ether (previously saturated at 0° with hydrogen chloride) and allowed to stand for twenty-four hours or longer, with occasional shaking, until all of the oxide was dissolved. A yellow solution resulted. The solvent was then evaporated under reduced pressure and the residue heated at 75° under water pump vacuum until the hydrogen chloride was completely expelled (about three hours). The residue was recrystallized from ethyl acetate–petroleum ether mixtures; yield 40 g. of pure ethenol (80%) of m. p. 88–89° (corr.). Repeated crystallizations by this method and also from ethanol did not change the melting point nor remove the last faint trace of halogen (flame test). Chlorine analyses showed, respectively, 0.0 and 0.1% chlorine, which is negligible.

Dibenzoylethenol or dibenzoylethylene chlorohydrin (IV) react with ethereal hydrogen chloride in the same way as the oxide and may be substituted in the above reactions.

The intermediate chlorohydrin is unstable and loses hydrogen chloride spontaneously with such ease that the compound has not yet been isolated in a pure state. When the ethereal hydrogen chloride solution (above) was allowed to evaporate in a current of air it was obtained as a colorless crystalline residue which was recrystallized from ether by adding petroleum ether; it melted at 75–80°, and gave a chlorine analysis of 7.9% (calcd., 12.3). On further crystallizations, or when warmed gently alone or in solvents, it loses hydrogen chloride, going finally into dibenzoylethenol. When refluxed in methanol or ethanol it gives nearly theoretical yields, respectively, of 1,4-diphenyl-4-methoxy-3-butene-1,2-dione and the ethoxy analog. (Dibenzoylethenol reacts similarly with methanol or ethanol containing a small amount of hydrogen chloride.)

Stability of *dl* and *meso* Dibenzoyldichloroethanes toward Phosphorus Pentachloride, Thionyl Chloride and Acetyl Chloride.—These tests were made because of their importance in connection with the mechanism of reaction between these reagents and various saturated and unsaturated 1,4 diketones. These dichlorides were recovered nearly quantitatively, unchanged, (a) when heated for one hour at 100° with phosphorus pentachloride, with or without added phosphorus oxychloride and gaseous hydrogen chloride, and (b) when heated in thionyl chloride (with a stream of hydrogen chloride and sulfur dioxide passing through), refluxing for one hour.

The *meso* dichloride was recovered unchanged upon standing for fifteen minutes in 10 cc. of acetyl chloride containing 5–6 drops of concd. sulfuric acid, but the *dl* isomer under these conditions was converted nearly quantitatively into diphenyldichlorofuran.

Summary

The preparation and typical reactions of dibenzoylethylene oxide and chlorohydrin are described, including their conversion into dibenzoylethenol.

UNIVERSITY, VIRGINIA

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Some Physical Constants of Anabasine

BY O. A. NELSON

Anabasine, an isomer of nicotine, and present to the extent of approximately 2% in *Anabasis aphylla* L., has been found to be toxic to a number of insects.[1,2] In view of the available supply and its promise as a valuable insecticide it was considered advisable to prepare a sample of high purity, and to determine some of the more important physical constants.

Purification of Material.—The commercial material from which the anabasine was obtained was a solution containing approximately 44% total alkaloids in water. The solute consisted of 72% anabasine, the remainder being lupinine, other alkaloids and miscellaneous plant materials not identified.

The mixture was treated with strong caustic solution and centrifuged. The resulting mixture of alkaloids and other impurities was separated from anabasine by converting the latter into the nitroso derivative, after which the anabasine was recovered by treatment with hydrochloric acid followed by sodium hydroxide.

The dark brown product obtained at this stage was freed from tarry material by distillation at 10–15 mm. pressure, and an attempt was made to purify it further by fractionation in a 23-plate column under pressure of 2–2.5 mm., at which pressure about 88% distilled at a temperature of 104 ± 1°. It was observed, however, that the distillate was not miscible in all proportions with water, as it should have been, indicating that some change had taken place during the fractionation. The plates of the fractionation column were made from nickel gauze, therefore dehydrogenation may have taken place. The composition of the water-insoluble compound was not ascertained, but it was found to be readily removed by extracting the aqueous solution with ether, which took up very little of the anabasine.

Final purification was accomplished by means of a Hickman still at a temperature of 40–50° and under a pressure of 4×10^{-4} to 2.5×10^{-4} mm. The anabasine obtained was water white and on cooling in a carbon dioxide–alcohol trap solidified to a viscous mass which appeared to crystallize after remaining at the low temperature overnight.

The pure anabasine was miscible in all proportions in water, and showed the following constants: specific gravity $^{20}_{20}$ 1.0481; n^{20}_{D} 0.5443; $[\alpha]^{20}_{\mathrm{D}}$ −59.66°. A. Oréchoff

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(1) F. L. Cambell, W. N. Sullivan and C. R. Smith, *J. Econ. Entomol.*, **26**, 500 (1933).

(2) P. Garman, *Conn. Agr. Exp. Sta. Bull.*, **349**, 433 (1933).

and G. Menschikoff[3] reported: specific gravity $^{20}_{20}$ 1.0455; n^{20}_{D} 1.5430; $[\alpha]^{20}_{D}$ −82.20°.

Vapor Pressure of Anabasine.—The vapor pressure of the purified anabasine was determined by the same method used in previous work on vapor pressure of fumigants.[4]

Table I shows the vapor pressures obtained at a number of temperatures from 79.0 to 280.6°. The boiling point was found to be 280.9° compared with 276.0° reported by Oréchoff and Menschikoff[3] and 280–282° reported by C. R. Smith.[5] The vapor pressure can be represented with an accuracy of about 5% up to 100° and to better than 0.10% for the remainder of the temperature range investigated by the empirical equation $\log P_{\text{mm.}} = 7.2423 - (2416.14/T_{K})$.

Optical Rotation of Anabasine.—The optical rotation was determined at 20°, and for the pure material it was found to be $[\alpha]^{20}_{D}$ −59.66°.

TABLE I

VAPOR PRESSURE OF ANABASINE

Temp., °C.	Press. obs., mm.	Temp., °C.	Press. obs., mm.
79.0	2.5	218.6	211.5
100.0	6.0	280.6	756.8
137.1	31.6	280.9	760.0
184.2	85.4	282.4	776.1

Optically active anabasine sulfate has been found to racemize by heating in a sealed tube. Menschikoff, Gregorovitch and Oréchoff[6] observed that when a dilute solution of the sulfate had been heated in a sealed tube at 200° for seventy hours and the anabasine freed, the rotation had changed to $[\alpha]^{20}_{D}$ −25° from presumably $[\alpha]^{20}_{D}$ 82.20°, while after heating for 120 hours $[\alpha]^{20}_{D}$ was −3.0°. About ten months after the rotation of −59.66° was measured another sample was purified but this showed a rotation of $[\alpha]^{20}_{D}$ −51.93°, thereby indicating auto-racemization at room temperature. Further work is being done on this constant, and will be reported in a subsequent contribution.

Summary

Anabasine was carefully purified and the following constants determined: specific gravity, refractive index, optical rotation, vapor pressures at different temperatures, and its boiling point. An equation was obtained that represents the change of vapor pressure with change in temperature to a high degree of accuracy.

WASHINGTON, D. C.

RECEIVED JUNE 13, 1934

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(3) A. Oréchoff and G. Menschikoff, *Ber.*, **64**, 266 (1931).

(4) O. A. Nelson, *Ind. Eng. Chem.*, **20**, 1380 (1928).

(5) C. R. Smith, THIS JOURNAL, **53**, 277 (1931).

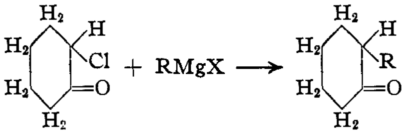
(6) G. Menschikoff, Gregorovitch and A. Oréchoff, *Ber.*, **65**, 1126 (1932).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

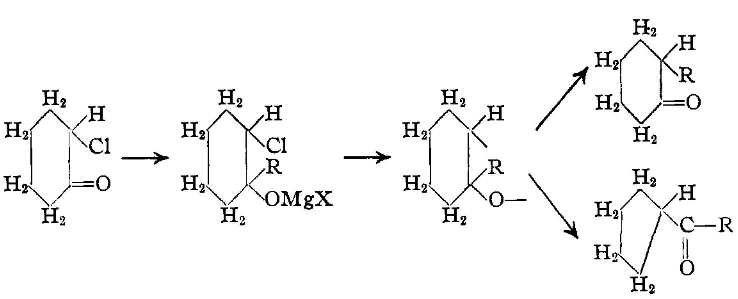
Cis- and *Trans*-Chlorohydrins of Δ^1-Methylcyclohexene[1]

BY PAUL D. BARTLETT AND ROBERT H. ROSENWALD

The reaction of Grignard reagents with 2-chlorocyclohexanone was reported by Bouveault and Chereau[2] to take the following course:



In a very recent paper, Tiffeneau and Tchoubar[3] have shown that this reaction represents a special case of the behavior established years ago for chloroacetone[4] with phenylmagnesium bromide. The first step in the reaction is normal addition of the Grignard reagent to the carbonyl group, and the resulting magnesium derivative of a chlorohydrin is rearranged, by heating, into a 2-alkylcyclohexanone and a smaller amount of an alkyl cyclopentyl ketone. As formulated by Tiffeneau the reactions are



In investigating the mechanism of this reaction shortly before the appearance of the paper by Tiffeneau and Tchoubar, we had obtained results similar to theirs. The isolation of the chlorohydrin (I) in yields up to 82%, from the reaction of 2-chlorocyclohexanone with methylmagnesium bromide, and the isolation of the corresponding bromohydrin from the reaction using 2-bromo-

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(1) From a thesis presented by Robert H. Rosenwald in partial fulfilment of the requirements for the degree of Master of Science at Minnesota, 1934.

(2) Bouveault and Chereau, *Compt. rend.*, **142**, 1986 (1906).

(3) Tiffeneau and Tchoubar, *ibid.*, **198**, 941 (1934).

(4) Tiffeneau, *Ann. chim.*, [8] **10**, 367 (1907).