NOTES

New Types of Racemization Reactions

By Ernst Bergmann and Alfred Bondi

To the number of racemization reactions which obviously are of fundamental importance for our knowledge of the stability of spacial configurations, three new types have recently been added: (a) the racemization of methylalkyliodomethanes by interaction with iodide ions,[1] (b) the racemization of 2-bromohexane during its conversion into the Grignard compound,[2] and (c) the racemization occurring during the interaction between active ethyl propylmethylacetate and phenylmagnesium bromide.[3] Only the first of these three types has so far a theoretical and experimental treatment.

For case (b) one would perhaps be inclined to assume that racemization is due to electrolytic dissociation of the Grignard compound. But this assumption seems inadmissible, since negative carbonium ions seem to be sufficiently stable,[4] while positive ions of carbon are unstable.[5] Therefore one has probably to conclude that the racemization belongs to type (a): the bromide is racemized by bromide ions, which are formed by the ordinary equilibrium reaction $2RMgBr \rightleftharpoons R_2Mg + MgBr_2$. The case, therefore, is analogous to the racemization of phenylmethylchloromethane by interaction with magnesium or sodium metal.[1,6]

For case (c) the following suggestion has been advanced by Bergmann and Hartrott.[3] The ester does not undergo racemization—it is unstable only in alkaline solution[7]—but the carbinol is subjected to an equilibrium $(Me)(Pr\text{-}\alpha)CH\text{-}C(OH)Ph_2 \rightleftharpoons H_2O + (Me)(Pr\text{-}\alpha)C{=}CPh_2$, whereby the asymmetry is destroyed. It is well known that diphenylalkylcarbinols are easily dehydrated. If this explanation is correct, ethyl propylmethylacetate should give optically active carbinols with simple aliphatic alkylmagnesium halides, since compounds like (2-pentyl)-diethylcarbinol, $(Me)(Pr\text{-}\alpha)CHC(OH)Et_2$, do not lose water so easily. The conclusion has been confirmed by experiment. Into a solution of ethylmagnesium bromide (from 2.5 g. of magnesium and 11 g. of ethyl bromide), active methyl propylmethylacetate (4 g., rotation in acetone, $l = 1$, $c = 2.70$, α_D $-0.19°$; hence $[\alpha]_D$ $-7.04°$) was introduced. The rather violent reaction was completed by boiling for thirty minutes, then the mixture was decomposed with ice and ammonium chloride and the ethereal layer dried with anhydrous sodium sulfate and evaporated. The (2-pentyl)-diethylcarbinol boiled at 92–93° (32 mm.); yield 2.9 g. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 75.8, 75.4; H, 14.4, 14.1. Rotation in acetone: $l = 1$, $c = 2.80$, $\alpha^{22}D$ $-0.365°$; hence $[\alpha]^{22}D$ $-13.04°$.

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(1) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20B**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936).
(2) Porter, This Journal, **57**, 1436 (1935).
(3) Bergmann and Hartrott, *J. Chem. Soc.*, 1218 (1935).
(4) Wallis and Adams, This Journal, **54**, 4753 (1932); **55**, 3838 (1933).
(5) Bergmann and Polanyi, *Naturwissenschaften*, **21**, 378 (1933).
(6) Ott, *Ber.*, **61**, 2124 (1926).
(7) Menon and Peacock, *J. Ind. Chem. Soc.*, **12**, 268 (1935).

The Preparation of Pure Apocodeine and its Hydrochloride

By Karl Folkers

Early preparations of apocodeine were complex mixtures.[1] Knorr obtained "pseudoapocodeine"[2] by melting codeine with oxalic acid, and later he showed[3] that his apocodeine was identical with the monomethylation product of apomorphine; although this latter product had been reported earlier by Pschorr,[4] but with widely different physical properties. Later methods[5] of making apocodeine from codeine with zinc and sodium chlorides still introduced apomorphine impurities, which necessitated the use of a troublesome perchlorate, chromate or phosphate salt for purification.

Nevertheless, a certain confusion exists in the

(1) Small, "Chemistry of the Opium Alkaloids," Supp. No. 103, Public Health Reports, 1932, pp. 183, 362.
(2) Knorr and Roth, *Ber.*, **40**, 3355 (1907). The name pseudoapocodeine was introduced by Knorr as he believed pseudocodeine to be an intermediate in the transformation of the morphine nucleus to the aporphine nucleus. Apocodeine is the generally accepted name, and it suggests the same relationship to codeine that apomorphine has to morphine.
(3) Knorr and Raabe, *ibid.*, **41**, 3050 (1908).
(4) Pschorr, Jaeckel and Fecht, *ibid.*, **35**, 4377 (1902).
(5) German Patent 489,185, *Frdl.*, **16**, 2485.