nitrotrichloromethane" **PA-FRL-TN-91** (Sept 1961) 5) J.A. Castro & H. Godoy, AnalChimActa **33**, 679 (1965)
Bromonitromethane. This article supplements the material in Vol **2**, B312-R under Bromomethane and Derivatives; CA Registry No 563-70-2. The IR and UV spectra are given in Ref 3. In polarographic analysis a two electron reduction to $CH_2NO_2^-$ and Br^- is indicated (Ref 4). It can be quanty detd by treatment with concd sul-

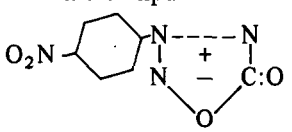
furic acid, then resorcinol, to give a colored complex which can be measured spectrophotometrically (Ref 2)
Refs: 1) Beil **1**, {115} & ⟨106⟩ 2) L.R. Jones & J.A. Riddick, AnalChem **24**, 1533 (1952) 3) V.I. Slovetskii et al, IzvestAkadNOtdel-KhimNauk **1961**, 683 & CA **55**, 23048 (1961) 4) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966)
Bromodifluoronitromethane. $BrCF_2NO_2$, mw 175.94, N 7.96%; CA Registry No 354-42-7. It has been patented as an insecticide, fungicide, and nematocide
Refs: 1) Beil – not found 2) E.E. Kenaga, USP 3445575 (1969) & CA **71**, 37905r (1969)
Bromodichloronitromethane. $BrCCl_2NO_2$, mw 208.86, N 6.71%; bp at 22mm, 52°; d at 20°, 2.073g/cc. It is prepd by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 33.2%
Refs: 1) Beil – not found 2) G.A. Burk & R.A. Davis, USP 3159686 (1965) & CA **62**, 3937d (1965)
Dibromonitromethane. Br_2CHNO_2, mw 218.86, N 6.40%; a liq; bp at 13mm, 58.5–60° (Ref 2); RI at 25°, 1.5757 (Ref 4); CA Registry No 598-91-4. It was first prepd by the action of Br on bromonitromethane in basic soln (Ref 2), and later by the similar bromination of nitroacetamide (Ref 3). In polarographic analysis a two electron reduction to $BrCHNO_2^-$ and Br^- is indicated (Ref 5)
Salts, Ammonium Salt. It is formed with Amm bromide by the action of liq ammonia on tribromonitromethane. The crude salt mixt is obtd as a yellow powd which gives free dibromonitromethane by the action of aq hydrobromic acid (Ref 4)
K salt. It is obtained as an orange powd which decomps suddenly on heating with formation of K bromide, but does not deton (Ref 3)
Refs: 1) Beil **1**, 57, [43] & ⟨106⟩ 2) R. Scholl, Ber **29**, 1822 (1896) 3) R.C. Schreyer, JACS **73**, 2962 (1951) 3) S.K. Brownstein, JOC **23**, 113 (1958) 4) J. Armand, BullFr **1966**, 574 & CA **64**, 17040e (1966)
Dibromofluoronitromethane. $FCBr_2NO_2$, mw 236.86, N 5.91%. It is claimed to reduce hydrocarbon emissions from automobile exhaust when added to the fuel at 3.3% by vol
Refs: 1) Beil – not found 2) C.P. Parsons & C.T. Pumpelly, USP 3413105 (1969) & CA **70**, 30633w (1969)
Chlorodibromonitromethane. $ClCBr_2NO_2$, mw 253.30, N 5.53%; a heavy oil; bp at 22mm, 67–69°; d at 25°, 2.398g/cc (Ref 3). It is prepd by the action of Br on chloronitromethane in aq K hydroxide (Ref 2), or by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 35.4% (Ref 3)
Refs: 1) Beil **1**, 77 2) J. Tscherniak, Ber **8**, 610 (1875) 3) G.A. Burk & R.A. Davis, USP 3159686 (1965) & CA **62**, 3937d (1965)
Tribromonitromethane. This article supplements the material in Vol **2**, B312-L under Bromoform and Derivatives; CA Registry No 464-10-8. The IR and UV spectra are given in Ref 4. In polarographic analysis a two electron reduction to $Br_2CNO_2^-$ and Br^- is indicated (Ref 5). It adds to olefins to form 1,1,1-tribromo-2-nitroalkanes. The authors found that it is the only halonitroalkane to react in this way (Ref 3). When added to liq ammonia it forms a mixt of the Amm salt of dibromonitromethane and Amm bromide (see above) (Ref 2)
Refs: 1) Beil **1**, {115} & ⟨106⟩ 2) S.K. Brownstein, JOC **23**, 113 (1958) 3) Yu.A. Baskakov & N.M. Mel'nikov, ZhObshchKhim **29**, 1233 (1959) & CA **54**, 8599i (1960) 4) V.I. Slovetskii et al, IzvestAkadNOtdelKhim-Nauk **1961**, 683 & CA **55**, 23048g (1961) 5) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966)
Iodonitromethane. ICH_2NO_2, mw 186.95, N 7.49%; OB to CO_2 –8.56%, an unstable, lacramatory oil, odor unpleasant (Refs 2 & 3); CA Registry No 25538-43-6. It is prepd by the action of Ag nitrite on methylene iodide in the presence of a trace of I (Ref 2), or by the action of I on NMe in cold alkali (Ref 3). It is reduced electrolytically to iodide and NMe (Ref 4). A Na salt has been prepd as a white solid which explds on heating (Ref 2).
Refs: 1) Beil **1**, 77 & {115} 2) A. Russanow, Ber **25**, 2632 (1892) 3) C.D. Nenitzescu & D.A. Isacescu, Ber **63**, 2484 (1930) 4) S. Tribalat & M. Grall, CR Series C **269**, 83 (1969) & CA **71**, 97712k (1969)

Dinitromethane (DNMe). $CH_2(NO_2)_2$, $CH_2N_2O_4$, mw 106.04, N 26.42%, OB to CO_2 +15.09%. It

is stored and handled in the form of salts, but has recently been obtd as an unstable oil, mp −15° (Ref 3); bp at 4mm, 39–40°; d at 20°, 1.524g/cc, RI at 20°, 1.4480 (Ref 16); CA Registry No 625-76-3. It was first prepd by the action of aq Amm sulfide on bromodinitromethane (Ref 2); and by the action of cold concd sulfuric acid on the di-K salt of symdinitroethane (Ref 4), isolated as the K salt. It is best prepd by the reduction of dibromodinitromethane with As trioxide in cold aq K hydroxide and isolated as the K salt (Ref 3). The pure material has been regenerated from the K salt by treatment with anhyd hydrogen fluoride in abs eth (Ref 16)

Ionization. The pK_a at 25° in w is 3.60, 50% aq et alc 4.11, et alc 7.5, and me alc 7.2 (Ref 17)

Reactions. It reacts with benzenediazonium chloride to give yellow crysts, mp 75° with gas evolution, whose structure was first thought to be $(PhN{:}N)_2C(NO_2)_2$ (Ref 3). More recently the reaction with p-nitrobenzenediazonium fluoroborate was examined in greater detail (Ref 11). The first prod isolated was the hydrazone $p\text{-}O_2NC_6H_4NHN{:}C(NO_2)_2$, orange-red crysts, mp 120–25° with decompn. It deflagrates when heated on a spatula, and its solns decomp slowly in the cold and more rapidly on heating, with evolution of oxides of N. From the mother-liquor was obtained another compd, mp 164°, which was considered to be a meso-ionic compd:



For a discussion of these type compds see Ref 12. The chemistry and technology of DNMe has been reviewed in Ref 9 with emphasis on its use as an intermediate for the prepn of nitropolymers, especially thru 2,2-dinitro-1,3-propanediol (code name A-diol)

Spectra. The UV spectra in w, acid, and base are given in Ref 5. The proton nuclear magnetic resonance spectrum shows a sharp singlet at 3.90ppm from tetramethylsilane (Ref 15)

Salts. **Ammonium Salt.** Obtained as bright yellow fine needles, expl at 105° (Ref 3). It is completely ionized in w at 25° (Ref 20)

Ba salt. Bright yellow needles, insol in w or et alc (Ref 3)

Cs Salt. Its IR and UV spectra are given in Ref 19

Li Salt. Its IR spectrum is given in Ref 13

HgCl+ Salt. It is prepd by the action of Hg(II) chloride on the K salt in w (Ref 6)

Phenylhydrazine Salt. It is prepd by the action of phenylhydrazine on dinitromethane in anhyd eth and obtd as intense yellow needles, mp 101° with gas evoln (Ref 3)

Piperidine Salt. The ionization constant in w at 25° is 3.37±0.01 (Ref 20)

K Salt. DNMe is stored and handled as the K salt which is obtd as brown-yellow feathery crysts, expln temp 218° (Ref 4). It is also prepd by the action of excess K cyanide or K thiosulfate on dibromodinitromethane (Ref 7). Best lab prepn: K nitrite (25g) in 40ml of w is added to 24g of chloronitromethane in 50g of me alc at 0°. To this soln is added with good stirring 16.5g of K hydroxide in 50g of me alc as the temp is held betw 0 and −5°. The stirring is contd for 5 hours, the pptd solid filtered off, and recrystd from w to give 8.4g of K dinitromethane, yield 23.3%, expln temp 208° (Ref 8). More recently it is conveniently prepd on a lab and comml scale by the interaction of NMe and Na nitrite with a Ag salt, most commonly the nitrate. This reaction, developed by Shechter and Kaplan of the Purdue Research Foundation, is called the Shechter-Kaplan reaction (Ref 14). The IR spectrum is given in Ref 13. The ionization constant in w at 25° is 2.26±0.01 (Ref 20). It readily adds to activated olefins (Ref 10)

Rb Salt. Its IR and UV spectra are given in Ref 18. The ionization constant in w at 25° is 0.602±0.004 (Ref 20)

Ag Salt. It is formed from the K salt and Ag nitrate in w, decomps at 135° (Ref 3). The IR and UV spectra are given in Ref 18. It reacts with Me iodide to give 1,1-dinitroethane (Ref 3)

Na Salt. The IR spectrum is given in Ref 13. It is estimated to be 100% ionized in w at 25° (Ref 20)

Refs: 1) Beil **1**, 77, (24), [44], {115} & ⟨107⟩ 2) S.M. Losanitsch, Ber **16**, 51 (1884) 3) P. Duden, Ber **26**, 3003 (1893) 4) R. Scholl & A. Schmidt, Ber **35**, 4288 (1902) 5) A. Hantzsch & K. Voigt, Ber **45**, 112 (1912) 6) W. Prager, Monatsh **33**, 1285 (1912) & CA **7**, 589 (1913) 7) R.A. Gotts & R. Hunter,

JCS **125**, 449 (1924) 8) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and their Application to Solid Smokeless Propellants", AerojetEngrgCorp, Azusa, Calif, Quarterly Report 345, Contr No N7-onr-462 (4 Jan 1949), p 54 9) L. Herzog & K. Klager, "A Review of Dinitromethane and 2,2-Dinitroethanol", AerojetEngrgCorp, Special Report 461, Contr No N7-onr-462 (20 July 1950) 10) L. Herzog et al, JACS **73**, 749 (1951) 11) S. Hünig & O. Boes, Ann **579**, 46 (1953) & CA **49**, 7518i (1955) 12) W. Baker & W.D. Ollis, QuartRevs **11**, 15 (1957) 13) V.I. Slovetskii et al, IzvestAkadNOtdelKhimNauk **1963**, 57 & CA **57**, 10874e (1963) 14) H. Shechter & R.B. Kaplan, USP 2997504 (1963) & CA **58**, 5515h (1963) 15) W. Hofman et al, JACS **86**, 555 (1964) 16) G.Ya. Legin et al, IzvestAkadNSerKhim **1965**, 2220 & CA **64**, 11073e (1966) 17) V.I. Slovetskii et al, TetrahedronLett **1966**, 1746 18) V.I. Slovetskii et al, ZhOrganKhim **2**, 1445 (1966) & CA **66**, 59654v (1967) 19) I.N. Shokhor et al, ZhOrganKhim **3**, 489 (1967) & CA **67**, 81695p (1967) 20) V.I. Slovetskii et al, IzvestAkadNSerKhim **1968**, 1004 & CA **69**, 54836v (1968)

Halogen Dinitro Derivatives of Methane

All 14 possible halogen derivs of dinitromethane have been reported in the literature. They are sens to friction, shock, and impact, as well as being toxic and skin irritants (Ref 5)

Fluorodinitromethane. $FCH(NO_2)_2$, $CHFN_2O_4$, mw 128.04, N 21.88%, OB to CO_2 18.74%, fr p −24.5°; bp at 20mm 35–38°, d at 20°, 1.5955 g/cc; RI at 20°, 1.4054 (Ref 4); pK_a at 20° 7.70 (Ref 2); CA Registry No 7182-87-8. It is prepd by the fluorination of the Amm salt of dinitromethane at 2–3° in w, yield 90% (Ref 4); by the action of H peroxide and K hydroxide on fluoronitroform in me alc; or by the fluorination of the K salt of ethyl dinitroacetate (Ref 5)

Hg Salt. It is prepd by the action of Hg(II) monoxide in eth on the free nitro compd, yield 86%, mp 147° (Ref 6). It reacts with K hydroxide or K iodide to give the K salt of fluorodinitromethane, and with H chloride or w to regenerate the free nitro compd (Ref 3)

Refs: 1) Beil – not found 2) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966) 3) L.V. Okhlobystina et al, DoklAkadN **176**, 1086 (1967) & CA **68**, 78397h (1968) 4) L.T. Eremenko & F.Ya. Natsibullin, IzvestAkadNSerKhim **1968**, 912 & CA **69**, 35315b (1969) 5) M.J. Kamlet & H.G. Adolph, JOC **33**, 3073 (1968) 6) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50160p (1969)

Difluorodinitromethane. $F_2C(NO_2)_2$, $CF_2N_2O_4$, mw 146.03, N 19.19%; bp 34°; d at 10°, 1.5644 g/cc; RI at 10°, 1.3640 (Ref 4); CA Registry No 1185-11-1. It is prepd by the reaction of di-N tetroxide with difluorodiazirine (Ref 2); by the fluorination of a mixt of K nitroform and Na fluoride at −12 to −6° in a Cu vessel (Ref 4); or by the action of anhyd K fluoride on fluoronitroform in sulfolane at 150°, yield 58.7% (Ref 5). A mixt of 0.249p to one p of ammonia has been claimed as a liq rocket proplnt (Ref 3)

Refs: 1) Beil – not found 2) R.A. Mitsch, JHeterocyclicChem **1**, 233 (1964) 3) H.W. Bost & R.C. Doss, USP 3127736 (1964) & CA **61**, 5445a (1964) 4) L.T. Eremenko et al, IzvestAkadNSerKhim **1968**, 429 & CA **69**, 18508f (1968) 5) M.J. Kamlet & H.G. Adolph, JOC **33**, 3073 (1968)

Chlorodinitromethane. This article supplements the material in Vol **3**, C259-L under Chloromethane and Derivatives; CA Registry No 921-13-1. Its pK_a in w at 20° is 3.53–3.80 (Refs 1 & 3). The K salt has a mp of 85° with decompn (Ref 2). The Hg salt is prepd from chlorodinitromethane and the Hg salt of fluorodinitromethane. It reacts with aniline to form $PhNHC(NO_2)_2Cl$, yield 59.1%, mp 125° with decompn (Ref 4)

Refs: 1) T.N. Hall, JOC **29**, 3587 (1964) 2) V.I. Erashko et al, IzvestAkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 3) A.I. Ivanov et al, ZhFizKhim **40**, 2298 (1966) & CA **66**, 14512v (1966) 4) L.V. Okhlobystina et al, DoklAkadN **176**, 1086 (1967) & CA **68**, 78397h (1968)

Chlorofluorodinitromethane. $FCCl(NO_2)_2$, $CClFN_2O_4$, mw 158.49, N 17.68%; OB to CO_2 20.19%, bp at 752mm 85–87°; d at 20°, 1.6162 g/cc, RI at 20°, 1.3992 (Ref 5); CA Registry No 19845-51-3. It is prepd by the action of di-N tetroxide on chlorofluoronitroacetic acid in an autoclave at 80–90° (Ref 3); by the action of Li

chloride in dimethylformamide on fluoronitroform, yield 35% (Ref 4); or by the action of Cl in anhyd eth on the Hg salt of fluorodinitromethane, yield 72% (Ref 5). The thermal decompn has been studied betw 170 and 240°. The plot of log k vs 1/T was found to be a straight line from which the activation energy was calcd to be 41.5kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) I.V. Martynov et al, USSR-Pat 20788 & CA **69**, 35407q (1968) 4) A.A. Fainzil'berg et al, IzvestAkadNSerKhim **1969**, 476 & CA **70**, 114505u (1969) 5) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50169p (1969)

Dichlorodinitromethane. This article supplements the material in Vol **5**, D1213-R under Dichloromethane and Derivatives; bp at 50mm, 54–56°; d at 20°, 1.6643g/cc; RI at 20°, 1.5460 (Ref 2); CA Registry No 1587-41-3. It is prepd by refluxing trichloroethylene with a 3 mole excess of 70% nitric acid (Ref 1); or by the action of Cl on the K salt of dinitromethane in aq K hydroxide (Ref 2). The thermal decompn betw 115 and 150° was found to be 1st order and homogeneous, the plot of log k vs 1/T gave a straight line (Ref 3). It is a useful herbicide for water weeds (Ref 1).

Refs: 1) H. Johnston, USP 3054828 (1963) & CA **58**, 3315e (1963) 2) V.I. Erashko et al, IzvestAkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 3) G.M. Nazin et al, Combstn-&Flame **12**, 102 (1968)

Bromodinitromethane. This article supplements the material in Vol **2**, B312-R under Bromomethane and Derivatives; the pK_a in w at 20° is 3.47–3.60 (Refs 4 & 6); in the UV the λ_{max} is at 385mμ (Ref 6); CA Registry No 996-67-8. The Amm salt is formed by the action of liq ammonia on dibromodinitromethane (Ref 2). The K salt is a yellow solid, mp 152° with decompn (Ref 5). It is formed by the action of phenylhydrazine in aq K hydroxide on dibromonitromethane (Ref 2)

Refs: 1) Beil **1**, {115} 2) A.K. Macbeth & W.B. Orr, JCS **1932**, 540 3) F.C. Schmidt et al, JOC **9**, 421 (1944) 4) T.N. Hall, JOC **29**, 3587 (1964) 5) V.I. Erashko et al, Izvest-AkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 6) A.I. Ivanov et al, ZhFizKhim **40**, 2298 (1966) & CA **66**, 14514v (1966)

Bromfluorodinitromethane. $BrCF(NO_2)_2$, $CBrFN_2O_4$, mw 202.94, N 13.81%; bp at 40mm, 35–36°; d at 20°, 1.8722g/cc; RI at 20°, 1.4351 (Ref 3); CA Registry No 22632-20-8. It is prepd by the action of Br in anhyd eth on the Hg salt of fluorodinitromethane, yield 76.4% (Ref 3). The thermal decompn was studied betw 170 and 210°. The plot of log k vs 1/T was a straight line from which the activation energy was calcd as 39.5kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50160p (1969)

Bromochloronitromethane. $BrCCl(NO_2)_2$, $CBrClN_2O_4$, mw 219.41, N 12.77%; a heavy oil, suffocating odor; mp 9.2–9.3°, bp at 15mm, 75–76°; d at 10°, 2.0394g/cc; RI at 20°, 1.4739 (Ref 4); CA Registry No 33829-48-0. It is prepd by the action of aq Cl on the K salt of bromodinitromethane (Ref 2), yields are improved by the addn of Na acetate (Ref 3)

Refs: 1) Beil **1**, 78, [45] & ⟨115⟩ 2) S.M. Losanitsch, Ber **17**, 848 (1884) 3) R.A. Gotts & L. Hunter, JCS **125**, 447 (1924) 4) F.C. Schmidt et al, JOC **9**, 421 (1944)

Dibromodinitromethane. $Br_2C(NO_2)_2$, $CBr_2N_2O_4$, mw 262.87, N 10.66%; a heavy yellow oil, solidifies to white leaflets; fr p 6°, mp 10° (Ref 5); bp at 19mm, 78–80° without decompn, expl at 158° (Ref 6); d at 25°, 2.3946 g/cc; RI at 20°, 1.5215 (Ref 9). It is insol in w, miscible with et alc, and volat in steam (Ref 2); CA Registry No 2973-00-4. It has been prepd by the action of Br in w (Ref 7) or aq K hydroxide (Ref 11) on the K salt of dinitromethane; or by the introduction of Br vapors into a w soln of equal parts of the di-K salt of sym-tetranitroethane and Na acetate (Ref 8). It is one prod isolated from the action of concd nitric acid on Br-contg compds such as ethylene dibromide (Ref 3), sym-tribromoaniline (Ref 2), p-bromophenol, and dibromo-p-toluidine (Refs 3 & 4). The experimental details for its prepn from sym-tribromoaniline and concd nitric acid are given in Ref 10

Reactions. For reactions see above under Dinitromethane and Bromodinitromethane

Refs: 1) Beil **1**, 78 & [44] 2) S.M. Losa-

nitsch, Ber **15**, 472 (1883) 3) S.M. Losanitsch, Ber **16**, 51 (1884) 4) S.M. Losanitsch, Ber **16**, 2731 (1884) 5) L. Wolff, Ber **26**, 2217 (1893) 6) R. Scholl & M. Brenneisen, Ber **31**, 651 (1898) 7) R. Scholl & A. Schmidt, Ber **35**, 4291 (1902) 8) L. Hunter, JCS **125**, 1483 (1924) 9) E. Schmidt et al, Ber **59**, 1887 (1926) 10 F.C. Schmidt et al, JOC **9**, 420 (1944) 11) V.I. Erashko et al, Izvest-AkadNSerKhim **1965**, 2060 & CA **64**, 6447g (1966)

Iodonitromethane. $ICH(NO_2)_2$, $CHIN_2O_4$, mw 231.96, N 12.08%, OB to CO_2 10.35%; CA Registry No 29610-14-8. The K salt is formed by the action of I in aq K hydroxide on dinitromethane (Ref 2). It is obtained as yellow tablets which darken on standing and expl at 154° (Ref 3). The Ag salt is obtd as pale yellow leaflets which expl at 109–10° (Ref 3)

Refs: 1) Beil **1**, 79 & [45] 2) S.M. Losanitsch, Ber **16**, 51 (1884) 3) R.A. Gotts & L. Hunter, JCS **125**, 443 (1924)

Fluoroiododinitromethane. $FCI(NO_2)_2$, $CFIN_2O_4$, mw 249.96, N 12.08%; it is a liq which decomps slowly on standing in the dark, rapidly in light; bp at 27mm, 59–9.5°; d at 20°, 2.3541g/cc; RI at 20°, 1.4998 (Ref 3); CA Registry No 22632-21-9. It is prepd by the action of I in anhyd eth on the Hg salt of fluorodinitromethane, yield 74% (Ref 3). The thermal decompn was studied betw 160 and 197°. The plot of log k vs 1/T gave a straight line from which the activation energy was calcd as 39.7kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50169p (1969)

Chloroiododinitromethane. $ClCI(NO_2)_2$, $CClIN_2O_4$, mw 265.42, N 9.05%; a colorl oil, characteristic odor; d at 12°, 2.1424g/cc; CA Registry No 40956-65-8. It is prepd by the action of aq Cl on the K salt of iododinitromethane

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Bromoiododinitromethane. $BrCI(NO_2)_2$, $CBrIN_2O_4$, mw 310.88, N 8.01%; an unstable oil, odor disagreeable; CA Registry No 40956-66-9. It is prepd by the action of aq Br on an ice cold soln of the K salt of iododinitromethane

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Diiododinitromethane. $I_2C(NO_2)_2$, $CI_2N_2O_4$, mw 357.87, N 7.83%; an extremely unstable oil, odor disagreeable; CA Registry No 40956-64-7. It is prepd by the acidification of an ice cold soln of the K salt of iododinitromethane. It decomps on standing with the evolution of I and oxides of N

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Trinitromethane (Nitroform, TNMe). Trinitromethan or nitroform (Ger), Nitroforme (Fr); $CH(NO_2)_3$, CHN_3O_6, mw 151.04, N 27.82%, OB to CO_2 +37.08%; a colorl to pale yellow solid, a pale yellow liq; mp 26.3 ± 0.1° (Ref 46). It can also be obtained in a higher melting form, mp 50°, which was assumed by the authors to be the aci-form (Ref 15); bp at 22mm, 45–7° (Ref 16); d at 24.3°, 1.5967g/cc; RI at 24.3°, 1.44174 (Ref 11). The pH of a satd soln in w was measured with a glass electrode and found to be 0.6 (Ref 25, p 2); CA Registry No 517-25-9. The Hercules Powder Co of Wilmington, Del has been granted a trademark for *Nitroform*®, a synthetic w-insoluble compd for controlled release of N for agricultural use (Ref 40). This should not be confused with TNMe

Historical. It was first prepd by the action of nitric acid (d 1.52 g/cc) on acetylene (Ref 5), and this is the basis for one industrial process for mfg TNMe (Refs 10, 29 & 35). This reaction was first examined on a large scale in Ger during WWII, where it was used to prepare TNMe and TeNMe for use as intermediates for the prepn of expls (Ref 18)

Preparation. A continuous process is described in Ref 26 for its prepn from nitric acid and acetylene. Other prepns on both lab and industrial scales are by the action on Tetranitromethane (TeNMe) of K hydroxide in aq glycerol (Ref 16), aq $HOCH_2SO_3Na$, or 30% aq H peroxide (Ref 19a) to give the K salt which is treated with sulfuric acid (Ref 16), syrupy phosphoric acid (Ref 20), or best by passing gaseous HCl thru a suspension of the K salt in anhyd eth (Ref 19a). It has also been prepd by the action of nitric acid on malonamide,

yield 58% (Ref 34); Ac_2O (Ref 27); the di-K salt of dinitroacetic acid, yield 54% (Ref 28); or ethylene (Ref 12)

Laboratory Preparation. A soln of 168g of K hydroxide in 350ml of w is cooled to 5° and 120g of 30% aq H peroxide added with stirring. Next is added, with stirring, 189g of TeNMe at a rate which keeps the temp at 20–5°. It is then allowed to rise to 30° over 15min, the bright yellow solid collected on a glass frit, washed with anhyd me alc, then anhyd eth, and air dried to give 100% of the K salt of TNMe. The salt is suspended in anhyd eth and anhyd HCl passed in until the yellow color disappears. The white ppt of KCl is filtered off and washed with anhyd eth. The eth is evapd from the filtrate and addnl washings at reduced press give 85–95% of crude TNMe which can be purified by sublimation (Ref 19a, p 79)

Chemical Reactions. TNMe is a strong acid and forms salts with metals and bases (see below). It readily reacts with formaldehyde to form trinitroethanol (Ref 16). It adds to activated double bonds, such as α,β-unsaturated carbonyl compds and vinyl ethers (Ref 19b). It forms a complex with dioxane contg 2 moles of TNMe to one of dioxane, mp 44–4.5°, bp at 8mm, 61–2° (Ref 19a, p 33). It reacts with aromatic diazonium salts to give compds of the type $ArN{:}NC(NO_2)_3$. The compds are relatively unstable and their expl props have not been examined (Ref 12). It reacts with N-hydroxymethyl compds to form adducts of the type $RNHCH_2C(NO_2)_3$. The same compds are formed from TNMe, formaldehyde, and the amine; or from trinitroethanol and the amine (Ref 31). It forms complexes with N-contg heterocyclics whose expl props have not been examined (Ref 42). It forms complexes with benzene and methylbenzenes. The formation constants for these complexes vary from 8.46 for the benzene complex to 279.4 for the hexamethylbenzene complex (Ref 49)

Analytical. It can be titrated with std base to a salmon colored phenolphthalein endpoint; and can be quanty pptd from aq solns with tetraphenylarsonium chloride; K_{sp} of the complex in w is 6.9×10^{-9} (Ref 22). This procedure can be adapted to the analysis of compds, such as bis-(trinitroethyl) urea, which regenerate TNMe on alkaline hydrolysis. In an ion exclusion-partition chromatographic method for the sepn of acids, TNMe emerged from the column betw citric and itaconic acids (Ref 36)

Impact Sensitivity. On the BRL machine (1kg wt), using a noisemeter to detect explns, the 50% expln height was found to be 218cm. A 50/50 mixt with kerosene had a 50% expln height of 130cm (Ref 21)

Power by Ballistic Mortar. 125–37% of TNT (Ref 24)

Spectrum, Ultraviolet. It shows a plain shoulder in eth, and in w shows a broad maximum at 3400Å (Ref 7)

Stability. It may be stored indefinitely at 0° in sealed glass ampules (Ref 20)

Toxicity. The toxic concns in air for mice are: LD (minimum) 0.7, LD50 0.8, and LD100 1.0mg/ℓ; the max acceptable concn is suggested to be 0.0005mg/ℓ (Ref 37). There is a large amt of toxicological info on the effects of TNMe in this Ref

Uses. It was found to be a poor gelling agent for NC (Ref 14). Its principal use is as an intermediate for the prepn of other expl compds.

Salts, **Ammonium Salt.** Yellow needles from w (Ref 6). It is prepd by the action of w or et alc on trinitroacetonitrile (Ref 2), or by the action of ammonia on TeNMe (Ref 6). The Q_c was found to be 1108.6 ± 1.3cal/g. From this was calcd the Q_f as −47.3 ± 0.2kcal/mole at 1 atm and 25°, and the energy of the bond betw Amm and the nitroformate ion to be 24.8 ± 0.7kcal/mole (Ref 47). It is 100% ionized in w at 25° (Ref 50). It has been patented as an ingredient in high energy proplnts (Ref 32)

Ba Salt. Fine pale yellow crysts, prepd by the action of Ba oxide on TeNMe in aq glycerol (Ref 13). A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

Ca Salt. A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

2,4-Dinitrophenylhydrazine Salt. It is prepd by the addn of the hydrazine in iso-Pr alc to TNMe in the same solv, mp 120–23° (Ref 48)

Guanidine Salt. It was first prepd in Ger during WWII by the addn of a guanidine salt to the K salt of TNMe in w. The hydrate is obtained as needles, mp 122–24°; the anhyd salt mp 128°. Impact sensy (2.5kg wt) 50% expln height,

17cm; deton vel at a loading d of 1.66g/cc, 8200m/sec; cryst d 1.643g/cc; vacuum stability: gas evoln 1.39cc/g in 48 hours at 90°; mixed with Al powd, 1.70cc/g in 48 hours at 90°. It detond after 30 hours at 100° (Ref 25)

Hydrazine Salt. Fine yellow crysts, mp 123° with decompn (Ref 25). It is prepd by the addn of hydrazine hydrate to TNMe in w (Ref 25), or by the addn of anhyd hydrazine to TNMe in iso-Pr alc (Ref 48). The cryst structure and X-ray diffraction pattern of the pure salt are given in Ref 45. Impact sensy (2.5kg wt), the 50% expln height was found to be 10cm (Ref 25). It is stable to 100° (Ref 48). It is claimed as an ingredient in a thixotropic proplnt formulation (Ref 41)

Li Salt. A complex with 2 moles of hydrazine is obtained as an orange-yellow solid, mp 70° with decompn (Ref 39). It is claimed as an oxidizer in proplnt formulations (Ref 39). It is 100% ionized in w at 25° (Ref 50)

Hg Salt. Colorl crysts, slightly sol in org solvs; prepd by the action of Hg oxide on an eth soln of TNMe (Ref 4). It reacts with olefins to form adducts contg one or 2 trinitromethyl groups, depending on reactant ratios (Ref 33). The ionization const in w at 25° is 6.04×10^{-3} (Ref 50)

Mg Salt. It forms an orange-yellow complex with hydrazine, mp 88° with decompn, d 1.68 g/cc, impact sensy 11.7cm (2kg wt). The salt has been patented as a proplnt ingredient (Ref 39)

Methylamine Salt. A yellow solid; mp 126–28° with decompn; ign temp 112°; vacuum stab 1.64cc/g of gas evolved at 60° in 2 hours, 2.04cc/g at 60° in 48 hours (Ref 43). It has been patented as an expl ingredient (Ref 44) and a proplnt ingredient (Ref 41)

K Salt. A yellow cryst solid, prepd by the action of basic K salts on TeNMe in the presence of reducing agents (see also above under TNMe). Some which have been used are: K methoxide in me alc (this proc is subject to dangerous explns) (Ref 8); K cyanide in me alc (Ref 23); a satd aq soln of K ferrocyanide (Ref 9); or K nitrite in w, yield 80% (Ref 38). It has also been prepd by the action of K nitrite on dibromodinitromethane (Ref 13). Its expln temp is 97–98° (Ref 3); and its impactg sensy, using a noisemeter to detect explns, was found to be 44.3cm (50% expln height, 1 kg wt) (Ref 21). The soly in w and et alc was detd betw 0 and 60° (Ref 13). It is 100% ionized in w at 25° (Ref 50). It is claimed as a corrosion inhibitor when added at a level of 0.05–0.1% to liq rocket proplnts (Ref 30)

Piperidine Salt. Its ionization constant in w at 25° is 0.288±0.001 (Ref 50)

Rb Salt. It is prepd from TNMe and Rb hydroxide in w, decomps at 157–59°. The ionization constant in w at 25° is 0.613±0.003 (Ref 50)

Ag Salt. It is prepd by the action of Ag oxide on TNMe in eth, mp 100° (Ref 3). It reacts with benzyl halides to form trinitroethyl derivs (Ref 17). Explodes mildly on rapid heating (Ref 3)

Na Salt. It is prepd by the action of Na nitrite on TeNMe in me alc or et alc (Ref 38). It is completely ionized in w at 25° (Ref 50). A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

Refs: 1) Beil **1**, 79, (21), [45], {116} & ⟨107⟩ 2) L. Schiskoff, Ann **101**, 216 (1857) 3) A. Hantzsch & A. Rinckenberger, Ber **32**, 631 (1899) 4) H. Ley & H. Kissel, Ber **32**, 1366 (1899) 5) Baschieri, AttiRealeAccadLincei-(Rendiconti) [5] **9**, I, 392 (1900) 6) E.C. Franklin & C.A. Kraus, JACS **27**, 213 (1905) 7) E.P. Hedley, Ber **41**, 1200 (1908) 8) A.K. Macbeth, Ber **46**, 2537 (1913) 9) F.D. Chattaway & J.M. Harrison, JCS **109**, 171 (1916) 10) K.J.P. Orton & P.V. McKie, JCS **117**, 283 (1920) 11) K. vonAuwers & L. Harres, Ber **62**, 2287 (1929) 12) A. Quilico, Gazz **62**, 912 (1932) & CA **27**, 1348 (1933) 13) A.K. Macbeth & W.B. Orr, JCS **1932**, 543 14) L. Médard, MP **25**, 451 (1932–33) & CA **28**, 5660 (1934) 15) L.W. Andrew & D.L. Hammick, JCS **1934**, 244 16) C.D. Hurd, "Report on the Preparation and Properties of Nitroform", OSRD **144**, 20 Sep 1941 (ATI-29966), p 11 17) W.S. Reich et al, JCS **1947**, 1235 18) K.F. Hager, IEC **41**, 2169 (1949) 19a) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and their Application to Solid Smokeless Propellants", Aerojet Engrg Corp Quarterly Summary Report 371, Contr N7onr-462 (15 Apr 1949) 19b) R.D. Geckler & M.H. Gold, Quarterly Summary Report 404 (12 Sep 1949), p 53 20) W.L.

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Halogen Derivatives of Trinitromethane

Fluorotrinitromethane. $FC(NO_2)_3$, mw 169.03, N 24.85%. A colorl to pale yellow liq, bp 84.2°; d at 20°, 1.795g/cc; RI at 25°, 1.3944; Q_f at 25°, −51.99kcal/mole (Ref 3); CA Registry No 1840-42-2. It has been prepd by the action of F in N 1:6 on a mixt of 20g of solid K salt of TNMe, 40g of K fluoride, and 50g of Cu turnings at −12 to −6° in a Cu vessel (Ref 4); by the action of 10% F in He on the K salt of TNMe in w, yield 48%, purity by gas chromatography 99.42 mole% (Ref 3); by the action of F on the Na salt of TNMe in aq Na hydroxide (Ref 5); or by the action of KF on TeNMe in dimethylformamide (Ref 6). It could not be detond with a hammer blow (Ref 2). It is a useful oxidizer in monoproplnts or hypergolic biproplnts (Ref 6). Calcd Isp with fuels are as follows: 0.304:1 with ammonia, 265; 0.469:1 with hydrazine, 281; 0.151:1 with triptane, 270; 0.262:1 with acetonitrile, 267; 0.313:1 with me alc, 261; and 0.185:1 wt ratio with 1,2-bis(dimethylamino)propane, 271 lb-sec/lb (Ref 2). It does not react at ambient temp with acetonitrile, triptane, acet, me alc, benzene, nitrobenzene, and cyclohexane (Ref 2)

Refs: 1) Beil – not found 2) H.W. Bost & R.C. Doss, USP 3127736 (1964) & CA **61**, 5445a (1964) 3) M.F. Zimmer et al, JChemEngrgData **11**, 577 (1966) 4) L.T. Eremenko et al, IzvestAkadNSerKhim (1968), 429 & CA **69**, 18565 (1968) 5) V. Grakaus-

kas & K. Baum, JOC **33**, 3080 (1968) 6) R.C. Doss, USP 3419625 (1969) & CA **70**, 77293 (1969)

Chlorotrinitromethane. $ClC(NO_2)_3$, mw 185.46, N 22.65%. A very pale yellow oil, freezes to a white solid, insol in w, sol in org solvs (Ref 3). Its odor is penetrating and unpleasant, resembling chloropicrin; and it is a lacrymator (Ref 3). Mp 5.75° (Ref 8); bp at 9mm, 35° (Ref 3); d at 20° 1.6769g/cc (Ref 6); RI at 20°, 1.4471 (Ref 8); dipole moment at 25°, 2.17 debye (Ref 5); heat capacity 0.21cal/g/deg; Q_v 10.86kcal/mole; Q_f at 25 , −5.57 ±0.18 cal/mole (Ref 8); CA Registry No 1943-16-4. It is prepd by the action of Cl on the K salt of TNMe in ice cold eth (Ref 2), or in w (Ref 3); or by the slow addn of acet to a mixt of nitric acid and HCl (Ref 4). Its IR and UV spectra are given in Ref 7. It reacts with K hydroxide in w or et alc to give the K salt of TNMe (Ref 4). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen chloride, and Cl (Ref 9)

Refs: 1) Beil **1**, [46] & {116} 2) E. Schmidt et al, Ber **54**, 1483 (1921) 3) A.K. Macbeth & D.D. Pratt, JCS **119**, 354 (1921) 4) W.J. Boyd, JSCI **44**, 222T (1925) & CA **19**, 2188 (1925) 5) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 15036b (1961) 6) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 22096i (1961) 7) V.I. Slovetskii et al, IzvestAkadNOtdKhimNauk **1961**, 683 & CA **55**, 23048g (1961) 8) M.F. Zimmer et al, JChemEngrgData **9**, 527 (1964) 9) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 315 & CA **69**, 66758j (1968)

Bromotrinitromethane. $BrC(NO_2)_3$, mw 229.95, N 18.23%. A faintly greenish yellow liq; mp 9.5–10°; bp at 8mm, 59° (Ref 4); d at 20°, 2.0313g/cc; RI at 20°, 1.4808 (Ref 7); dipole moment at 25°, 2.56 debye (Ref 6); CA Registry No 560-95-2. It has been prepd by the action of Br on TNMe in sunlight (Ref 2); in nitric acid (Ref 4); on the K salt of TNMe in ice cold eth, yield 90% (Ref 7); or on the Hg salt of TNMe in acet, yield 87% (Ref 5). It reacts with K hydroxide in et alc to give the K salt of TNMe (Ref 3), and with olefins to form 2-bromo-1-nitronate esters which can be hydrolyzed to the bromoalcohols (Ref 8). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen bromide, and Br (Ref 9)

Refs: 1) Beil **1**, 79, (21), [46] & {116} 2) L. Schischkoff, Ann **119**, 247 (1861) 3) A.K. Macbeth & D.D. Pratt, JCS **119**, 355 (1921) 4) A.K. Macbeth & D.D. Pratt, JCS **119**, 1356 (1921) 5) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1960**, 669 & CA **54**, 22331e (1960) 6) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 22331e (1961) 7) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 22096i (1961) 8) K. Torssel & R. Ryhage, ArkivKemi **23** 525 (1965) & CA **63**, 6893b (1965) 9) V.I. Slovetskii et al, IzvestAkadNSerKhim **1968**, 80 & CA **69**, 35191g (1968)

Iodotrinitromethane. $IC(NO_2)_3$, mw 276.46, N 15.19%. Bright yellow leaflets, insol in w, sol in hot et alc, benzene, or ligroin (Ref 2); mp 55–56°; bp at 13mm, 48–8.5° (Ref 3); dipole moment 3.79 debye (Ref 4); CA Registry No 630-70-6. It is prepd by the reaction betw I and the Ag salt of TNMe (Ref 2); or by the action of I on the K salt of TNMe in ice cold eth, yield 50% (Ref 5). It may expld violently on standing (Ref 3). It gives TeNMe on treatment with Ag Nitrite and the K salt of TNMe on treatment with aq K hydroxide (Ref 2). It reacts with ethylene and cyclohexene to form 2-iodonitronate esters which react further to form oxazolidines (Ref 6). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen iodide, and I (Ref 7)

Refs: 1) Beil **1**, 79 & [47] 2) A. Hantzsch, Ber **39**, 2478 (1906) 3) J. Mesenheimer & M. Schwarz, Ber **39**, 2551 (1906) 4) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 15036b (1961) 5) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 15036b (1961) 6) V.A.

Tartakovskii et al, IzvestAkadNSerKhim **1966**, 1290 & CA **65**, 16808 (1966) 7) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 315 & CA **69**, 66758j (1968)

Tetranitromethane (TeNMe). Tetranitromethan (Ger), Tétranitrométhane (Fr), Tetranitrometano (It), Tetranitrometan (Russ); $C(NO_2)_4$, mw 196.04, N 28.57%; OB to CO_2 +49%; a colorl to pale yellow liq, freezes to a colorl solid. Its odor is described as pungent (Ref 21). Pure TeNMe is said to be colorl, but becomes yellow on contact with w, due to hydrolysis to TNMe (Ref 5). Mp 14.2° (Ref 26); bp 125.7° (Ref 10); d at 25°, 1.62294g/cc; RI at 25°, 1.43822 (Ref 18). The dipole moment is essentially zero, indicating the structure to be symmetric, instead of $(O_2N)_3CONO$ as had been postulated to account for its reactivity (Ref 18); CA Registry No 509-14-8

Historical. It was first prepd by the action of nitric acid on TNMe (Ref 2). This reaction is the basis of large scale prepn in which acetylene is nitrated to TNMe and the latter treated with an excess of nitric acid to give TeNMe (Ref 26). As stated above under TNMe, in Ger during WWII, the prepn of TeNMe by this process was scaled up for use as an intermediate and as a substitute for nitric acid in the V-2 rocket (Ref 26). A pilot plant was built at Newark, NJ for prodn using this procedure. It was destroyed by an expln in 1953 and not rebuilt (Refs 33 & 44). Other prepns of lesser importance are by the action of Ag nitrite on iodotrinitromethane (Ref 3); by the action of 90% nitric acid and 25% oleum on malononitrile, yield 45% (Ref 40); by the action of mixed acid on a number of aromatic nitrocompounds, of which nitrobenzene, dinitrobenzene, and nitronaphthalene gave the best yields (Ref 13a); and by the action of nitryl chloride on salts of TNMe. The best yield, 95%, was obtained with the K salt (Ref 38). It is formed in small amts during the nitration of toluene to prepare TNT (Refs 37 & 38), and has been held responsible for explns which have occurred in TNT mfg plants. It has been postulated that mixts of TeNMe and toluene, which are as sensitive as NG, have condensed in off gas lines and detonated (Ref 37). Crude TNT, therefore, contains varying amts of TeNMe which, being highly toxic, accounts for conflicting reports as to the toxicity of TNT (Ref 37). By the use of C^{14}-labeled TNT, it was shown that 54.2% of the TeNMe came from the aromatic C attached to the Me group, 8.3% from each of the C atoms connected to nitro groups, 7.4% from each of the C atoms attached to H, and 6.1% from the Me group (Refs 37 & 38)

Laboratory Preparation. Anhydrous nitric acid (31.5g) in a 250ml 2-necked flask fitted with a dropping funnel and thermometer reaching to its bottom is cooled to 10°, and 51g of Ac_2O is added slowly at a rate which keeps the temp below 10°. After all is added, the funnel is removed and the flask allowed to warm slowly to room temp, allowed to stand a week, the contents poured into 300ml of w in a 500ml flask, and the TeNMe removed by steam distn. The lower layer of the distillate is sepd, washed with dil alkali, w, and dried over anhyd Na sulfate; yield 57–65% (Ref 32). *TeNMe should not be distd as it can expl with great violence, and distn residues are especially dangerous* (Ref 46). A continuous process using this reaction is described in Ref 34. A similar prepn is by heating acetyl nitrate with acet ac or Ac_2O (Ref 4)

Chemical Reactions. TeNMe gives TNMe or salts of TNMe under a variety of conditions (see above under TNMe). It is a mild oxidizing agent, converting hydroquinone to quinhydrone, N,N-dimethylaniline into crystal violet (Ref 8), and thiourea into $(H_2NCS)_2$ (Ref 14). It is

NH

a nitrating and nitrosoating agent (Ref 26), converting triethylamine into diethylnitrosamine (Ref 12). It is reduced to guanidine and ammonia with Zn (Ref 14) or Fe (Ref 13) and aq HCl

Analytical. A proc is described for the quant titrimetric analysis of TeNMe in nitric acid (Ref 35); and a spectrophotometric method is described in Ref 41 for the detn of small amts of TeNMe in air and w

Critical Diameter. The crit diam for deton propagation of TeNMe thickened with poly(methyl acrylate) and loaded with up to 75% inert solids was detd and found to decrease with increasing solids loading. It was postulated that the solids acted as reaction foci ahead of the deton front (Ref 45)

Explosion Temperature. It does not expl below 360° (Ref 21)
Heat of Combustion. 102.9kcal/mole (Ref 22)
Heat of Explosion. From a differential therm analysis exotherm at 310° the Q_e at 227° was calcd to be 557cal/g (Ref 39)
Heat of Formation. −8.9kcal/mole (Ref 22)
Impact Sensitivity. Described as "similar to TNT" (Ref 21). On BM app (2kg wt) the 50% expln height was found to be over 100cm (Ref 25)
Shock Wave Sensitivity. A test is described to detn the shock wave sensy of liq expls. A crit thickness is detd for which an impressed shock wave causes a deton. For TeNMe this was detd to be 3mm. An eqn is developed to relate this thickness with other parameters such as press and deton vel (Ref 42)
Spectra, Infrared. The IR spectra in the gas, liq, and solid states are in Ref 30
Ultraviolet. λ_{max} ca 275mμ, log ε 2.2 (Ref 19)
Thermal Stability. At 100° it evolves acid fumes in 30min, at 135° there is no expln after 300min (Ref 21)
Toxicity. It is a lacrymator and irritates the skin mucous membranes, especially of the respiratory tract (Ref 26). Prolonged exposure to vapors causes damage to liver, kidneys, and other organs. Concn in air of 0.1ppm is fatal and 3.3ppm or higher are rapidly fatal (Ref 47, p 1156). Its threshold limit value in air is set at 1ppm (Ref 47, p 22)
Trauzl Test. 21.4% of TNT when pure (Ref 26); for mixts see below
Uses. It does not gelatinize NC (Ref 15). It improves the octane rating of diesel fuels (Ref 26). It decreases the polymerization rate of methyl methacrylate (Ref 24), and styrene (Ref 23), but does not inhibit the reaction. A review of its use as an oxidizer in rocket proplnts is given in Ref 33. TeNMe gives yellow to orange colors with olefins and aromatic compds. This is used as a diagnostic test for the presence of these groups in org analysis (Refs 6, 9, 16, 17 & 29)
Explosive Mixtures with Organic Compounds. Mixts with org compds are more powerful and sensitive expls than TeNMe. Those whose expl props have been detd are listed below:
Benzene. A mixt of 2 moles of TeNMe and one of benz gave an expln temp of 163.3° (Ref 11). An 87:13 mixt with benz gave a Trauzl test of 134% of TNT (Ref 26). Mixts of from 65 to 90% by wt in benz had a card gap test of over 300 cards, indicating them to be very sens (Ref 36). The sensy of mixts with benz was found to be due to the formation and collapse of cavitation bubbles in the liq (Ref 43)
Ethylene Glycol. A 50% soln by wt had a card gap test of 270 cards (Ref 36)
Gasoline. Mixts with gasoline and diesel fuel were found to be powerful, but sens expls (Ref 26)
Hydrocarbons. Addn of metallo-org compds lowers the burning rate of TeNMe/hydrocarbon mixts to the point where they are useful monoproplnts (Ref 27)
Naphthalene. A mixt of 2 moles of TeNMe to one of naphthalene gave an expln temp of 160.4° (Ref 11)
Nitromethane. A mixt of 4 moles of NMe to one of TeNMe gave a maximum expansion of 30.62 in the Pb block expansion test (Ref 20). A mixt contg 40% TeNMe had a card gap test of 75 cards (Ref 36)
Paraffins. Mixts of 10–40% paraffins and 69–90% TeNMe are liq expls which are readily detond by expl shock, but are resistant to mech shock (Ref 28)
Sodium Methoxide. TeNMe explds violently in its presence (Ref 7)
TNT. The power by BalPend of mixts with TNT was 171, TNB 151, RDX 167, and EDNA 160% of TNT (Ref 31)
Toluene. A mixt with toluene expld at the Kaiser Wilhelm Inst in 1917, and in 1920 at the Univ of Münster a massive iron gas burner containing a residue of 10g of a TeNMe/toluene mixt decompd suddenly. The deton splintered the container, and of 300 students in the area, 10 were killed and 20 injured (Ref 13b). A mixt with toluene which has an OB of zero is called "Panclastite" in Fr. It has a deton vel of 8000 m/sec (NG 7000m/sec) and is more shock sensitive than NG (Ref 31)
Refs: 1) Beil **1**, 80, (21), [47], {116} & ⟨107⟩ 2) L. Schischkoff, Ann **119**, 246 (1861) 3) A. Hantzsch, Ber **39**, 2479 (1906) 4) A. Pictet & E. Khotinsky, Ber **40**, 1136 (1907) 5) F.D. Chattaway, JCS **97**, 2099 (1910) 6) I. Ostromisslenskii, JPraktChem (2) **84**, 489 (1911) & CA **6**, 1287 (1912) 7) A.K. Macbeth, Ber **46**,

2537 (1913) 8) J.N. Rakshit, JACS **36**, 1221 (1914) 9) A.K. Macbeth, JCS **107**, 1826 (1915) 10) A.W.C. Menzies, JACS **41**, 1337 (1919) 11) G. Tammann, NachGesWissGöttingen **1919**, 220 & CA **14**, 3532 (1920) 12) E. Schmidt & R. Schumacher, Ber **54**, 1418 (1921) 13) T. Henderson et al, JCS **123**, 1136 (1925) 13a) P.V. Mckie, JSCI **44**, 430T (1925) & CA **19**, 3373 (1925) 13b) A. Stettbacher, SS **25**, 439 (1930) & CA **25**, 1647 (1931) 14) A.K. Macbeth & W.B. Orr, JCS **1932**, 542 15) L. Médard, MP **25**, 451 (1932–33) & CA **28**, 5660 (1934) 16) T.T. Davies & D.L. Hammick, JCS **1938**, 763 17) H. Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen", Springer (1938), p 773 18) G.L. Lewis & C.P. Smyth, JACS **61**, 3067 (1939) 19) G. Kortüm, ZPhysChem(Leipzig) **B43**, 271 (1939) & CA **33**, 8115 (1939) 20) H.B. Hass, "The Synthesis of Certain Aliphatic Nitro Compounds", OSRD **154** (18 Oct 1941), p 19 21) R. McGill, "Evaluation of Explosives Submitted to the Explosives Research Laboratory in 1941", OSRD **830** (25 Aug 1942), p 56 22) W.A. Roth & K. Isecke, Ber **77**, 537 (1944) 23) G.V. Schulz et al, JMakrChem **2**, 127 (1944) 24) G.V. Schulz, Ber **80**, 241 (1947) 25) A.J. Clear & W.R. Tomlinson, Jr, "Development of Standard Tests, Application of the Impact and Sand Tests to the Study of Nitroglycerin and Other Liquid Explosives", PATR **1738** (13 June 1948), Table I 26) K.F. Hager, IEC **41**, 2185 (1949) 27) J.A. Hannum, USP 2559071 (1951) & CA **45**, 9836d (1951) 28) J.A. Hannum, USP 2560439 (1951) & CA **46**, 739b (1951) 29) E. Heilbronner, Helv **36**, 1121 (1953) & CA **47**, 11980i (1947) 30) P.H. Lindenmeyer & P.M. Harris, JChemPhys **21**, 408 (1953) 31) H. Muraour, MAF **28**, 520 (1954) & CA **49**, 2753b (1955) 32) P. Liang, "Tetranitromethane" in OrgSynColl Vol **3** (1955), p 803 33) J.G. Tshinkel, IEC **48**, 732 (1956) 34) F.C. Anderson et al, "Explosives Research", AGC **1200**, Contr N7onr-46208 (21 Dec 1956), p 10 35) I. Sakamaki et al, BunsekiKagaku **6**, 626 (1957) & CA **52**, 13540e (1958) 36) J.G. Tshinkel & C.R. Morrison, Chem & Eng Data Series **3**, 350 (1958) 37) F.S. Holahan et al, "The Use of Carbon-14 as a Tracer to Study the Origin of Tetranitromethane in TNT Manufacture", PATR **2695** (July 1960) (AD 241129 & PB 148304) 38) F.S. Holahan et al, JACS **84**, 756 (1962) 39) R.S. Bohon, AnalChem **35**, 1845 (1963) 40) H.G. Clark et al, USP 3067261 (1963) & CA **58**, 8904b (1963) 41) D.J. Glover & S.G. Landsman, AnalChem **36**, 1690 (1964) 42) I.M. Voskoboinikov et al, DoklAkadN **167**, 610 (1966) & CA **64**, 19366a (1966) 43) V.E. Gordeev et al, DoklAkadN **172**, 383 (1967) & CA **66**, 77920v (1967) 44) Urbański **3** (1967), 299 45) R.Kh. Kurbangalina, ZhPriklMekhTekhFiz **1969**, 133 & CA **71**, 126697s (1969) 46) Houben **X/1** (1971), p 11 47) Sax (1975)

METHANE, NITROSO. CH_3NO; mw 45.04, N 31.10%, OB to CO_2 –88.81%. It is a blue gas at room temp, its solns in hydrophobic solvs are blue, in w and hydrophilic solvs are colorl (Ref 2); CA Registry No 865-40-7

Preparation. It was first prepd by the irradiation of tert-butyl nitrite with a Hg-vapor lamp and isolated as a colorl dimer which, when heated above its mp of 122.0–2.2°, is converted to the blue monomer; prolonged heating of the dimer converts it to the insoluble trimer of formaldehyde oxime (Ref 2). It has also been prepd in varying yield by the irradiation of compds capable of producing Me radicals, such as dimethyl mercury (Ref 5), tert-butyl peroxide (Ref 8), azomethane, or Me iodide (Ref 10) in the presence of nitric oxide

Reactions. Monomeric nitrosomethane is condensed out at liq N temp to a pale blue solid which converts to the colorl dimer upon warming to room temp (Refs 6 & 7), and to formaldehyde oxime at higher temps (Ref 7). The structure proposed for the dimer is $CH_3N{:}NCH_3$ (O O) which can exist in cis and trans forms (Ref 6). The low yield of nitrosomethane in irradiation expts has been explained by its reactn with excess nitric oxide to form N dioxide, N, and polymeric prods (Ref 9)

Spectroscopic Data. Freshly prepd nitrosomethane has an IR absorption band at 6.3–6.4μ which slowly decays and is replaced by a band at 11μ characteristic of formaldehyde oxime (Ref 8). The visible absorption λ_{max} is 287mμ in eth and at 266–7mμ in w (Ref 4)

Refs: 1) Beil **1**, {105} & ⟨99⟩ 2) C.S. Coe

& T.F. Doumani, JACS **70**, 1516 (1948) 3) J.R. Raley et al, JACS **70**, 88 (1948) 4) H.T.J. Chilton & B.G. Gowenlock, JCS **1954**, 3174 5) W.A. Bryce & K.U. Ingold, JChemPhys **23**, 1968 (1955) 6) B.G. Gowenlock & J. Trotman, JCS **1955**, 4190 7) L. Batt & B.G. Gowenlock, TrFaradSoc **56**, 682 (1960) 8) J.G. Calvert et al, JACS **82**, 1 (1960) 9) M.I. Christie et al, JCS **1964**, 3147 10) M.I. Christie et al, TrFaradSoc **61**. 674 (1965)

Nitroso Halogen Derivatives of Methane

Difluoronitrosomethane, F_2CHNO, mw 81.03, N 17.29%; prepd by the photolysis of a mixt of chlorodifluoromethane & nitric oxide

Refs: 1) Beil – not found 2) M.G. Bellas et al, CanJChem **43**, 1022 (1965)

Trifluoronitrosomethane. F_3CNO; mw 99.01, N 14.15%; a deep blue solid, liq, or gas. The color of the liq is described as that of a concd ammoniacal Cu soln (Ref 2). The odor is described as earthy or similar to sewage sludge (Ref 2). Mp –196.6°, bp –84° (Refs 1 & 2); CA Registry No 334-99-6

Preparation. It was first isolated as a by-prod from the fluorination of Ag cyanide. Its formation was attributed to the presence of Ag nitrate or Ag oxide in the tech grade Ag cyanide used (Ref 2). The first prepn in good yield was by the irradiation in a sealed tube of a mixt of nitric oxide and trifluoromethyl iodide plus a small amt of Hg with the light from a Hg vapor lamp, yield 75% (Ref 3). The same workers also prepd trifluoronitrosomethane by the reaction of Ag trifluoroacetate with nitrosyl chloride (ClNO), yield 13% (Ref 5). More recent work indicated that this reaction proceeds thru the intermediate formation of the mixed anhydride of nitrous and trifluoroacetic acids ($F_3C\overset{\displaystyle O}{\overset{\|}{C}}ONO$) (Ref 11).

Another prepn reported is by heating trifluoroacetohydroxamic acid ($F_3CCONHOH$) to 85° at 30–40mm of Hg, yield 63% (Ref 10)

Chemical Reactions. It is readily oxidized with hydrogen peroxide to the nitro compd (Ref 4). It is stable in the absence of light or air for 3–5 years; but sunlight or irradiation with UV light converts it to o-nitroso-N,N-bis(trifluoromethyl)-hydroxylamine, $(F_3C)_2NONO$ (Ref 8). It reacts with perfluoroethylene to give a mixt of perfluoro-2-methyl-1,2-oxazetidine and a linear copolymer (Ref 6). This polymer, whose structure was shown to be $(CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{N}}O)_x$, has been been found to be an elastomer with very good chem resistance and low temp props. For a review of this type of elastomer see Ref 11

Heat of Vaporization. 4133cal/g, Trouton const 21.9 (Ref 7)

Spectra. Infra Red. The IR spectrum of a highly purified sample in the gas phase with assignment of bands is given in Ref 7

Visible. The intense blue color of the compd is due to a broad absorption band at 6800–40Å, ε_{max} = 19.0 (Ref 4). This band is present in the gas phase and in solns (Ref 9)

Toxicity. Its inhalation causes headaches and an unwell feeling (Ref 2)

Refs: 1) Beil **1**, {105} & ⟨99⟩ 2) O. Ruff & M. Giese, Ber **69**, 598 (1936) 3) R.N. Hazeldine, JCS **1953**, 2075 4) J. Banus, JCS **1953**, 3755 5) R.N. Hazeldine & J. Jander, JCS **1953**, 4172 6) D.A. Barr & R.N. Hazeldine, JCS **1955**, 1881 7) J. Mason & J. Dunderdale, JCS **1956**, 754 8) R.N. Hazeldine & B.J.H. Mattison, JCS **1957**, 1741 9) J. Mason, JCS **1957**, 3904 10) I.L. Knunyants & G.A. Sokol'skii, DoklAkadN **132**, 602 (1960) & CA **54**, 24366f (1960) 11) M.C. Henry et al, "Synthesis, Compounding, and Properties of Nitroso Rubbers" in P.R. Tarrand, ed, Fluorine Chemistry Reviews **1**, 1 (1967)

Chloronitrosomethane. See Chloromethane and Derivatives in this Vol

Chlorodifluoronitrosomethane. $ClCF_2NO$, mw 115.47; N 8.24%; a dark blue liq or gas; bp ca –35° (Refs 1, 2 & 6); CA Registry No 421-13-6

Preparation. It has been prepd by reactions analogous to those for prepn of trifluoronitrosomethane (Refs 2 & 5). It has also been prepd by the action of 33% aq nitric acid on chlorodifluorosulfenyl chloride ($ClCF_2SCl$) (Ref 3), and by the action of hot concd HCl on difluoronitroacetic acid (Ref 4). Its props and reactions are similar to trifluoronitrosomethane

Refs: 1) Beil **1**, ⟨99⟩ 2) R.N. Hazeldine, JCS **1953**, 1075 3) N.N. Yarovenko & S.P. Moronyi, ZnObsKhim **30**, 4066 (1960) & CA **55**, 20928e (1961) 4) A.V. Fokin et al,

ZhObshchKhim **36**, 540 (1966) & CA **65**, 613e (1966) 5) R.N. Hazeldine, USP 3083327 (1964) & CA **60**, 1588d (1964) 6) C.W. Taylor, USP 3342874 (1968) & CA **68**, 21546b (1968)

Dichlorofluoronitrosomethane. $FCCl_2NO$, mw 131.93, N 10.61%; a blue liq, bp 12° (Ref 2); CA Registry No 1495-28-9. It is prepd by the action of 33% nitric acid on $FCCl_2SCl$, yield 8% (Ref 2); and by the action of K chloride on fluorochloronitroacetic acid (Ref 3)

A soln of the compd in eth was treated overnight with hydrogen sulfide in a sealed tube to give FClC:NOH which polymerized in a few days (Ref 2)

Refs: 1) Beil – not found 2) N.N. Yarovenko & S.P. Motornyi, ZhObshchKhim **30**, 4066 (1960) & CA **55**, 20928e (1961) 3) I.V. Martynov & Yu.L. Krugylak, ProblOrganSinteza-AkadNaukSSSR, OtdObshchITeknKhim **1965**, 56 & CA **64**, 8022h (1964)

Trichloronitrosomethane. Cl_3CNO, mw 148.39, N 9.51%, OB to CO_2 −10.78%; a deep blue liq, comparable in color to ammoniacal Cu solns; freezes at liq N temp to a violet-blue solid; bp 57–58°; d at 20°, 1.500g/cc (Refs 1, 2 & 3); CA Registry No 3711-49-7

Preparation. It was first prepd by the action of 10% nitric acid on Na trichloromethanesulfonate (Cl_3CSO_2Na) (Ref 2). It has also been prepd by the reduction of chloropicrin (Cl_3CNO_2) at a Pt cathode in 40% aq sulfuric acid contg et alc (Ref 4); by heating trichloroacetohydroxamic acid ($Cl_3CCONHOH$) to 90° and 20–30mm, yield 62% (Ref 5); and by the interaction of Na trichloromethanesulfonate and nitrosyl chloride in a sealed tube (Ref 7). Most interesting is the report that when nitric oxide was passed thru C tetrachloride while being irradiated with high-energy electrons, the soln turned dark blue, and a 50% yield of trichloronitrosomethane was obtd (Ref 6)

Chemical Reactions. It decomps slowly on standing, more rapidly on heating in the absence of air to form nitrosyl chloride, nitric oxide, chloropicrin, & trichloromethyldichloromethyl-eneimine ($Cl_3CN{:}CCl_2$) (Ref 2). It deflagrates in the presence of O_2 at 120° to give N dioxide, chloropicrin, and hexachloroethane (Ref 2). It is reduced to Me amine with Fe turnings and acet ac (Ref 2); and to phosgene oxime ($Cl_2C{:}NOH$) with hydrogen sulfide in Me alc (Ref 2), or Sn dichloride and HCl (Ref 3)

Solubility. It is insol in w, sol in org solvs (Ref 2)

Refs: 1) Beil **1**, [39], {105} & ⟨99⟩ 2) W. Prandtl & K. Sennewald, Ber **62**, 1754 (1929) 3) W. Prandtl & W. Dollfus, Ber **65**, 754 (1932) 4) H. Brintzinger et al, ZElektrochem **53**, 109 (1949) & CA **43**, 8915 (1949) 5) I.L. Knunyants & G.A. Sokol'skii, DoklAkadN **132**, 602 (1960) & CA **54**, 23466f (1960) 6) A. Hengleim, LargeRadiationSourcesInInd, ProcCong-Warsaw **2**, 139 (1959) & CA **55**, 19762c (1961) 7) H. Sutcliffe, JOC **30**, 3221 (1965)

Bromodifluoronitrosomethane. $BrCF_2NO$, mw 159.93, N 8.76%; it is a dark blue solid & liq; bp ca −12°. It is prepd by the irradiation of a mixt of bromodifluoroiodomethane and nitric oxide in a sealed tube in the presence of Hg, yield 50%

Refs: 1) Beil **1**, ⟨100⟩ 2) R.N. Hazeldine, JCS **1953**, 2075

Bromodichloronitrosomethane. $BrCCl_2NO$, mw 192.84, N 7.26%; it is a dark blue liq of unpleasant odor, fr p −80°, bp 21° at 24mm. It is prepd by the action of Br and Na acetate on phosgene oxime ($Cl_2C{:}NOH$). It decomps on attempted distn at atm press. It is reduced to phosgene oxime with hydrogen sulfide in Me alc, and warming with Br produces dichlorodibromomethane

Refs: 1) Beil **1**, {105} 2) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

Chlorodibromonitrosomethane. $ClCBr_2NO$, mw 237.31, N 5.90%; it is a dark blue liq of unpleasant odor, it freezes at −80°, bp 24° at 20mm; it can only be distd in a vacuum. It is prepd by action of Br and Na acetate in w on bromochloroformoxime (BrCCl:NOH). Heating with Br forms chlorotribromomethane

Refs: 1) Beil **1**, {105} 2) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

Tribromonitrosomethane. Br_3CNO, mw 281.77, N 4.97%; it is a dark blue liq of unpleasant odor; bp 36–38° at 14mm, decomps above 50°. It is prepd by the action of K hypobromite on MF (Ref 2), or by the action of KBr and Na acetate on MF (Ref 3). Upon warming with w forms tetrabromomethane and cyanogen bromide (Ref 3)

Refs: 1) Beil **1**, {106} 2) G. Endres & H. Bottmann, Ber **65**, 67 (1932) 3) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

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