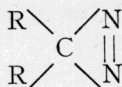


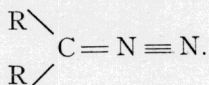
A DIAZO COMPOUND DERIVED FROM CAMPHOR WITH A VERY HIGH OPTICAL ROTATION.*

W. A. NOYES AND F. E. KENDALL, UNIVERSITY OF ILLINOIS.

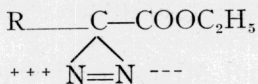
Two formulas have been proposed as representing the structure of aliphatic diazo compounds. The formula



proposed by Curtius, the discoverer of this class of compounds, was accepted as correct for about twenty years until, in 1907, Angeli suggested that the structure might be



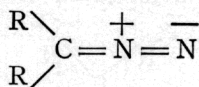
The usual method of preparation of diazo esters by the treatment of α -amino esters with nitrous acid suggested that the two nitrogen atoms might be expected to be different, one of them coming from the amino ester, a derivative of ammonia, in which nitrogen is negative, being combined with three positive hydrogens, and the other nitrogen coming from nitrous acid in which it has a valence of plus three. Thus the diazo ester might be written



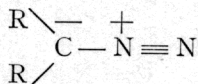
Such a compound could exist in two optically active forms which would differ only in the charges upon the two nitrogen atoms. Recent evidence based upon the reactions of these compounds makes it probable that the Angeli-Thiele formula is correct. In this formula one of the nitrogens has a valence of five. If it can be considered analogous to the nitrogen in ammonium salts

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in which nitrogen has a valence of five, four of the bonds differ from the fifth one. Four of the bonds are shared electrons while the fifth is a polar bond. Two possible structures exist with such valencies. The first one has been proposed by Langmuir who writes it in this way:



with a polar bond between the nitrogen atoms. If this structure is correct, such a compound cannot exist in optically active forms. The other formula

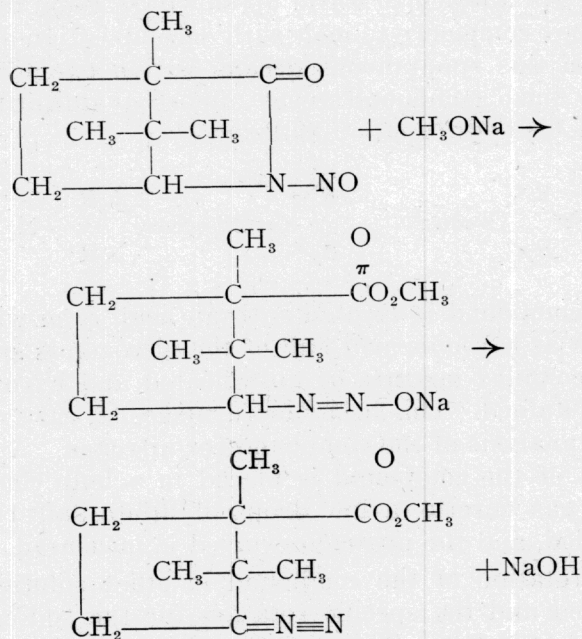


does permit the existence of optically active forms if the electrons represented by the negative charge upon the carbon are fixed upon one of the corners of the carbon tetrahedron.

Evidence is furnished by the reactions of diazo compounds that they actually exist in these two forms in equilibrium with each other. However under certain conditions of structure the second form may be the stable form and exist in optically active forms. Noyes and Chiles report six different diazo esters having specific rotations varying from -2° to $+2^\circ$ for different compounds. Levene and Mikeska have confirmed these results in part. However, all the compounds investigated were oils difficult to purify without decomposition and the results were widely questioned on the ground that the rotations obtained were possibly due to some impurity in the diazo ester. For that reason this work was undertaken with the hope of obtaining a crystalline diazo compound.

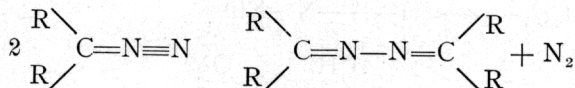
Previous work of W. A. Noyes with Coss and Ross has indicated that the nitroso derivative of the anhydride

of aminocamphonic acid gives a diazo compound when treated with alkali—



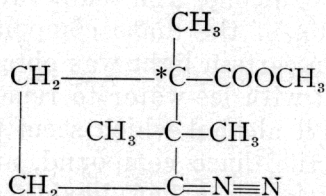
Work was continued upon this compound. By treating a solution of the nitroso anhydride dissolved in dry ether with about $\frac{1}{4}$ of a mole of sodium methylate in methyl alcohol at a temperature of -20°C a deep red solution of the diazo compound, showing a blue fluorescence in certain light was obtained. This solution was washed with ice-water to remove sodium hydroxide and methyl alcohol which seem to catalyze the decomposition of the diazo compound, and then cooled to -80° in a mixture of carbon dioxide snow and ether to freeze out the water. Usual methods of drying solutions with anhydrous CaCl_2 and Na_2SO_4 cause a rapid decomposition of this diazo compound. The solution was then filtered without exposure to moist air and concentrated to a small volume by drawing a current of dry, carbon dioxide-free air through the solution under diminished pressure. Upon cooling again to -80° the diazo compound crystallizes out in large, rouge-colored,

hexagonal needles. The crystals melt sharply at 30° if they are very rapidly heated to that temperature, but if they are allowed to warm up slowly to room temperature, they commence to melt with decomposition at about 10°. In this spontaneous decomposition two molecules of the diazo compound react almost quantitatively to form a bis-hydrazone or ketazine—



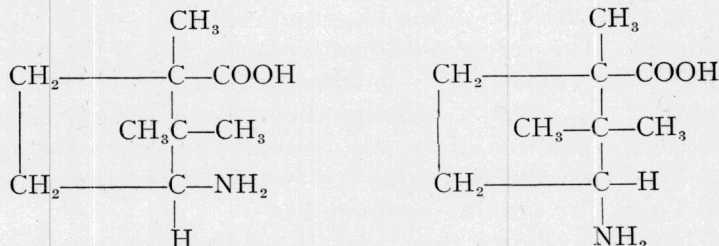
If the compound is treated with an acid, even with one as weak as carbonic acid—all of the nitrogen is split out and a complex mixture of unsaturated and hydroxy esters is obtained. This behavior furnishes an easy method for the analysis of the compound for nitrogen. A known amount of the compound is placed in a bulb connected with a gas burette, a few drops of dilute sulfuric acid are added, and the nitrogen evolved is measured.

The rotation of the compound in ether solution was measured and the specific rotation for the sodium line found to be +410°. This exceedingly high value did not necessarily show that the rotation was due to asymmetry of the diazo group; because the compound contains a second optically active carbon atom.



But, as no other compound in this series shows a specific rotation higher than 80°, it was felt that this high rotation indicated optical activity due to the diazo group. In order to show whether this was true or not a diazo compound was prepared from trans-aminocamphonic acid which differs from the cis-aminocamphonic acid

used as starting point in the first synthesis, only in having the amino group on the opposite side of the ring—



cis-aminocamphonic acid trans-aminocamphonic acid
 If the high optical activity was due to the diazo group, this compound should give a correspondingly high negative rotation.

After much investigation to find a suitable method of preparation, the diazo compound was finally obtained by the action of sodium methylate upon the nitroso derivative of symmetrical di-trans-amino methyl camphionate urea. This diazo compound showed a specific rotation of $+410^\circ$, identical to that of the compound for the corresponding cis ester.

In order to explain the high optical rotation of these compounds a series of readings of the rotation of the compounds using light of differing wave lengths was made. The relation between rotation and the wave length of light is given by Drude's equation which holds for normal compounds—

$$[\alpha] = \frac{K}{L^2 - L_0^2}$$

The term L_0 has the physical significance of representing the position of an absorption band in the absorption spectrum of the compound. If L approaches L_0 then the rotation becomes very high. It has been suggested that the constant K furnishes a much more accurate measure of the rotatory power of a compound than does the rotation measured at a given wave length because it corresponds to a value so far over in

the infra red that an absorption band in visible or near ultra violet spectrum has very little effect. Specific rotations varying from $+150^\circ$ in the red to $+1100^\circ$ in the green, very near 0° in the blue and -400° in violet were obtained. The values obtained from the red to the green coincide very closely with values calculated from Drude's equation. L_0 , 5380 Å, calculated corresponds very closely with the position of an absorption band in the absorption spectrum and the value for K , 26, represents a normal value for similar compounds.

This work shows then that the diazo compounds of this series do not exist in optically active forms and explains the high observed rotation of the compounds as being due to measurement near the absorption band in the spectrum of the compound.