aldehyde by nitric oxide is also probably initiated by oxidation processes. The inhibition of the thermal decomposition of dimethyl ether by nitric oxide is, however, a very important addition to those facts which we have enumerated, which serve to distinguish this process from the thermal decomposition of acetaldehyde. Taking all these facts together, it does not seem possible to distinguish either process as being the only one which is influenced by chain mechanism.

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¹ *Proc. Roy. Soc., A*, **154**, 335, and *J. Chem. Soc.*, 812 (1936).

² *NATURE*, **137**, 906 (1936); **138**, 26 (1936).

Use of Deuterium as an Indicator in Stereochemical Investigations

1. It is known that optically active compounds under different influences undergo racemization. Various theories have been put forward to explain the mechanism of these changes.

A. Werner¹ took the view that the extreme oscillation of the molecules led apparently to an unravelling of the tetrahedral configuration. Other authors assume that the racemization is brought about through the formation of an enol². Taking as an example mandelic acid, it is assumed that the following equilibrium goes over from the keto-form to the enol-form; that is, there is a change from an asymmetrical to a symmetrical molecule:

The use of heavy water (D_2O) enabled us to decide experimentally between the various opinions, for we know from other examples³ that the OH group of the enol-forms is exchanged with D_2O . If the racemization in heavy water takes place through the enol-form, then the racemized mandelic acid will show a corresponding high content of the D-atom.

In the control experiment, mandelic acid was recrystallized out of heavy water by heating to 60°C ., an operation in which the optical activity is fully retained. The resulting mandelic acid contained, according to isotope analysis⁴, $x = 1.7$ D-atom (corresponding to $t = 1.9$)⁵, which corresponds to an exchange of two hydrogen atoms.

This result was confirmed by many experiments and is explained by the formation of the acid

In the racemization experiment, mandelic acid, dissolved in heavy water, was warmed to a temperature of 140°C . over a period of 51 hours. The acid isolated was optically completely inactive. The isotope analysis of the racemized mandelic acid, carefully purified, freed from all traces of benzoic acid, gave, however, $x = 1.7$, $t = 1.9$ also, corresponding to two interchangeable hydrogen atoms, although if we assume enolization, at least $t = 2.7$ was to be expected. This result, accordingly, is in favour

of the Werner-Hund conception of the mechanism of racemization.

A racemization experiment with a mandelic acid in a solution of NaOD also resulted after 16 hours heating at a temperature of 100°C . in a fully racemized acid. Purified and recrystallized from D_2O , the isotope analysis of this acid gives $x = 2.06$, $t = 2.34$.

Since the value of t here is again less than 2.7, it cannot be supposed that racemization and enol formation is the same reaction.

2. There exist the results of a series of experiments concerning the preparation of compounds of the type C.R'R''HD . These communications are partly of negative⁶ content and partly positive⁸. In this paper we only want to report on two such experiments. We allowed benzene to react with the optically active compound

in the presence of zinc; the resulting acid,

was optically inactive.

Experiments in which an attempt was made to split up the acid with the aid of alkaloids have also not succeeded in obtaining one isomer from the separated alkaloid salt and its antipodes from the mother liquor. All observed rotation of the plane of polarized light could be traced to impurities. Further experiments are still in process.

However, we have shown with *l*-mandelic acid that the substitution of H by D in an optically active molecule can have an influence on the optical rotation. When *l*-mandelic acid, which is not subject to racemization at 60°C ., was allowed to react with heavy water at that temperature, it showed 1.7 D-atoms by the isotope analysis. The measurement of the optical activity of this acid (D) and of the original, untreated *l*-mandelic acid (H), both in dry acetophenone, gave the following results:

	H	D
$[\alpha]_D^{20}$	$-179.10^\circ \pm 0.13$	$-173.27^\circ \pm 0.13$
$[\alpha]_{\text{Hg}}^{20}$	$-216.34^\circ \pm 0.13$	$-211.43^\circ \pm 0.13$

The complete communication will appear in the *Helv. chim. Acta*.

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¹ A. Werner, "Stereochemie", **49** (1904); see also F. Hund, *Z. Phys.*, **43**, 805 (1927).

² A. McKenzie and H. Wren, *J. Chem. Soc.*, **117**, 680 (1920); T. A. Smith, *Ber.*, **64**, 430 (1931); Th. Wagner-Jauregg, "Stereochemie" (Freudenberg), 858 (1933).

³ See A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen", 200 (1935); H. Erlenmeyer, A. Epprecht, H. Lobeck and H. Gärtner, *Helv. chim. Acta*, **19**, 354, 543 (1936).

⁴ H. Erlenmeyer and H. Gärtner, *Helv. chim. Acta*, **19**, 129 (1936).
⁵ The difference from the value 2 is caused by the rates of dissociation; see *Helv. chim. Acta*, **19**, 354 (1936).

⁶ W. F. K. Wynne-Jones, *Chem. Rev.*, **17**, 122 (1935).

⁷ H. Erlenmeyer and H. Gärtner, *Helv. chim. Acta*, **19**, 145, 331 (1936); J. B. M. Coppock and S. M. Partridge, *NATURE*, **137**, 907 (1936).

⁸ E. Billmann, K. A. Jensen and E. Knuth, *Ber.*, **69**, 1031 (1936); J. R. Clemo and S. McQuillen, *J. Chem. Soc.*, 808 (1936); *Chem. and Indust.*, **55**, 441 (1936).

⁹ Rothe, *Ber.*, **47**, 843 (1914).