

est refractive index,  $\alpha$ , lies in the main prism face at right angles to the prism length. The other two vibration directions  $\beta$  and  $\gamma$  are parallel to the thickness and length of the crystal but could not be identified as the crystal is almost uniaxial. This agrees with Crowfoot's determination of the sign of the birefringence as negative.

The "c" axis was found to be 111 Å. and corresponds in direction to  $\alpha$ , the crystal width. The crystal length, "a," is 60 Å. and the thickness "b" is 62 Å. These values agree very well with Crowfoot's cell values 110, 60 and 63 Å., respectively. This identifies the material as the lactoglobulin that Crowfoot studied, and, therefore, her unit cell measurements 154, 67.5 and 67.5 for the wet crystals can be used to determine cell shrinkage in the various crystal directions. The agreement between these shrinkages and those observed by McMeekin and Warner on the actual crystal is very good. It is also interesting to note that the approximate uniaxial optic character of the crystal agrees with the approximate tetragonal shape of the unit cell. This may, of course, be only a coincidence and have no bearing on any characteristics of the molecular arrangement.

ANDERSON INSTITUTE FOR BIOLOGICAL RESEARCH  
RED WING, MINNESOTA, AND THE  
DEPARTMENT OF PHYSIOLOGY  
UNIVERSITY OF MINNESOTA  
MINNEAPOLIS, MINN.

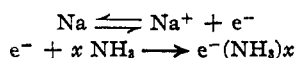
RECEIVED JULY 9, 1942

## The Hydrogenation of Disubstituted Acetylenes

BY KENNETH W. GREENLEE AND W. CONARD FERNELIUS

Campbell and Eby<sup>1</sup> have recently shown that the treatment of dialkylacetylenes with sodium in liquid ammonia produces the pure *trans* forms of the corresponding olefins. These investigators offer no explanation for this startling phenomenon. The following suggested mechanism seems to account satisfactorily for the observed results.

A solution of sodium in liquid ammonia contains electron ions<sup>2</sup>

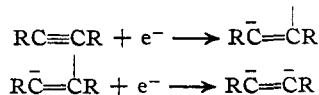


The reaction of sodium with double and triple bonds consists in the addition of electrons<sup>3</sup>

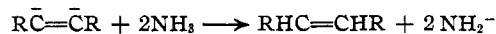
(1) K. N. Campbell and L. T. Eby, *THIS JOURNAL*, **63**, 216-219 (1941).

(2) For references see W. C. Fernelius and G. W. Watt, *Chem. Reviews*, **20**, 195-258 (1937).

(3) For a review of reactions of solutions of metals see Fernelius and Watt, *ref. 2*.



followed by partial or complete ammonolysis



In the ionic intermediate, the electrons would repel each other into positions as far apart as possible, *i. e.*, the *trans* form. The configuration once fixed in the ion (either before or after the addition of the second electron), persists in the ammonolysis (or hydrolysis) product. The pic-

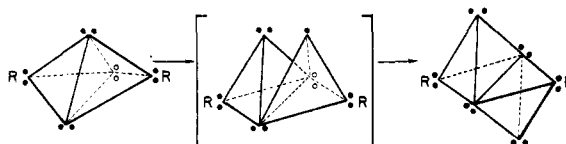


Fig. 1.

ture of one of the carbon tetrahedra turning inside out like the frame of an umbrella is the same mechanism as that frequently offered for the Walden inversion.<sup>4</sup>

(4) W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1936, pp. 331-336.

DEPARTMENT OF CHEMISTRY  
THE OHIO STATE UNIVERSITY  
COLUMBUS, OHIO

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## The Nitration of 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET AND HARRIS O. VAN ORDEN

Earlier studies on the bromination of esters containing diphenyl groups, including the bromination of 4-phenylphenyl benzoate,<sup>1</sup> have been reported from this Laboratory.<sup>2</sup> In the work here reported an attempt was made to compare the nitration of an ester with the bromination of the same compound. Methods of investigation were essentially the same as in previously reported work.<sup>2</sup> For reference compounds, the nitrophenylphenols were prepared by methods on record, and the corresponding benzoates were prepared by the action of benzoyl chloride on the nitrophenols.

Nitration of 4-phenylphenyl benzoate was effected under conditions somewhat similar to those employed in the bromination which was reported earlier,<sup>1</sup> and 4-(4-nitrophenyl)-phenyl benzoate resulted. The course of this nitration, then, is strictly parallel to the analogous bromination.

(1) Hazlet, Alliger and Tiede, *THIS JOURNAL*, **61**, 1447 (1939).

(2) Cf. Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942), for the last paper in this series.

TABLE I  
 BENZOATES OF THE NITROPHENYLPHENOLS

Nitrophenylphenol used	Yield, %	Solvent	M. p., °C.	Analyses, %			
				Calcd.	Found	Calcd.	Found
				C	H	C	H
2-Nitro-4-phenyl- <sup>3</sup>	82	Ethanol	111 <sup>6</sup>				
4-(4-Nitrophenyl)- <sup>4</sup>	Quant.	Propanol	209-210	71.4	4.1	71.2	4.8
2,6-Dinitro-4-phenyl- <sup>5</sup>	91.5	Propanol	157-158	62.6	3.3	62.4	4.1
2-Nitro-4-(4-nitro-phenyl)- <sup>4</sup>	Quant.	Propanol	151-152	62.6	3.3	62.5	4.0
2,6-Dinitro-4-(4-nitrophenyl)- <sup>6</sup>	60	Propanol	168	55.8	2.7	55.4	3.3

Acknowledgment is gladly made to the Dow Chemical Company, Midland, Michigan, for the supply of 4-phenylphenol used in this work.

**The Nitrophenylphenyl Benzoates.**—These benzoates were prepared by treating the necessary phenols with benzoyl chloride in the presence of pyridine. The individual compounds are described in Table I.

**Nitration of 4-Phenylphenyl Benzoate.**—Ten grams of 4-phenylphenyl benzoate<sup>1</sup> dissolved in 80 ml. of glacial acetic acid was treated with a mixture of 5 ml. of fuming nitric acid and 2.5 ml. of concentrated nitric acid, which was added slowly at room temperature. The mixture was stirred and heated gently for a short time on an electric heater. After cooling, filtering and one recrystallization from glacial acetic acid, 4.8 g. of product was obtained. Several more recrystallizations from glacial acetic acid gave lustrous colorless plates which melted at 208-210°. A mixture of equal amounts of this product and 4-(4-nitrophenyl)-phenyl benzoate melted without depression at 209-211°.

(3) Raiford and Colbert, *THIS JOURNAL*, **47**, 1457 (1925).

(4) Bell and Kenyon, *J. Chem. Soc.*, **129**, 3048 (1926).

(5) Bandú and Guiteras, *Anales soc. españ. fis. quim.*, **21**, 126 (1922).

(6) Colbert, Meigs and Stuerke, *THIS JOURNAL*, **56**, 2129 (1934).

DEPT. OF CHEMISTRY

STATE COLLEGE OF WASHINGTON

PULLMAN, WASHINGTON

RECEIVED JULY 22, 1942

### Some Reactions of Morpholine<sup>1</sup>

BY ALVIN R. INGRAM<sup>2</sup> AND W. F. LUDER

In the course of an investigation of the conductivity of morpholine solutions, the following reactions were observed.

Morpholine, a weak base, reacts with the acidic stannic chloride<sup>3,4</sup> to give the expected addition compound  $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_9\text{NO}$ . It is similar to the compounds of morpholine prepared by Haendler and Smith.<sup>5</sup> Dilute solutions of morpholine and stannic chloride in carbon tetrachloride were mixed in a ratio of two moles of morpholine to one

of stannic chloride. A white precipitate formed immediately. This product was washed in carbon tetrachloride, absolute alcohol and petroleum ether. It was insoluble in the common organic solvents, water and dilute acids, but it dissolved with decomposition in hot concentrated acids. It melted with decomposition between 215° and 235°. *Anal.* Calcd. for  $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_9\text{NO}$ : Sn, 27.3; Cl, 32.7. Found: Sn, 27.3; Cl, 32.0.

Morpholine also reacts with carbon tetrachloride and chloroform to give morpholinium chloride. Similar reactions have been observed previously with piperidine to form piperidinium chloride.<sup>6</sup> Because these reactions of morpholine with carbon tetrachloride and chloroform were of no concern to the investigation under way, no attempt was made to isolate other products in addition to morpholinium chloride. However, from the work of Powell and Dehn,<sup>6</sup> the principal ones may be N-trichloromethyl and N-dichloromethyl morpholine.

A 4.5% by weight solution of morpholine in carbon tetrachloride, made up for another purpose, contained a large quantity of needle-like crystals when noticed about four months later. The crystals melted at 177° and when dissolved in water gave a white precipitate with silver nitrate. Mixed melting points, using morpholinium chloride prepared by the reaction of dry hydrogen chloride with morpholine, confirmed the conclusion that the crystals were morpholinium chloride. When approximately equal volumes of morpholine and carbon tetrachloride were warmed to temperatures from 50 to 100°, the morpholinium chloride was formed in a few hours, and the remaining liquid became yellow or brown depending on time and temperature. Distillation of the colored liquid gave a colorless distillate which deposited more morpholinium chloride immediately upon cooling. The residue was viscous and dark brown. When mixed in a ratio of two moles of morpholine to one mole of carbon tetrachloride (both being dried over calcium chloride or calcium sulfate)

(1) Abstracted from a portion of a thesis presented by Alvin R. Ingram to the faculty of Northeastern University in partial fulfillment of the requirements for the M.S. degree, June, 1942.

(2) Present address: General Chemical Defense Corporation, Claymont, Delaware.

(3) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(4) W. F. Luder, *Chem. Rev.*, **27**, 547 (1940).

(5) H. M. Haendler and G. McP. Smith, *THIS JOURNAL*, **63**, 1164 (1941).

(6) S. G. Powell and W. M. Dehn, *ibid.*, **39**, 1717 (1917).