

est refractive index, α , lies in the main prism face at right angles to the prism length. The other two vibration directions β and γ 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 α , 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.

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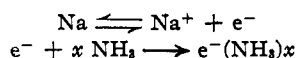
RECEIVED JULY 9, 1942

The Hydrogenation of Disubstituted Acetylenes

BY KENNETH W. GREENLEE AND W. CONARD FERNELIUS

Campbell and Eby¹ 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 ions²

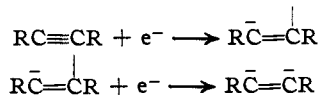


The reaction of sodium with double and triple bonds consists in the addition of electrons³

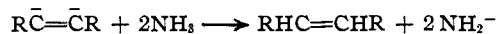
(1) K. N. Campbell and L. T. Eby, *THIS JOURNAL*, **63**, 216-219 (1941).

(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-

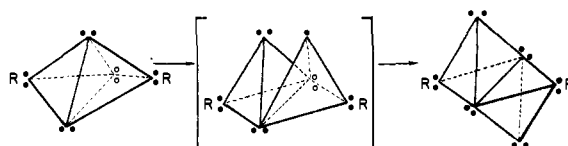


Fig. 1.

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.⁴

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

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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,¹ have been reported from this Laboratory.² 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.² 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,¹ 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.