Cis- and *Trans*-Chlorohydrins of Δ^1-Methylcyclopentene

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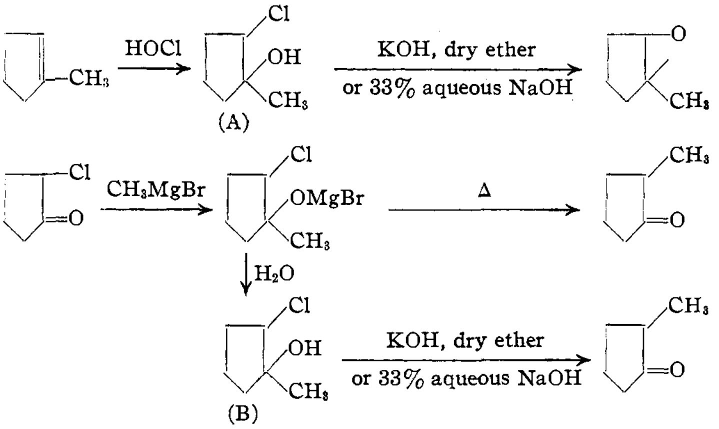
The isomeric chlorohydrins (A) and (B) have been obtained by methods parallel to those used in the cyclohexane series,[1] and are found to react as shown.



The (B) isomer alone is new, (A), m. p. 35–37°, having been studied by Chavanne and de Vogel.[2] In two respects these isomers contrast with the homologous compounds, previously described, containing the six-membered ring. (1) There is only one ketone formed from the B isomer, whatever method of dehydrohalogenation is employed, no ring contraction occurring. (2) These isomers show marked differences in their physical properties, which is not the case with the corresponding 6-ring compounds. If such differences (*e. g.*, in boiling point) are assumed due to some interaction of groups[3] in the *cis* compound which is impossible in the *trans*, then the absence of such effects in the cyclohexanes may be connected with the strainless 6-ring, which enables *trans* groups to approach each other as closely as *cis* groups.

Chavanne and de Vogel[2] obtained, along with our "Isomer A," an oil of b. p. 64–67.5° (10 mm.) which they believed to be an isomeric chlorohydrin. We also obtained a lower-boiling fraction (b. p. 38–43°, 8 mm.); it contained, however, 35.74% of chlorine, and did not react with boiling alcoholic alkali in thirty-five minutes. It was therefore not a chlorohydrin, and we believe that "Isomer A" represents the sole product of addition of hypochlorous acid to Δ^1-methylcyclopentene.

PROPERTIES OF THE ISOMERIC 2-CHLORO-1-METHYLCYCLOPENTANOLS

Isomer	B. p., °C.	d_{24}	n^{24}_{D}	Cl, % (calcd. 26.37)
A	61–64 (7 mm.)	1.131[a]	1.477[a]	26.28
B	50–57 (8 mm.)	1.059	1.4709	26.55

[a] Supercooled.

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[1] Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[2] Chavanne and de Vogel, *Bull. soc. chim. Belg.*, **37**, 141–152 (1928).

[3] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1927, p. 147.

COMMUNICATIONS TO THE EDITOR

THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF WEAK BASES BY THE SILVER IODIDE ELECTRODE

Sir:

Among electrodes of the second kind, sufficiently insoluble in ammonia and organic bases to be used in the determination of their dissociation constants without liquid junctions, the silver–silver iodide electrode offers interesting possibilities. To avoid technical difficulties associated with the use of dilute hydriodic acid, the normal potential (E^0) may be obtained in alkaline solutions. The method is essentially a comparison of the silver iodide and silver chloride electrodes. Preliminary values of E^0 have been determined in borax buffers by reversing the calculation for the ionization constant of boric acid [Owen, THIS JOURNAL, **56**, 1695 (1934)], and should likewise be obtainable in solutions of a strong base from the ionization constant of water [Harned and Hamer, *ibid.*, **55**, 2194, 4496 (1933)]. Using the cell

$$H_2/NH_4OH(m_1),\ NH_4I(m_2)/AgI,\ Ag$$

in connection with the extrapolation function $\log K - B\mu = (E - E^0)/0.05915 + \log K_{H_2O}$

$+ \log (NH_4^+)(I^-)/(NH_4OH) - 0.5/\sqrt{\mu}$, $K = 1.75 \times 10^{-5}$ was obtained for ammonium hydroxide at 25°. Since this result depends upon a single series of measurements, and a preliminary determination of E^0, it can only be regarded as tentative, but it is sufficiently close to the accepted value, 1.81×10^{-5} ["Int. Crit. Tables," Vol. VI], to demonstrate the potential usefulness of the indirect procedure herein outlined. Further work on this problem is in progress.

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THE EMISSION OF γ-RAYS IN NUCLEAR REACTIONS

Sir:

It has been shown recently[1] that all known nuclear reactions which result in actual disintegration, and which are induced by a nuclear projectile of ordinary energy (up to 8 to 15 mev) are of the type of a chemical double decomposition or metathesis. Thus: $A + B \longrightarrow AB^* \longrightarrow C^* + D$. Here C is starred to indicate the probability that at least one of the products is activated and shows either γ-ray activity or the emission of an electron or positron, which, since it is commonly delayed, is considered as an artificial radioactivity.

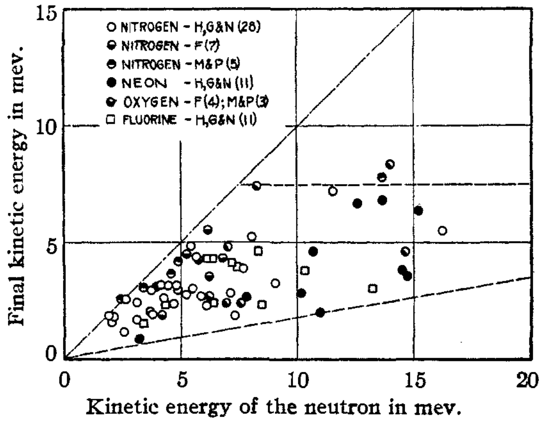

Fig. 1.—H,G & N, Harkins, Gans and Newson; F, Feather; M & P, Meitner and Philipp.

It is now possible to collect complete data where the projectile is a neutron for 71 such reactions, many of which were obtained in this Laboratory, and the others by Feather [*Proc. Roy. Soc.* (London), **A136** (1932); **142**, 689 (1933); *Nature*, **130**, 237 (1932)] and Meitner and Philipp [*Z. Physik*, **87**, 484 (1934); *Naturwissenschaften*, **20**, 929 (1932)]. One such event, obtained by Kurie [*Phys. Rev.*, **43**, 672 and 771 (1933)], was not included since the nature of the reaction involved is supposed by him to be uncertain.

These reveal relations of considerable interest (Fig. 1).

1. Kinetic energy disappears in every reaction, or is rarely conserved.

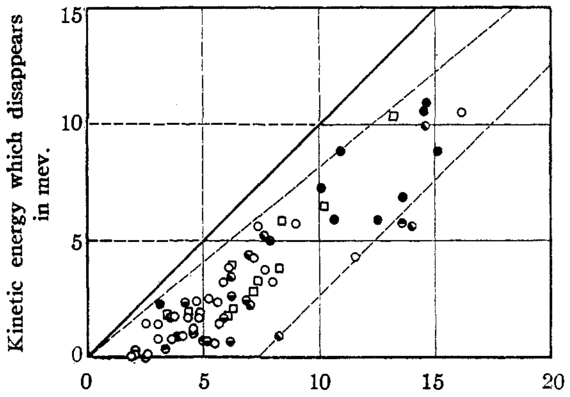

Fig. 2.

2. Though the kinetic energy of the neutron rises as high as 15 mev or slightly more, the maximum kinetic energy retained by the products of the reaction (C and D) is 8.5 mev.

3. The kinetic energy which disappears ($-\Delta KE$) in the reaction rises rapidly with the kinetic energy of the neutron, which is the initial kinetic energy of the system, since the velocity of the atom of A is relatively very small

4. The minimum kinetic energy which remains in the system (ordinates Fig. 1) increases with the kinetic energy of the neutron.

It may be assumed that some or all (depending on the mass change in the reaction) of the kinetic energy decrement is emitted as γ-rays, which are given off either by the atom AB^*, which has an excessively short life, or by the atom C^*. In experiments with fluorine, Harkins, Gans and Newson [*Phys. Rev.*, **44**, 945 (1933)] considered that if C^* is nitrogen 16, a new isotope found by them, it would be likely to be unstable and emit an electron to form oxygen 16. This has been verified by Fermi [Fermi, Amaldi, D'Agostino, Rasetti and Segrè, *Proc. Roy. Soc.* (London), **146**, 483 (1934)], who finds nitrogen 16 to be radioactive.

The ordinate of Fig. 2 ($-\Delta KE$) plus a con-

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[1] Harkins and Gans, *Phys. Rev.*, **46**, 397 (1934).