the diffusion constant D_{20} 1.09×10^{-7}, corresponding to an axial ratio of about 390.

This work, which will later be reported in detail, has been supported by a research grant from the U. S. Public Health Service.

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RECEIVED MARCH 17, 1947

THE SYNTHESIS OF CYCLOÖCTATETRAENE FROM PSEUDOPELLETIERINE

Sir:

Validity of the synthesis of cycloöctatetraene from the pomegranate bark alkaloid pseudopelletierine by Willstätter, Waser and Heidelberger[1] has been questioned because their product resembled styrene in some physical and chemical properties,[2] and on the basis of studies of model compounds.[3] The synthesis has not been repeated, presumably because pseudopelletierine was not available. Development of a catalytic synthesis of cycloöctatetraene from acetylene in Germany[4] has renewed interest in the hydrocarbon.

We have repeated the Willstätter synthesis of cycloöctatetraene, beginning with synthetic pseudopelletierine,[5] through the following steps. Pseudopelletierine → N-methylgranatoline (82%) → N-methylgranatenine (85%) → methiodide (97%) → α-des-dimethylgranatenine (I) (82%) → methiodide (92%) → cycloöctatriene (II) (70%) → dibromide (not isolated) → bis-(dimethylamino)-cycloöctadiene (III) (47%) → di-methiodide (97.5%) → cycloöctatetraene (7–9%). Physical constants of the intermediates corresponded closely to those reported originally.[1] Ultraviolet absorption spectra were consistent with conjugated diene structures for I and III, and a conjugated triene structure for II ($\lambda_{max.}$ 2650 Å., log ϵ 3.57).

The cycloöctatetraene which was obtained gave a satisfactory analysis (calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.47; H, 7.91), and had the following properties: m. p. (capillary) −5.8 to −5.4°[6]; $n^{25}D$ 1.5342; m. p. (hot stage) of the maleic anhydride adduct 166.7–168.2°; per cent. hydrogen absorbed in catalytic hydrogenation over platinum 101.5%. The m. p. of the cycloöctatetraene and its maleic anhydride adduct were not depressed by mixture with a sample prepared from acetylene and its corresponding derivative, respectively. Cycloöctatetraene from the two sources had identical ultraviolet absorption spectra, and showed no important differences in infrared absorption spectra.[7]

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[1] Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

[2] Noted by Vincent, Thompson and Smith, *J. Org. Chem.*, **3**, 603 (1939). Also, dehydrogenation of cycloöctene yields styrene; Goldwasser and Taylor, THIS JOURNAL, **61**, 1260 (1939).

[3] Hurd and Drake, *ibid.*, **61**, 1943 (1939). Investigation of other models led to a different conclusion; Hurd and Ensor, paper presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, September, 1946 (Abstracts, page 24M). For a review see Baker, *J. Chem. Soc.*, 258 (1945).

[4] Reported in "German Synthetic Fiber Developments," p. 631 (translation of an article by W. J. Reppe), Textile Research Institute, New York, N. Y., 1946 (PB. 7416) and other Department of Commerce reports.

[5] Prepared by modifications of the small-scale synthesis of Schöpf and Lehmann, *Ann.*, **518**, 1 (1935).

[6] Ref. 1 reports m. p. −27°. Other physical properties are in fair agreement.

[7] We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared data.

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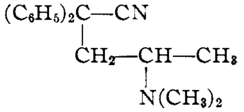
RECEIVED MARCH 18, 1947

SOME ISOMERS OF AMIDONE AND RELATED COMPOUNDS

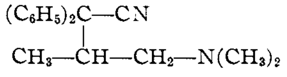
Sir:

It has recently been shown that the reaction between diphenylacetonitrile and 1-dimethylamino-2-chloropropane results in a mixture from which two isomeric aminonitriles (I and II) have been isolated.[1] The higher melting nitrile (I) reacts with ethylmagnesium bromide to yield Amidone (III). We have now found that the lower melting nitrile (II) reacts with ethylmagnesium bromide to give a ketimine (IV) which was isolated as the sesquioxalate (m. p. 145–146°. *Anal.* Calcd. for $2C_{21}H_{28}N_2 \cdot 3H_2C_2O_4$: C, 64.99; H, 7.05; N, 6.32; $H_2C_2O_4$, 30.45. Found: C, 65.15; H, 6.96; N, 6.36; $H_2C_2O_4$, 30.50). This was also characterized as the dihydrochloride (m. p. 200–202°dec. *Anal.* Calcd. for $C_{21}H_{28}N_2 \cdot 2HCl$: C, 66.13; H, 7.93; N, 7.35; Cl, 18.59. Found: C, 66.00; H, 7.75; N, 7.30; Cl, 18.43) and the dipicrate (m. p. 140–141°. *Anal.* Calcd. for $C_{21}H_{28}N_2 \cdot 2C_6H_3O_7N_3$: C, 51.69; H, 4.47; N, 14.62. Found: C 51.65, 51.75; H, 4.54, 4.38; N, 14.41, 14.58).



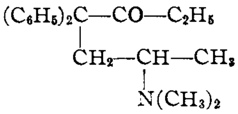
$(C_6H_5)_2C(CN){-}CH_2{-}CH(N(CH_3)_2){-}CH_3$

I



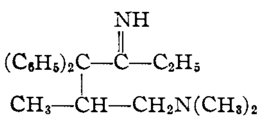
$(C_6H_5)_2C(CN){-}CH(CH_3){-}CH_2{-}N(CH_3)_2$

II



$(C_6H_5)_2C(CO{-}C_2H_5){-}CH_2{-}CH(N(CH_3)_2){-}CH_3$

III



$(C_6H_5)_2C(C({=}NH){-}C_2H_5){-}CH(CH_3){-}CH_2N(CH_3)_2$

IV

This ketimine was found to be remarkably resistant to hydrolysis, being only partially converted to the ketone (Isoamidone II, V) by boiling for five hours with an excess of 20% hydrochloric

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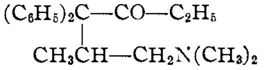
[1] E. M. Schultz, C. M. Robb and J. M. Sprague, THIS JOURNAL, **69**, 188 (1947).

acid. The ketone was isolated as the sesquioxalate (m. p. 162–163°. *Anal.* Calcd. for $2C_{21}H_{27}ON \cdot 3H_2C_2O_4$: C, 64.86; H, 6.76; N, 3.15; $H_2C_2O_4$, 30.41; neut. equiv., 148. Found: C, 65.2; H, 6.66; N, 3.43, 3.39; $H_2C_2O_4$, 30.40; neut. equiv., 149). This was further characterized as the base (oil, b. p. 215° under 12 mm. *Anal.* Calcd. for $C_{21}H_{27}ON$: C, 81.50; H, 8.80; N, 4.53. Found: C, 81.50; H, 8.90; N, 4.54, 4.52), the hydrochloride (m. p. 189–191°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot HCl$: C, 72.92; H, 8.16; N, 4.05; Cl, 10.25. Found: C, 72.95; H, 8.14; N, 4.02, 4.08; Cl, 10.24), the picrate (m. p. 149–150°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot C_6H_3O_7N_3$: C, 60.22; H, 5.58; N, 10.41. Found: C, 59.95; H, 5.54; N, 10.55, 10.52) and the methiodide (m. p. 263–264°. *Anal.* Calcd. for $C_{22}H_{30}ONI$: C, 58.54; H, 6.70; N, 3.10; I, 28.11. Found: C, 58.45; H, 6.78; N, 3.06; I, 28.25, 28.35).



$$\begin{array}{l}(C_6H_5)_2C—CO—C_2H_5 \\ \qquad\;| \\ CH_3CH—CH_2N(CH_3)_2\end{array}$$

V

When the crude mixture obtained by the condensation of diphenylacetonitrile with 1-dimethylamino-2-chloropropane was treated with ethylmagnesium bromide, there was formed, among other products, another isomer of amidone, which has been designated as Isoamidone I. This was isolated as the binoxalate (m. p. 158–160°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot H_2C_2O_4$: C, 69.15; H, 7.32. Found: C, 69.20; H, 7.06). This was also characterized as the base (oil, b. p. 164–167° under 3 mm. *Anal.* Calcd. for $C_{21}H_{27}ON$: C, 81.50; H, 8.80; N, 4.53. Found: C, 81.35; H, 8.84; N, 4.76, 4.73), the hydrochloride (m. p. 172–173°. *Anal.* Calcd. for $C_{21}H_{27}ON \cdot HCl$: C, 72.92; H, 8.16; N, 4.05; Cl, 10.25. Found: C, 73.05; H, 8.21; N, 4.25, 4.22; Cl, 10.25) and the methiodide (m. p. 195–196°. *Anal.* Calcd. for $C_{22}H_{30}ONI$: C, 58.54; H, 6.70; I, 28.11. Found: C, 58.65; H, 6.85; I, 28.40, 28.50). From this, it appears that there is a third aminonitrile formed in the original condensation.

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RECEIVED MARCH 18, 1947

THE CATHODIC PROTIUM-TRITIUM SEPARATION FACTOR

Sir:

Protium–tritium separation factors of 13.4 and 14.7 were observed in the electrolysis at 20.0° of a 10% sodium hydroxide solution at a smooth platinum foil cathode using a current density of 0.1 amp./sq.cm. The alkaline solution contained approximately 10^{-11} atom fraction tritium and had a normal deuterium content. Protium–deuterium separation factors of 6–8 have been reported for smooth platinum cathodes in both acid and alkaline media.[1]

Tritium activity was measured using a counting gas mixture consisting of hydrogen, ethyl alcohol, and argon at 25, 20 and 20 mm. partial pressure at 25° in a glass envelope copper gauze cathode Geiger counter having an effective counting volume of about 200 cc. Approximately 2×10^{-3} mole of hydrogen was produced in an electrolytic run, the isotopic composition of the medium remaining practically constant. Under these conditions the isotope separation factor equals the tritium–protium concentration ratio in the alkaline solution divided by that for the cathode gas. Water vapor was stripped from the latter using a liquid air trap and traces of oxygen were removed by combustion over a glowing nichrome wire. The tritium activity of the alkaline solution was determined by quantitatively converting the hydrogen in 0.05-g. samples of solution to hydrogen gas over magnesium at 630° in an analytical train previously "seasoned" at this activity. Table I summarizes the pertinent data.

TABLE I

Hydrogen source		Tritium activity in counts per minute per mm. at 25° of hydrogen gas	Isotope separation factor
Alkali solution		574 (Average, 571)	
		568	
Cathode gas	Electrolysis 1	38.9	14.7
	Electrolysis 2	42.7	13.4

The equilibrium constant at 20.2° for the reaction

$$HT + H_2O \rightleftharpoons H_2 + HTO$$

has been reported to be 6.47 ± 0.12 by Black and Taylor.[2] Libby[3] calculated a value of 6.24 for this equilibrium at 20°. The protium–tritium ratio for the hydrogen gas in the electrolyses reported above is thus slightly more than twice that corresponding to thermodynamic equilibrium conditions prevailing at the electrode interface. A detailed description of the analytical techniques developed for this study will be reported elsewhere. This investigation was supported by a grant from the Research Corporation.

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[1] B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934); A. Eucken and K. Bratzler, *Z. physik. Chem.*, **A 174**, 269 (1935).

[2] J. F. Black and H. S. Taylor, *J. Chem. Phys.*, **11**, 395 (1943).

[3] W. F. Libby, *ibid.*, **11**, 101 (1943).

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RECEIVED MARCH 8, 1947

TAUTOMERISM IN CYCLOHEXANE DERIVATIVES; REASSIGNMENT OF CONFIGURATION OF THE 1,3-DIMETHYLCYCLOHEXANES

Sir:

It is now established that cyclohexane has predominantly the chair configuration.[1] Except for

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[1] R. Rassmussen, *J. Chem. Phys.*, **11**, 249 (1943), and others there cited.