

1930

Decomposition of Optically Active Diazo Compounds

Francis Earl Ray
Grinnell College

Martha G. Hemphill
Grinnell College

Let us know how access to this document benefits you

Copyright ©1930 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

Recommended Citation

Ray, Francis Earl and Hemphill, Martha G. (1930) "Decomposition of Optically Active Diazo Compounds," *Proceedings of the Iowa Academy of Science*, 37(1), 235-236.

Available at: <https://scholarworks.uni.edu/pias/vol37/iss1/44>

This Research is brought to you for free and open access by the Iowa Academy of Science at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact scholarworks@uni.edu.

DECOMPOSITION OF OPTICALLY ACTIVE DIAZO
COMPOUNDS *

FRANCIS EARL RAY AND MARTHA G. HEMPHILL

In 1921, Levene and Mikeska,¹ and in 1922, Noyes and Chiles² prepared optically active esters in which the only possible asymmetric carbon was that doubly bound to diazo nitrogen. Due to this double bond being semipolar the nitrogen loses an electron to the carbon. The asymmetry of the carbon atom would result from the localization of this electron much the same as the localization of the ordinary bond is considered to cause asymmetry.

The work mentioned has been criticized 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 optically active diazo derivatives from both camphoric acid and 1-isocamphoric acid. Camphoric acid and its derivatives, however, contain two asymmetric carbon atoms but when strain is introduced into the molecule the secondary carbon only is racemized and the 1-isocompound is formed. Though Kendall prepared optically active diazo derivatives from both types of compounds, their instability precluded any decision as to the activity of the secondary carbon which was attached to the diazo group.

Skinner⁴ has studied quite thoroughly the decomposition of aminolauronic ester, derived from the *cis* acid by substitution of the amino group for the secondary carboxyl; and Skinner and Noyes⁵ have studied the decomposition of the *trans* amino ester, similarly derived from the 1-isocamphoric acid. They found for the decomposition of the *cis* amino ester, 40 parts of hydroxy to 60 parts of unsaturated esters, and for the *trans* amino ester, 60 parts of hydroxy to 40 parts of unsaturated esters. An ether acid

* Since this paper was read before the Academy we have secured additional evidence that the two diazo compounds differ. Kendall showed that the *cis* diazo compound decomposes to form the bis-hydrazone of Noyes and Taveau (*Am. Chem. J.*, **32**, 287 (1914) melting at 99°. On allowing the *trans* diazo compound to warm up and decompose we obtained a compound that melted at 71° and gave a molecular weight of about 330. A mixture of the two compounds melted at 60-62° showing that the two products obtained by spontaneous decomposition of the two diazo compounds are different. The compounds may be *cis-trans* isomers. This work is being continued.

F. E. RAY

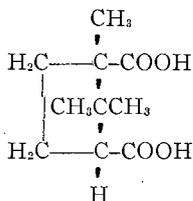
¹ Levene & Mikeska, *J. Biol. Chem.* **45**, 592 (1911); **52**, 485 (1922).

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

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

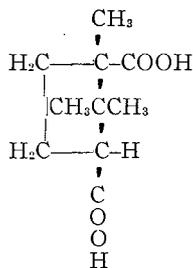
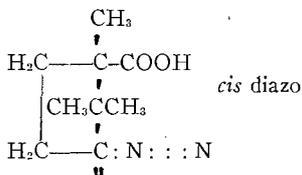
⁴ Skinner, *J. A. C. S.*, **45**, 1498 (1923).

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



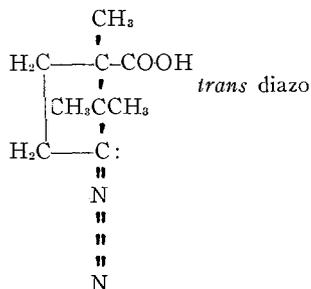
CAMPHORIC ACID

cis



1-ISOCAMPHORIC ACID

trans



was found only in the decomposition of the *trans* compound. There is, however, no direct proof that in these decompositions, diazo compounds are formed as intermediates.

In this work we undertook to prepare and decompose the actual diazo compounds and to study their decomposition products. From the decomposition of 20 grams of the *cis* diazo compound we found 60.5% of unsaturated ester. This corresponds to the amount found by Skinner for the *cis* amino compound. No ether acid was found.

In the decomposition products of the *trans* diazo derivative we isolated the ether acid that Skinner found only in the decomposition of the *trans* amino ester. The unsaturated ester was present to the extent of 27 percent.

As the two diazo compounds give different products the diazo carbon must retain its asymmetry as that is the only manner in which the two compounds can differ.

SUMMARY

It has been shown that an asymmetric carbon atom retains its asymmetry when converted into a diazo derivative.

GRINNELL COLLEGE,
GRINNELL, IOWA.