the importance of the steric factor. This was also pointed out by Preckel and Selwood.[4]

Another point which should be emphasized is that there is a difference in the di- and tetra-substituted β-naphthyl derivatives (6 and 13%), whereas in the alkyl substituted compounds in this general series these differences between di- and tetra-substituted compounds were not found.[1] However, the hexa-substituted derivatives in the alkyl and aryl series all seem to fall in about the same range (25–35%). From the data of Gomberg and Schoepfle[7] it seems likely that our 0.1 M solutions of di-α-naphthyltetraphenylethane were supersaturated.

All of the aryl-substituted ethanes except tetra-p-biphenyldiphenylethane were relatively stable as indicated by the constant value for their magnetic susceptibilities over twenty-four hour periods. Tetra-p-biphenyldiphenylethane solutions deposited heavy white crystalline precipitates in twenty-four hours. Hexa-β-naphthylethane showed a decrease in color and a change in magnetic susceptibility on exposure to diffused daylight over a period of one week.

(7) Gomberg and Schoepfle, This Journal, **39**, 1652 (1917).

The following new compounds were characterized:

Phenyldi-β-naphthylmethylperoxide, m. p. 168–169°.

Anal. Calcd. for $C_{34}H_{38}O_2$: C, 90.25; H, 5.30. Found: C, 90.12; H, 5.84.

Phenyldi-p-biphenylmethylperoxide, m. p. 151–152°.

Anal. Calcd. for $C_{12}H_{46}O_2$: C, 90.51; H, 5.59. Found: C, 90.54; H, 5.94.

Phenyldi-β-naphthylmethylchloride, m. p. 159–160°.

Anal. Calcd. for $C_{27}H_{17}Cl$: Cl, 9.42. Found: Cl, 8.92.

Summary

The degrees of dissociation of several hexaphenylethanes combining α-naphthyl, β-naphthyl and p-biphenyl radicals have been examined by the magnetic susceptibility method. The dissociations observed are lower than reported in the older literature. The difference in the effect of an α- and a β-naphthyl group on the degree of dissociation is very marked.
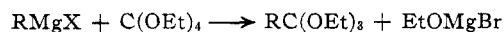

The Preparation of Orthoesters

BY S. M. MCELVAIN AND J. WALTER NELSON

The work in this Laboratory to date indicates that the only general method that is available for the preparation of ketene acetals of the type $RCH=C(OEt)_2$ involves the elimination of the elements of ethyl hypohalite from an α-halogenated orthoester by the action of metallic sodium.[1] Consequently, the preparation and study of these higher ketene acetals are dependent upon the availability of the corresponding orthoesters as starting materials. The present paper is a summary of a large number of experiments which had as their objective practical and reliable procedures for the preparation of the esters of ortho acetic acid, certain of its derivatives and higher homologs.

Two methods of preparation of orthoesters that would seem to be of general applicability have been reported in the literature. One of these is

(1) Walters and McElvain, This Journal, **62**, 1482 (1940).

the Tschitschibabin procedure[2] which involves the reaction of a Grignard reagent with ethyl orthocarbonate

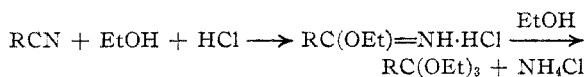$$RMgX + C(OEt)_4 \longrightarrow RC(OEt)_3 + EtOMgBr$$

This procedure is analogous to the widely used Tschitschibabin method for the preparation of acetals by the reaction of a Grignard reagent with ethyl orthoformate, $HC(OEt)_3$. While the latter reaction is a very useful preparational method, all of the experience in this Laboratory points to the conclusion that the reaction between a Grignard reagent and orthocarbonic ester is not a satisfactory method of preparation of orthoesters. Instead of the desired orthoester the reaction products are practically wholly a mixture of the ketal $R_2C(OEt)_2$ and the ether R_3COEt and all attempts to alter this result have been consistently unsuccessful.[3]

(2) Tschitschibabin, *Ber.*, **38**, 563 (1905).
(3) McBane, M.S. Thesis, University of Wisconsin, 1941.

The other general method that appears in the literature was originated by Pinner[4] and involves the alcoholysis of an iminoester hydrochloride which is obtained from a nitrile. These reactions are

$$RCN + EtOH + HCl \longrightarrow RC(OEt){=}NH{\cdot}HCl \xrightarrow{EtOH} RC(OEt)_3 + NH_4Cl$$

Reiter and Hess[5] used Pinner's method and reported 40–64% yields of ethyl orthoacetate from the alcoholysis of the iminoester hydrochloride over a period of eight to fourteen days. Sah[6] used this procedure for the preparation of a number of alkyl esters of orthoacetic acid. He allowed the alcoholysis of the iminoester salt to proceed at room temperature for a period of two weeks. Brooker and White[7] have reported the preparation, by the same procedure, of the methyl esters of orthopropionic, -n-butyric, -n-valeric, -n-caproic and -isocaproic acids. With the exception of the propionate (69% yield) the yields of the orthoesters from the iminoester salts were quite low (9–40%) and the time required for the alcoholysis varied from five to thirty-five days.

In the work which is now reported it has been found possible to shorten considerably the time required for the alcoholysis of the iminoester hydrochlorides and to increase materially the yields of the esters of orthoacetic acid and certain of its higher homologs. This has been accomplished by carrying out the alcoholysis of these salts in a refluxing ether solution. Under these conditions the alcoholysis is complete in six to twenty-eight hours and the reaction temperature is kept below the point (60–80°) at which the competing decomposition of iminoester hydrochloride into the amide and ethyl chloride, $RC(OEt){=}NH{\cdot}HCl \rightarrow RCO{-}NH_2 + EtCl$, occurs. In marked contrast to these results is the strange fact that the iminoester hydrochloride derived from the negatively substituted acetonitrile, chloroacetonitrile, gives a better yield of the orthoester if the alcoholysis is carried out simply with the alcoholic solution of the hydrochloride stirred at a temperature of approximately 40°. In this case the use of ether is detrimental to the yield of the orthoester.[8]

Table I is a summary of (a) the reaction time

(4) Pinner, Ber., **16**, 356, 1644 (1883).

(5) Reiter and Hess, ibid., **40**, 3020 (1907).

(6) Sah, This Journal, **50**, 516 (1928).

(7) Brooker and White, ibid., **57**, 2485 (1935).

(8) Messrs. H. I. Anthes and P. M. Walters in this Laboratory have had similar experiences in the preparation of two other negatively substituted orthoacetates, ethyl orthophenylacetate and ethyl orthoethoxyacetate.

required for the alcoholysis of the iminoester hydrochlorides when a ratio of 15 moles of alcohol to 1 mole of the salt is used (this ratio of alcohol to salt is necessary to completely dissolve the salt), (b) the optimum ratio by volume of alcohol to ether, (c) the reaction temperature (which is the refluxing temperature when ether is used) and (d) the yields of ammonium chloride and the orthoesters. Each entry in this table covers at least eight runs. When the amount of ether in the alcoholysis mixture was less than the optimum ratio shown in Table I, the yields of the first six unsubstituted orthoesters dropped markedly. When no ether was used the yields were generally 30–50% of those shown in Table I. The yields of ethyl orthochloroacetate varied from 40% with an alcohol–ether ratio of 1:2 through 50% for a 1:1 ratio and up to the yields indicated in Table I when no ether was used.

TABLE I

ALCOHOLYSIS OF IMINOESTER HYDROCHLORIDES, $RC(OEt){=}NH{\cdot}HCl$

R is	Reaction time, hr.	Alcohol ether ratio	Reaction temp., °C.	Yield, % NH₄Cl	Yield, % RC(OEt)
CH₃	6	1:1	46	100	75–78
C₂H₅	9	1:2	42	95	75–78
n-C₃H₇	18	1:3	41	96	60–63
i-C₃H₇	24	1:5	39	54	27–30
n-C₄H₉	12	1:3	42	88	59–61
i-C₄H₉[a]	28	1:5	39	56	21–23
ClCH₂	6	1:0	40	89	70–73

[a] This ester was prepared by Robert L. Clarke. In addition to the orthoester a 14% yield of isovaleramide and a 21% yield of ethyl isovalerate were isolated.

It is seen from the data in Table I that under these optimum reaction conditions the alcoholysis of those iminoester hydrochlorides in which R is a primary and normal alkyl group is quite complete. The yield of ammonium chloride is obviously the most accurate measure of this reaction since it is obtained by simply filtering off the salt from the alcoholysis reaction mixture. The nitrogen that is not in the form of ammonium chloride appears as the amide, $RCONH_2$, and in those cases (R is a branched chain) in which the yield of the ammonium salt is low, the amide is a troublesome factor in the purification of the orthoester. While the yield of the orthoester theoretically should be the same as that of the ammonium chloride, it is generally considerably lower due, quite probably, to some hydrolysis to the normal ester, RCOOEt, during the necessary washing of the ethereal reaction mixture to remove

any unchanged salt and amide as well as to the incomplete separation of the orthoester by fractionation.

Experimental

Iminoester Hydrochlorides.—The following general procedure was followed for the preparation of these salts. To an ice-cooled solution of 1 mole of the appropriate nitrile (distilled from phosphorus pentoxide) in 1.1 moles of absolute alcohol, dry hydrogen chloride was added until 1.1 moles had been absorbed. The resulting solution then was allowed to stand at 0° in the refrigerator for the time indicated in the second column of Table II, after which time absolute ether was added in the quantity shown in the third column of Table II. In the cases of acetonitrile and chloroacetonitrile the precipitation of the hydrochloride was so rapid that it was found advisable to mix the ether with the alcohol solution of the nitrile *prior* to the addition of the hydrogen chloride in order to prevent the solidification of the reaction mixture before the addition of the hydrogen chloride was completed; upon cooling to −30° the first crop of crystals of these hydrochlorides could be filtered off immediately. In the cases of the other imino

TABLE II
IMINOESTER HYDROCHLORIDES, RC(OEt)=NH·HCl

R is	Reaction time at 0°	Alcohol–nitrile ether ratio[a]	Yield, %, hydrochloride
CH₃	2 hr.	1:0.5[b]	85–95
C₂H₅	6 hr.	1:4	85–95
n-C₃H₇	4 days	1:4	65–70
i-C₃H₇	4 days	1:4	70–90
n-C₄H₉	5 days	1:4	70–80
i-C₄H₉	6 days	1:6	35–40
ClCH₂	..	1:8[b]	80–90

[a] This is the ratio *by volume* of the alcohol–nitrile mixture to ether. [b] In these runs the ether was added to the alcohol solution of the nitrile before the addition of the hydrogen chloride.

and phosphorus pentoxide after which it was triturated under sufficient cold (−40°) anhydrous ether to cover it and again filtered and dried in the desiccator. On standing for a few more days in the refrigerator the mother liquor generally yielded additional crops of crystals. After the ether washing the salt does not give an acid reaction to moistened congo red paper and is in the proper condition for alcoholysis. If placed in tightly stoppered bottles or in a vacuum desiccator it may be kept for several weeks without deterioration.

The conditions for the preparation and the yields of the various iminoester hydrochlorides are shown in Table II.

Preparation of Orthoesters.—A mixture of 0.2 mole of the iminoester hydrochloride and 3 moles of absolute alcohol in a flask of suitable size fitted with a reflux condenser, an efficient stirrer and a thermometer dipping into the reaction mixture was carefully protected against moisture and stirred until the salt went into solution. Then the quantity of anhydrous ether indicated in Table I was added through the neck holding the thermometer. The ethereal solution was refluxed (in the cases when ether was not used the alcohol solution was kept at 40°) by an electrically heated oil-bath for the time indicated in Table I. After this time the reaction mixture was cooled to 0° and the precipitated ammonium chloride filtered off by suction. The filtrate (50 ml. of ether was added before filtration in those cases in which ether was not used in the alcoholysis) was washed with an equal volume of 10% sodium carbonate solution and then with 50 ml. of a saturated solution of sodium carbonate and after drying over anhydrous potassium carbonate it was fractionated under about 10–30 mm. pressure. In the case of ethyl orthoacetate it was found necessary to carry out the fractionation at atmospheric pressure and with an efficient Widmer column to obtain the yields that are reported in Table I. The boiling points of the various orthoesters together with other properties and analyses of those not previously described in the literature are listed in Table III.

TABLE III
PROPERTIES AND ANALYSES OF ORTHOESTERS RC(OC₂H₅)₃

| | | B. p., | | | | | | Analyses, % | | | | |
| | | | | | | | Calcd. | | | Found | | |
R is	Formula	°C.	mm.	d²⁵₄	n²⁵D	C	H	EtO	C	H	EtO[a]
CH₃[b]	...	144–146	740	..	....	..	..	..	..	..	..
C₂H₅[c]	...	70–72	32	...	....	..	..	..	..	..	..
n-C₃H₇	C₁₀H₂₂O₃	58–59	7	0.875	1.4028	63.1	11.7	71.0	63.1	11.6	69.0
i-C₃H₇	C₁₀H₂₂O₃	50–51	7	.871	1.4002	63.1	11.7	71.0	63.4	11.5	68.5
n-C₄H₉	C₁₁H₂₄O₃	49–50	3	.873	1.4086	64.7	11.8	66.2	64.4	11.8	64.9
i-C₄H₉[d]	C₁₁H₂₄O₃	57–59	7	.869	1.4056	64.7	11.8	66.2	64.7	11.8	..
ClCH₂[e]	...	68–70	10	...	....	..	..	..	..	..	..

[a] Found ethoxy values of these orthoesters generally are lower than the theoretical just as they are with the ketene acetals. [b] Ref. 6. [c] Ref. 1. [d] Prepared and analyzed by Robert L. Clarke. [e] Beyerstedt and McElvain, THIS JOURNAL, **59**, 1273 (1937).

ester hydrochlorides the resulting ethereal solution[9] was allowed to stand in the refrigerator overnight after which it was cooled to −30° in dry-ice and the precipitated salt rapidly filtered by suction. The salt was dried in a vacuum desiccator over dishes of solid potassium hydroxide

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(9) The use of ether at this point is for the purpose of preventing the formation of a hard cake and to cause the salt to precipitate as small and more pure crystals.

Summary

The conversion of acetonitrile, certain of its higher homologs and chloroacetonitrile into iminoester hydrochlorides, and the alcoholysis of these salts to the corresponding orthoesters in good and reproducible yields are described.

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