[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Cyclohepta[de]naphthalene (Pleiadiene)

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A re-examination of the reaction between chloranil and 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (I) has shown that low yields of cyclohepta[de]naphthalene are produced. A brief discussion of the resonance stabilization of such compounds is presented.

An investigation of certain nonbenzenoid "aromatic" compounds, initiated in 1949,¹ was concerned primarily with the attempted synthesis of cyclohepta[de]naphthalene (III). Although initial attempts to synthesize III were unsuccessful,¹ an inconclusive experiment conducted in the course of that investigation suggested that III may have been formed, although in low yield, by the dehydrogenation of 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (I) using chloranil as the hydrogen acceptor.^{2,3,4} The present report is concerned with a re-examination of that reaction.

Since this work was completed, the synthesis of III, by more conventional methods, has been reported, along with chemical evidence pertaining to the question of resonance stabilization in that substance.⁵ These data⁵ and the results of the chloranil reaction suggest that such stabilization is slight, if present at all.

The conversion of I to olefin II by reaction with lead tetraacetate, although previously reported to be undependable, has proved to be entirely satisfactory. Further attempts to prepare III from II, however, have not been successful.



The synthesis of III was finally effected by the treatment of I with chloranil in refluxing xylene solution,² from which, I, II, and III were isolated by chromatography and fractional crystallization. The mobilities of these three substances on alumina were so similar that several chromatograms were required for effective separation. Based on unrecovered I (23% recovery), II was formed in 56% yield and III in 7.5% yield.

- (1) Gardner and Horton, J. Am. Chem. Soc., 74, 657 (1952).
- (2) Arnold, Collins, and Zenk, J. Am. Chem. Soc., 62, 983 (1940).
- (3) Braude, Linstead, Mitchell, and Woolridge, J. Chem. Soc., 3595 (1954).

(4) Treibs, Steinert, and Kirchhof, Ann., 581, 54 (1953).
(5) Boekelheide and Vick, J. Am. Chem. Soc., 78, 653

(1956).

Pleiadiene (III) which appears to possess little resonance stabilization contains 14 π electrons. Acepleiadylene (IV), on the other hand, contains 16 π electrons and appears to possess significantly greater stabilization than III.⁵ These facts would appear discordant with the Hückel requirement⁶ of $4n + 2\pi$ electrons for resonance stability.⁵ It is implied, however, in the model used by Platt⁷ that in such systems peripheral electrons play a dominant role in resonance stabilization. Structures III and IV contain one and two "internal" carbon atoms, respectively. If the π electrons associated with "internal" carbon atoms be ignored and only peripheral p orbitals are considered to interact normally, then the peripheral system of III does not comply with the rule, while that of IV satisfies it. Superimposed on this is the interaction of "internal" p orbitals with the peripheral system.



This secondary interaction is less easily described with regard to type and degree and, although it could be calculated on the basis of molecular orbital theory, assumptions inherent in such applications of the theory would render the results questionable.

EXPERIMENTAL⁸

7,8-Dihydrocyclohepta[de]naphthalene (II). A solution comprised of 6.85 g. (0.014 mole) of lead tetraacetate and 2.31 g. of I dissolved in 55 ml. of purified⁹ acetic acid was heated, protected from atmospheric moisture, for 1.2 hr. The mixture was chilled, diluted with 300 ml. of water and extracted with several portions of ether. Washing with water and aqueous sodium hydrogen carbonate followed by

(8) Melting points are corrected.

⁽⁶⁾ Hückel, Z. Elektrochem., 43, 752 (1937).

⁽⁷⁾ Platt, J. Chem. Phys., 22, 1448 (1954). The relative importance of peripheral electrons in resonance considerations was first pointed out to us by a referee.

⁽⁹⁾ Purification by fractional distillation of a mixture of acetic acid and acetic anhydride from potassium permanganate.

drying and evaporation of solvent left the crude product as an oil. It was converted to the picric acid complex by dissolving it in 10 ml. of methanol containing 2.68 g. of picric acid. There was obtained 2.64 g. (51%) of red-brown complex, m.p. 129-132° (dec.) (lit.¹ 131-133°). Decomposition of a sample of the complex gave II, identified by m.p. and mixed m.p. Its ultraviolet absorption spectrum exhibited λ_{max} 229 m μ and 300 m μ , log ϵ 4.75 and 3.80, respectively (alcohol).

Cyclohepta[de]naphthalene. A suspension of 5.00 g. (0.0274 mole) of I and 13.52 g. (0.0548 mole) of recrystallized chloranil in 85 ml. of xylene was refluxed in a nitrogen atmosphere for 20 hr. The reaction mixture was transferred to a separatory funnel by repeated rinsing with petroleum ether (60-66°) and 10% aqueous sodium hydroxide and diluted with 700 ml. of water. After extracting the aqueous phase with several portions of ether, the combined organic solution was washed twice with dilute sodium hydroxide and then repeatedly with water. The dry (sodium sulfate) solution was distilled through a 2 ft. bead-packed column using a steam bath.

The residual oil was then dissolved in a minimum volume of petroleum ether $(60-66^{\circ})$ and charged to a column of acid-washed alumina $(1 \times 18 \text{ in.})$. The first eluate, containing I and II, appeared colorless in white light and blue in ultraviolet light. The red band (black in ultraviolet) contained III. The red eluate was concentrated using the bead column and the chromatography repeated. A third chromatogram afforded 0.454 g. of red liquid which was then dissolved in 20 ml. of ethanol and treated with 20 ml. of saturated alcoholic picric acid solution. The mixture was warmed until homogeneous, cooled, and filtered to yield 0.64 g. of brown-black complex, m.p. 186° (dec.) (7.5% based on unrecovered I). Repeated recrystallization from ethanol gave pure picric acid complex of III, m.p. 206– 208° (dec.).

Anal. Calc'd for $C_{20}H_{13}N_{3}O_{7}$: C, 58.96; H, 3.21. Found: C, 58.54; H, 3.09.

A sample (0.196 g.) of the complex was decomposed by washing an ethereal solution several times with aqueous sodium hydrogen carbonate. Isolation in the usual manner gave 0.084 g. of red solid (III), m.p. $88.5-90^{\circ}$ (with sintering at 86°). The sample for analysis was prepared by sublimation at 0.3 mm.

Anal. Cale'd for C₁₄H₁₂: C, 94.34; H, 5.66. Found: C, 94.20; H, 5.62.

A mixed melting point with material prepared by the other route^{5,10} was not depressed. Catalytic hydrogenation of a 2.8 mg. sample gave I. The ultraviolet absorption spectrum of III was virtually identical with that reported.⁵

The colorless eluates from all of the above chromatograms were combined and concentrated as before. To the residual oil thus obtained was added a solution of 5.0 g. of picric acid in 50 ml. of ethanol. Fractional crystallization gave a total of 4.82 g. (56% based on unrecovered I) of light red complex of II, m.p. 127-130° (dec.) (lit.¹ 131-133°). Further recrystallization gave material melting 130-132° (dec.). The bronze color previously reported for this complex was found to be due to a slight contamination by black solid. The pure hydrocarbon (II) was isolated and identified as described above, m.p. 44.5-46° (lit.¹ 43-45°).

The mother liquor of the above pieric acid complex was concentrated and cooled whereupon 2.63 g. (23%) of orange complex of I crystallized, m.p. 113-114°, characterized in the usual way.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. XXXIX. The Reaction of Diacetyl Peroxide with sec-Butyl Nitrite and 3-Amyl Nitrite

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The thermal decomposition of diacetyl peroxide in sec-butyl nitrite and 3-amyl nitrite results in the formation of a white solid of empirical formula CH_sNO . Cryoscopic molecular weight determination in benzene indicates that the material is a "dimer" (CH_sNO)₂. The Rast method (in camphor) indicated a molecular weight of 55. Upon hydrogenation of the "dimer" (CH_sNO)₂ a quantitative yield of methylamine was obtained. The "dimer" (CH_sNO)₂ forms a hydrochloride of the empirical formula (CH_3NO .HCl).

It was shown in previous publications that nitroso compounds² and nitrite esters³ are excellent inhibitors in the free radical bromination of aliphatic hydrocarbons. In the hope of elucidating the mechanism whereby nitrite esters act as inhibitors, the reactions of diacetyl peroxide with 3-amyl nitrite and *sec*-butyl nitrite, respectively, were investigated.

When diacetyl peroxide, dissolved in sec-butyl nitrite, was slowly added to sec-butyl nitrite, maintained at 73°, a reaction resulted (as indicated by an evolution of gas). Upon cooling the reaction mixture, a white solid, A, separated, and no additional amounts of this material were found on concentrating the filtrate. It was also established by conventional chemical methods that the filtrate contained

⁽¹⁾ The material presented in this paper formed part of a dissertation submitted in 1948 by Theodore H. Meltzer to the Graduate School of the University of Chicago in partial fulfillment of the requirements for the Ph.D. degree.

⁽²⁾ Kharasch, White, and Mayo, J. Org. Chem., 3, 33 (1938).

⁽³⁾ Kharasch, Hered, and Mayo, J. Org. Chem., 6, 818 (1941).