Bernal[2] concluded from X-ray data that the dodecyl alcohol molecule rotated around its long axis in the solid just below the melting point and not at lower temperatures. In agreement with the indications of the dielectric constant data, these facts indicate that, when the long axes of the molecules lie perpendicular to the planes in which their heads lie, they may rotate around their long axes, thereby permitting their dipoles to make some contribution to the dielectric constant and raise its value above that of a similar solid in which no molecular rotation is possible. This does not preclude the possibility of some slight intramolecular dipole orientation through turning of groups in the molecule as found by Bridgman and Williams[32] nor does it mean the complete absence of the orientation of an occasional molecule in the β-lattice. It does mean, however, that the major part of any excess of the polarization of these solids over that arising from mere electronic shifts is due to molecular rotation, and by molecular rotation is meant not necessarily completely free rotation about the long axis of the molecule but also an ability to rotate from one position of minimum potential energy in the lattice to another.

Summary

The dielectric constants of ethyl undecylate, palmitate and stearate and cetyl alcohol have been measured over a wide range of temperature and frequency in the liquid and solid states in order to investigate the possibility of molecular rotation in the solid forms. Ethyl undecylate shows no general freedom of molecular rotation in the solid, the melting temperature evidently being too low to permit the molecules to acquire sufficient rotational energy to overcome the intermolecular forces. Ethyl palmitate undergoes a solid α–β transition at its freezing point and, during the process, shows greater freedom of molecular rotation than in the liquid. It also shows a slight transition in the β-form not hitherto detected. Ethyl stearate shows molecular rotation around the long axis in the α-form. Cetyl alcohol shows molecular rotation in the α-form accompanied by strong anomalous dispersion of the dielectric constant. In the α-forms where the long molecules lie perpendicular to the planes in which their heads lie, rotation around the long axes of the molecules appears to be possible, but, in the β-forms where the molecules are tilted with respect to the planes and more closely packed, no general freedom of rotation is found.

PRINCETON, NEW JERSEY RECEIVED MARCH 7, 1938

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[32] Bridgman and Williams, THIS JOURNAL, **59**, 1579 (1937).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF CITY OF NEW YORK]

Alkanolamines. V. Reaction of *m*-Dinitrobenzene with Ethanolamines

BY M. MELTSNER, I. KIRSHENBAUM AND A. STEMPEL

Clark[1] reported that 2,4-dinitrochlorobenzene reacted with monoethanolamine to yield 2,4-dinitrophenylaminoethanol.

Raccui[2] found that 3,4,6-trinitrotoluene condensed with di- and triethanolamines to give addition compounds.

Inasmuch as no reduction products were reported, contrary to our experience with nitrobenzene and nitrochlorobenzene, as described in previous papers,[3] we thought it advisable to publish our results with *m*-dinitrobenzene and the ethanolamines.

3,3′-Dinitroazoxybenzene, 3,3′-diaminoazoxybenzene, 3,3′-diaminoazobenzene and an addition product containing 2 moles of 3,3′-diaminoazoxybenzene and 3 moles of triethanolamine were isolated as products of the reaction between the dinitro compound and the three ethanolamines. Traces of nitroaniline were found but no phenylenediamine. As each of the ethanolamines shows a different alkalinity, the yields of each product would vary with the type and concentration of each ethanolamine. Since previous experiments have shown that azo compounds can be reduced by ethanolamines to amines, the non-formation of phenylenediamine is probably due to decomposition at the temperature of the experiments. The formation of an addition product of the diaminoazoxybenzene would seem to indicate that addition precedes reduction.

Experimental

Reduction with Diethanolamine and Water.—Eighty-four grams of diethanolamine and 20 cc. of water were added

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[1] Clark, *Ind. Eng. Chem.*, **25**, 1385 (1933).

[2] Raccui, *C. A.*, **29**, 6217 (1935).

[3] Meltsner, *et al.*, THIS JOURNAL, **59**, 2660 (1937); Kremer, *ibid.*, **59**, 1681 (1937); Kremer and Kress, *ibid.*, **60**, 1031 (1938).

dropwise to 34 g. of melted *m*-dinitrobenzene. The mixture was refluxed carefully for three hours and then steam distilled to remove unreduced *m*-dinitrobenzene. The residue was extracted with hot benzene. The benzene was evaporated and the residue yielded a red compound. After recrystallization from alcohol and benzene, the compound, m. p. 140°, gave on analysis: C, 52.99; H, 2.92; N, 20.82. Calculated for dinitroazobenzene: C, 52.94; H, 2.94; N, 20.58.

Reduction with Diethanolamine.—Thirty-four grams of *m*-dinitrobenzene and 84 g. of diethanolamine were refluxed as above for three hours. Steam distillation yielded a distillate from which ether extracted a trace of a compound, m. p. 110°, which gave tests for the amino group. This compound is probably *m*-nitroaniline.

The residue from the steam distillation was cooled and filtered from the tarry solids which were then treated with hot benzene. There was finally obtained after recrystallization an orange compound, m. p. 145°, which formed a white hydrochloride charring at 240° and a diacetyl compound melting at 265° corresponding to 3,3′-diaminoazobenzene. A small amount of 3,3′-diaminoazoxybenzene was isolated.

Reduction with Triethanolamine.—One hundred and nineteen grams of triethanolamine and 34 g. of *m*-dinitrobenzene were refluxed for three hours at 160–170°. The mixture was treated with hot water and filtered. The insoluble solids were extracted with benzene, the benzene evaporated and the residue recrystallized from alcohol. There was thus obtained a red compound, m. p. 144°, insoluble in hydrochloric acid, and forming no acetyl derivative. The compound is probably 3,3′-dinitroazoxybenzene reported in the literature as having m. p. 143–146°.

The filtrate was steam distilled and the residue extracted with ether. Evaporation of the ether left an orange residue from which by recrystallization from water there was obtained a yellow compound, m. p. 109°. This compound gave the usual tests for an amino group: N, 21.31; calculated for $2NH_2C_6H_4 \cdot N_2OC_6H_4NH_2N(CH_2CH_2OH)_3$, *i. e.*, addition product of the azoxy compound and triethanolamine, N, 20.82. It formed an acetyl derivative corresponding to the aminoazoxy compound.

Reduction with Excess Triethanolamine.—The molar ratio of *m*-dinitrobenzene to triethanolamine was 1 to 6. The mixture was refluxed for three hours over a free flame. treated with hot water and allowed to stand. The water insolubles were filtered off and yielded 3,3′-dinitroazoxybenzene. The filtrate was extracted with ether. The residue obtained after evaporation of the ether was treated with hot water. The water-soluble portion upon cooling deposited the same addition compound as in the previous experiment while the insoluble portion yielded 3,3′-diaminoazobenzene.

Reduction with Monoethanolamine.—To 34 g. of molten *m*-dinitrobenzene was added slowly 48.8 g. of monoethanolamine and refluxed for three hours with a small flame. The mixture was treated with 200 cc. hot water and filtered. The filtrate was cooled and the solid that separated was extracted with benzene. Petroleum ether was added to the benzene extract. A crystalline precipitate of 3,3′-diaminoazobenzene settled out.

Summary

The ethanolamines reduce *m*-dinitrobenzene to the nitroazo, aminoazo, aminoazoxy stages. An addition compound of the aminoazoxy and triethanolamine was isolated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Application of the Cyano Ester Ring Closure to Five- and Six-Membered Rings

BY REYNOLD C. FUSON AND WAYNE COLE

A simple method of closing the cyclobutane ring was discovered by Fuson and Kao,[1] who prepared ethyl 1-cyano-1,2-cyclobutanedicarboxylate (II) by treating ethyl α,α′-dibromoadipate (I) with sodium cyanide.[2] That the reaction may prove to be generally useful in synthesizing cyclobutane derivatives has been indicated by its successful application in the preparation of a methylcyclobutanedicarboxylic acid[3] and norcaryophyllenic acid.[4] Where it is applicable, this synthesis is superior to other methods of closing the cyclobutane ring, because it affords higher yields and involves a comparatively simple procedure.

The present work was undertaken with the object of determining whether this method of ring closure could be extended to the synthesis of rings of other sizes. The attempts have been successful for cyclopentane and cyclohexane rings.

For the synthesis of a five-membered ring, ethyl α,α′-dibromopimelate (III) was employed. Treatment with sodium cyanide in absolute alcohol converted this ester into ethyl 1-cyano-1,2-cyclopentanedicarboxylate (IV) in yields of 80 to 88%. As was to be expected, these are somewhat

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[1] Fuson and Kao, THIS JOURNAL, **51**, 1536 (1929).

[2] The method is novel, but the reaction which it involves has long been known to take place with open chain compounds. See, for example, Franchimont, *Ber.*, **5**, 1048 (1872); Zelinsky, *ibid.*, **21**, 3160 (1888); Poppe, *ibid.*, **23**, 113 (1890); Bone and Perkin, *J. Chem. Soc.*, **69**, 253 (1896).

[3] Fuson, Kreimeier and Nimmo, THIS JOURNAL, **52**, 4074 (1930).

[4] Rydon, *J. Chem. Soc.*, 593 (1936).