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F. E. Ray
Grinnell College

W. R. Bunting
Grinnell College

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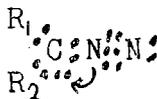
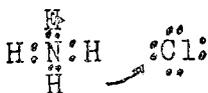
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THE DECOMPOSITION OF THE OPTICALLY ACTIVE DIAZO ESTER FROM AMINOLAURONIC ACID

F. E. RAY and W. R. BUNTING

In 1921 Levene and Mikeska,¹ and in 1922 Noyes and Chiles² prepared optically active esters in which the only asymmetric carbon was that doubly bound to diazo nitrogen. The theoretical explanation being: that of the five valences of the nitrogen, four are co-valences while the fifth is a Polar or ionizing valence. This may be illustrated by ammonium chloride.



Nitrogen loses one electron to the chlorine, but shares the others with hydrogen atoms. So in the diazo esters, one of the carbon-nitrogen bonds is a co-valence, and the other is a polar valence, the other three co-valences being nitrogen to nitrogen bonds. The carbon, therefore, gains an electron from the nitrogen; the four groups causing asymmetry are accordingly, R₁, R₂, N, and an electron.

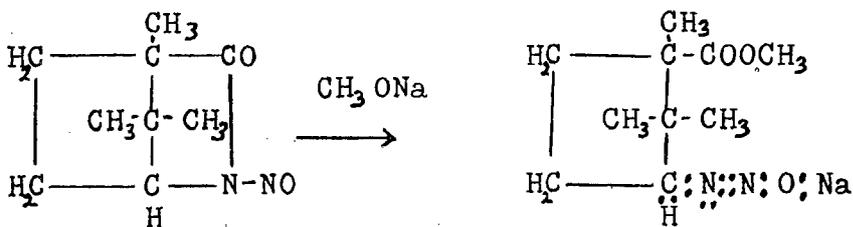
The work mentioned has been criticised because the rotations of the compounds investigated were so small that impurities might be the cause of the observed rotation.

In 1926 Kendall and Noyes³ obtained a crystalline optically active diazo compound from the nitroso derivative of aminolauronic acid with a rotation of about $[\alpha]_D + 400^\circ$. Camphoric acid and its derivatives contain two asymmetric carbon atoms and when sufficient strain is introduced into the molecule the secondary carbon is racemized and a trans acid is formed. Though Kendall prepared optically active diazo compounds from both the cis form and the trans form the instability of the diazo compounds obtained precluded any decision as to the activity of the diazo group.

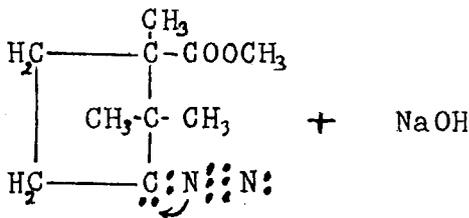
¹ Levene and Mikeska, *J. Biol. Chem.*, 45, 592 (1921); 52, 485 (1922).

² Chiles with Noyes, *J. A. C. S.* 44, 1798 (1922).

³ Kendall with Noyes, *J. A. C. S.* 48, 2404 (1926).



nitroso
derivative



diazo
compound

Now Skinner ⁴ has studied quite thoroughly the decomposition of aminolauroic acid (the cis compound) with nitrous acid, and Skinner and Noyes ⁵ have studied the decomposition of the trans-ester; and although recent work by Ray ⁶ has thrown doubt on the existence of an isomer of lauronic acid in the decomposition products, the ratio of saturated to unsaturated products is unaffected. Skinner found for the decomposition of the cis-amino camphononic acid 40 parts of hydroxy to 60 parts of unsaturated acids; and for the trans- 60 parts of hydroxy to 40 parts of the unsaturated. Some of the products were different.

There is, however, no direct proof that in this decomposition a diazo compound is formed as an intermediate.

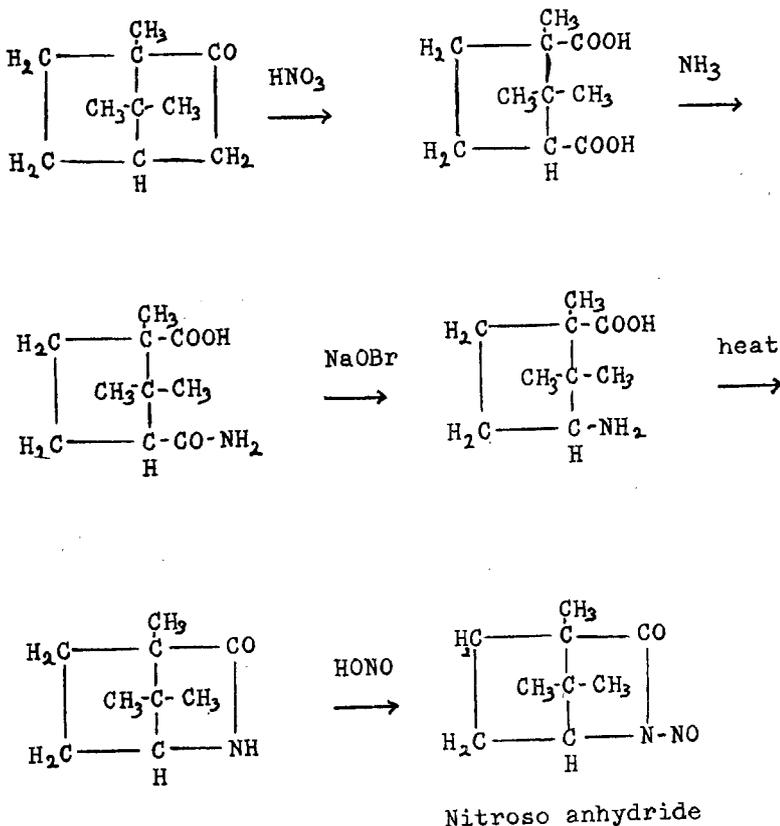
We therefore undertook to prepare the cis-diazo compound and to decompose it with dilute sulphuric acid at -20°C. and to examine the products to see if they corresponded to those obtained by Skinner. The work was somewhat complicated by the fact that the diazo compound decomposes if allowed to warm up to 0° C. Acids, salts, and CO₂ from the air also catalyse its decomposition.

⁴ Skinner, J. A. C. S. 45, 1498 (1923).

⁵ Skinner and Noyes, J. A. C. S. 39, 2692 (1917).

⁶ Ray, J. A. C. S. 50, 558 (1928); 51, 930 (1929).

The starting material was d-camphor and the formulae will make the course of the reactions clear:



At this time only a preliminary report can be given as we have not worked at all on the *trans*-compound.

We have prepared and decomposed about 20 grams of the diazo compound from the *cis*-acid. This gives, on distillation, an unsaturated fraction that corresponds to 60.5% of the distillate. We have not found any of the *ether* acid that Skinner found *only* in the decomposition of the *trans*-amino ester.

We have shown that the *cis*-diazo compound follows the same course in its decomposition as the *cis*-amino acid. It is reasonable to suppose that the *trans*-diazo compound will follow the course of the *trans*-amino ester. If the two diazo compounds give different products, it must be allowed that the diazo carbon retains its

asymetry, as that is the only manner in which the two compounds differ.

To complete the work the trans-diazo compound must, therefore, be prepared and decomposed. This work is now in progress.

GRINNELL COLLEGE,

GRINNELL, IOWA.