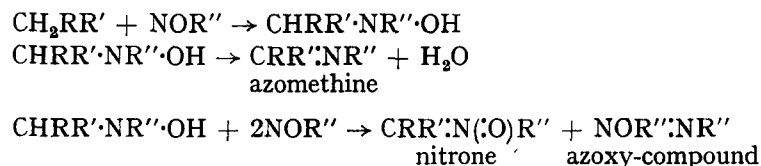


REACTIVE METHYLENE GROUPS. III.* THE EHRLICH-SACHS REACTION

By A. McGOOKIN

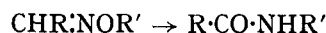
The Ehrlich-Sachs reaction generally results in the production of a mixture of azomethine(anil), nitrone and azoxy-compound. A method is described whereby the azomethine is the sole product.

The Ehrlich-Sachs reaction¹ consists in condensing a reactive methylene compound with an aromatic nitroso-compound in aqueous-alcoholic sodium carbonate. Varying quantities of nitrones† and azoxy-compounds are formed in addition to the azomethine(anil), and separation is often difficult. The reaction is generally expressed as follows:



and the presence of azoxy-compounds, in addition to nitrones, has been observed in confirmation. The nitrones have often been erroneously formulated but, since they are a type of *N*-oxide, their structure must be that indicated above.

A further complication, in some cases, is the conversion of the nitrone into the corresponding anilide:^{2, 3}



It has now been found that azomethines may be obtained in good yield, and free from other products, by a modification of the Ehrlich-Sachs method, namely by employing absolute methanol as solvent and anhydrous potassium carbonate as condensing agent, and by using equimolecular proportions of the two reactants.

Experimental

2 : 4-Dinitrobenzaldehyde-*p*-dimethylaminophenylazomethine.—2 : 4-Dinitrotoluene (13 g.) and pure *p*-nitrosodimethylaniline⁶ (10.7 g.) were dissolved in pure methanol (72 ml.) and anhydrous potassium carbonate (22 g.) was added. After refluxing for $\frac{1}{2}$ hour the solution turned reddish-brown. The solvent was removed *in vacuo* and the dark residue recrystallized from hot, dry acetone, then benzene, forming green leaflets, m.p. 211° (20.1 g., 90%).

Benzoyl cyanide *p*-dimethylaminophenylazomethine.—Benzyl cyanide (4.68 g.) and *p*-nitrosodimethylaniline (6.0 g.) were dissolved in methanol (50 ml.) and potassium carbonate (12 g.) was added. The mixture turned red immediately on heating. After refluxing for 1 hour the solvent was removed *in vacuo* and the crimson solid dried and recrystallized from methanol, forming clusters of brick-red prisms (9.95 g., 99%) with a blue reflex, m.p. 90°. Recrystallization from light petroleum (60–80°) or acetic acid did not raise the m.p. (Found: N, 17.07. Calc. for C₁₆H₁₆N₃: N, 16.8%).

Isatin-3-*p*-dimethylaminophenylazomethine.—Oxindole (1.23 g.), *p*-nitrosodimethylaniline (1.5 g.), methanol (20 ml.) and potassium carbonate (3 g.) were refluxed for 1 hour. The solvent was removed as before and the residue extracted with ethyl acetate. Recrystallization from aqueous pyridine afforded coppery needles (2.5 g., 94%), m.p. 220° (decomp.). The product was soluble in benzene, alcohol, chloroform, ethyl acetate and pyridine (Found: N, 15.83. C₁₆H₁₅ON₃ requires N, 15.84%). The azomethine (0.45 g.) was dissolved in benzene (50 ml.) and boiled with 50% hydrochloric acid for 2 hours. Recrystallization of the red solid from hot

* Part II: *J. Soc. chem. Ind., Lond.*, 1950, **69**, 186

† This name was originally suggested by Pfeiffer.⁴ Others⁵ have since been suggested but the original term is retained here.

water furnished red needles (0.24 g.), m.p. 200°, undepressed when mixed with an authentic specimen of isatin.

2 : 4 : 6-Trinitrobenzaldehyde-*p*-dimethylaminophenylazomethine.—2 : 4 : 6-Trinitro-toluene (2.27 g.), *p*-nitrosodimethylaniline (1.5 g.), potassium carbonate (5 g.) and methanol (20 ml.) were refluxed for 2 hours. On cooling, a black solid separated. Recrystallization from acetone-chloroform gave lustrous dark-green crystals (3 g., 95%), m.p. 268° (decomp.) (Found: N, 19.62. Calc. for $C_{18}H_{13}O_6N_5$: N, 19.5%).

Cyanoglyoxylamide-*p*-dimethylaminophenylazomethine.—Cyanoacetamide (2.1 g.), *p*-nitrosodimethylaniline (3.75 g.), potassium carbonate (10 g.) and methanol (20 ml.) turned dark red in the cold and became warm. After 1 hour under reflux the solvent was removed and the dark-red solid chromatographed on an alumina column by using benzene. Recrystallization from acetone or ethyl acetate afforded pale-brown plates, m.p. 172° (Found: C, 61.30; H, 5.62; N, 25.48. $C_{11}H_{13}ON_4$ requires C, 61.1; H, 5.56; N, 25.9%); yield 5 g. (92%). Sachs⁷ described this compound as of m.p. 220–221°. Possibly these compounds are stereoisomers.

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PHASE EQUILIBRIA IN SUGAR SOLUTIONS. VI.* THE QUATERNARY SYSTEM SUCROSE-FRUCTOSE-POTASSIUM CHLORIDE-WATER

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Equilibrium-phase relationships of the quaternary system sucrose-fructose-KCl-water have been determined at 30°. No double compounds or hydrates were identified. The total concentration of solute increased as conditions approached the quaternary point (Q.P.), but reached a maximum before actually reaching this point. This experience was independent of the direction of approach to the Q.P., although the actual point of highest solute concentration was for a solution in equilibrium with both fructose and KCl as solid phases. Results have been plotted by using a Jänecke type of projection on a triangular diagram with isohydrores defined quantitatively as solvent per 100 units of total dissolved solids.

Introduction

The three ternary systems sucrose-fructose-water, sucrose-KCl-water and fructose-KCl-water were investigated first, and the results have been published elsewhere.¹ This work has now been extended to include conditions under which all three of these solutes are in solution and saturated with respect to one or more of the solutes. From the study of the ternary systems it was expected that the quaternary system would be unlikely to include double compounds or hydrates. It was also expected that the solutions, particularly in the neighbourhood of the quaternary point (Q.P.), would be very viscous, and high in total solids concentrations. The only feature of the results not altogether expected was the observation that the Q.P. was not the point of maximum solute concentration. This was confirmed from a number of determinations made within the vicinity of the Q.P., and later work indicated that this system is not unique in this

* Part V: *J. appl. Chem.*, 1954, **4**, 411