

water. The gray, cupric complex which separated was collected on a filter, suspended in ether and shaken with two portions of dilute hydrochloric acid. Removal of the ether from the organic layer left 3.27 g. (38.8%) of a white solid melting over the range 166–172°. Two recrystallizations from ethanol gave white needles, m.p. 172–173.5°.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.08; H, 8.39. Found: C, 82.09; H, 8.58.

The infrared spectrum of the material is very similar

to that of the known 1,3-dimesityl-1,3-propanedione.¹³ The ether solution, from which the copper complex of the 1,3-diketone had been precipitated, was evaporated to dryness and the residue steam distilled. The unchanged acetodurene in the distillate, amounting to 6.04 g., was collected on a filter.

(13) R. C. Fuson, W. O. Fugate and C. H. Fisher, *ibid.*, **61**, 2362 (1939).

URBANA, ILLINOIS

[CONTRIBUTIONS FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

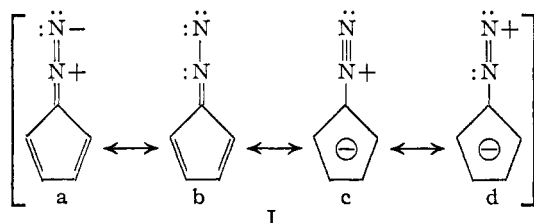
Diazocyclopentadiene¹

BY W. VON E. DOERING AND C. H. DEPUY

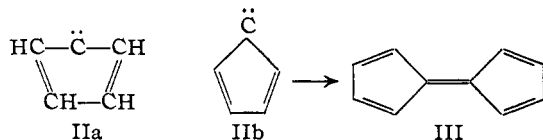
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By the novel reaction of cyclopentadienyllithium and *p*-toluenesulfonylazide, diazocyclopentadiene has been prepared. The structure of this stable, red diazo compound has been established.

Among various points of interest associated with the unknown diazocyclopentadiene (I), three are noteworthy. The arrangement of π -orbitals is



such that withdrawal of electrons from the diazo grouping to carbon leads to an aromatic resonance system of six electrons (Ic and Id).² This situation should be reflected in considerably different behavior from that shown by diazomethane. Related to diazocyclopentadiene by loss of nitrogen is a carbene, cyclopentadienylene (IIb), in which a linear arrangement (IIa) of divalent carbon and its bonded carbon atoms is denied by the small size of the ring. Finally, through its carbene or possibly



through another intermediate, I might be a precursor of fulvalene (III), hypothetically a non-benzenoid hydrocarbon of considerable resonance energy.³

Synthesis of I was first attempted from the dimer of cyclopentadienone oxime (IV, 1,8-dioximino-4,7-methano-3a,4,7,7a-tetrahydroindene) by way of the bis-hydrazone and the bis-diazo compound, the

dimer of I. Although this scheme was abandoned before completion in favor of another, a few observations are reported. The procedure of Thiele⁴ for the preparation of IV involved a method of purification which could not be reproduced and has therefore been replaced. One of the two oximino groups in IV was found to hydrolyze rapidly to a ketoxime, presumably 1-oximino-8-keto-4,7-methano-3a,4,7,7a-tetrahydroindene. IV showed the interesting property of subliming to an unstable, low-melting, yellow isomer which rapidly reverted to IV and may be a nitroso tautomer.

By means of the mechanistic theory outlined below, a new reaction was designed for the synthesis of I. In order to utilize the readily accessible cyclopentadienyllithium, a reagent, $N=N=A$, is required in which A must perform three functions: the negative charge introduced by the addition of the carbanion to the terminal nitrogen must be stabilized; the proton remaining at C₁ of the cyclopentadiene ring in this intermediate must be transferred to some atom in A so that, in the final stage AH^- may break away (as a relatively stable anion) from its bond to the second nitrogen atom, thereby removing the negative charge from the five-membered ring and forming I. Among the many groups, A, considered, $RSO_2N=$ represented an available reagent which satisfied the conditions not only in theory, as illustrated below, but in practice as well.⁵

Diazocyclopentadiene (I) is prepared in 35% of the theoretical amount by adding a suspension of cyclopentadienyllithium to *p*-toluenesulfonyl azide. As a by-product *p*-toluenesulfonamide is isolated in 29% of the theoretical yield.

The structure of I is consistent with several observations. Analysis and molecular weight point to $C_5H_4N_2$ as the empirical formula. Catalytic reduction to a hexahydro derivative which was shown to be identical with cyclopentanone hydra-

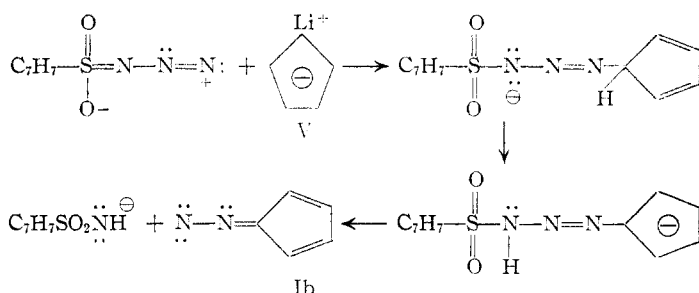
(4) J. Thiele, *Ber.*, **33**, 669 (1900).

(5) Stimulus for this conception was the work of M. Beringer and co-workers at the Polytechnic Institute of Brooklyn on the reaction of nitrous oxide with organometallic compounds [F. M. Beringer, J. A. Farr and S. Sands, *This Journal*, **75**, 3984 (1953)].

(1) Taken from a thesis submitted by C. H. DePuy to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. This work was supported in part by Contract DA-9-059-ORD-950 between the Office of Ordnance Research, U. S. Army, and Yale University.

(2) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

(3) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).



zone indicates a five-membered ring one atom of which is doubly bonded to a system of two nitrogen atoms. The strongest band in the infrared absorption spectrum (Fig. 1) lies at 2082 cm^{-1} ($4.80\text{ }\mu$) in a region generally associated with a triple bond or a system of two cumulated double bonds. Since both systems are excluded from a five-membered ring, only the two nitrogen atoms constituted as a diazo grouping can account for the band.⁶ Placement of the four hydrogen atoms in any way other than one on each of the four unsubstituted ring carbon atoms would lead to excessively strained structures.

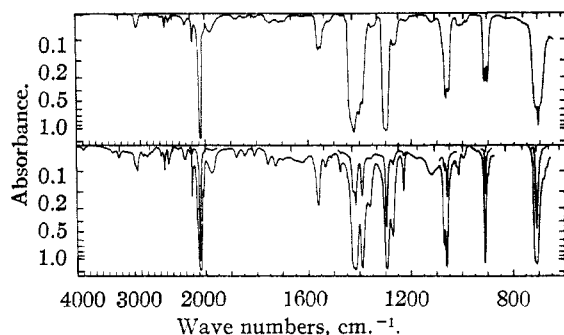


Fig. 1.—Lower curve, infrared absorption spectrum of diazocyclopentadiene in carbon tetrachloride (1.0 and 0.2 *M* in a 0.104-mm. cell) measured with a Perkin-Elmer Model 21 spectrophotometer, sodium chloride prism; upper curve, spectrum of the vapor (*ca.* 17 mm.) in an 8 cm. cell.

The ultraviolet spectrum (Fig. 2) of I has a maximum at $298\text{ m}\mu$ ($\log \epsilon 4.17$) and a long tailing absorption into the visible which is responsible for the red color of undiluted I. There can be no doubt that the spectrum results from a highly conjugated system.

Experimental⁷

1,8-Dioximino-4,7-methano-3a,4,7,7a-tetrahydroindene (IV).—A solution was prepared from 1 l. of absolute ethanol and 23 g. (1.0 mole) of sodium and cooled to 5° . A mixture of 71 g. (0.95 mole) of ethyl nitrite and 63 g. (0.95 mole) of freshly distilled cyclopentadiene was added to it dropwise and with stirring at such a rate that the temperature remained below 15° . After completion of the addition, which required 1 hr., the mixture was stirred an additional hour, diluted with 500 cc. of water and concentrated at 20 mm. in a bath at 40° to remove most of the ethanol. The remaining solution was extracted with ether until the extracts were colorless. Bubbling carbon dioxide into the aqueous solution precipitated black material which was

filtered and extracted continuously with ether overnight in a Soxhlet extraction apparatus. Concentration of this ether extract yielded 40 g. of slightly yellow solid. Continuous ether extraction of the aqueous filtrate yielded an additional 25 g. This material, m.p. $178\text{--}180^\circ$ (dec.), could not, as reported by Thiele,⁴ be purified by crystallization from water.

When 1 g. of the dioxime dissolved in 10 cc. of 20% sodium hydroxide was treated with 1.8 g. of benzoyl chloride, an oily precipitate was obtained which crystallized on heating in ethanol. Recrystallization from chloroform-ethanol afforded colorless crystals of the dibenzoate of the dioxime, m.p. $208\text{--}209^\circ$ as reported by Thiele.

In 95% ethanol the ultraviolet absorption spectrum of (IV) had a maximum at $261.5\text{ m}\mu$ ($\log \epsilon 3.40$).

Sublimation of IV at 1 mm. and 80° yielded a small amount of yellow crystalline material melting at $60\text{--}61^\circ$ to a yellow liquid which solidified at $110\text{--}115^\circ$ to colorless crystals, m.p. $155\text{--}157^\circ$ (dec.). The yellow solid dissolved very rapidly in ether and almost immediately deposited colorless crystals of IV; m.p. $179\text{--}180^\circ$ (dec.) showing no depression of m.p. in admixture with authentic IV. The yellow material was analyzed without further purification.

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{N}_2\text{O}_2$: C, 63.1; H, 5.3; N, 14.5. Found: C, 62.8; H, 5.5; N, 14.3.

Steam distillation of 1 g. of IV from aqueous oxalic acid gave a distillate of which the ether extractable material was sublimed. The 1-oximino-8-keto-4,7-methano-3a,4,7,7a-tetrahydroindene was obtained as colorless crystals (0.8 g.); m.p. $148\text{--}149^\circ$, $\lambda_{\text{max}} 261.5\text{ m}\mu$, $\log \epsilon 3.38$ (95% ethanol).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{NO}_2$: C, 68.5; H, 5.1; N, 8.0. Found: C, 68.4; H, 5.0; N, 8.0.

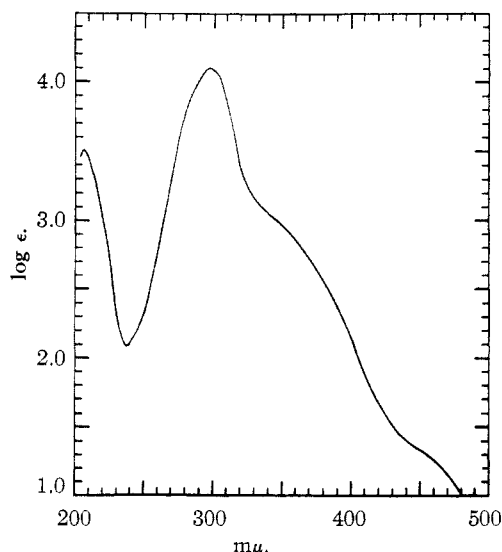


Fig. 2.—Ultraviolet absorption spectrum of diazocyclopentadiene in iso-octane solution measured with a Beckman Model DU spectrophotometer (with photomultiplier tube).

Diazocyclopentadiene (I).—*p*-Toluenesulfonyl azide was prepared in a modification of the procedure of Curtius and Kraemer⁸ by adding with swirling 70 g. of sodium azide in 200 cc. of water to 170 g. of freshly distilled *p*-toluenesulfonyl chloride in 1000 cc. of 95% ethanol. After standing one hour the mixture was poured into 4 l. of water. The separated oily sulfonyl azide was washed thrice with water and dried over sodium sulfate. Giving a negative test for chlorine it was used without further purification.

To a cooled solution of 0.5 mole of phenyllithium (prepared from 14 g. of lithium metal and 78 g. of bromobenzene according to the procedure of Gilman and Miller⁹ and filtered by forcing through a tube containing glass wool by

(8) T. Curtius and G. Kraemer, *J. prakt. Chem.*, **125**, 303 (1930).

(6) B. L. Crawford and W. H. Fletcher, *J. Chem. Phys.*, **19**, 406 (1951), report very strong absorption by diazomethane at 2101 cm^{-1} ($4.76\text{ }\mu$).

(7) Melting and boiling points are corrected. Analyses are by the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, New York.

(9) "Organic Reactions," Vol. VI, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 353-354.

(6) A. T. Carpenter and R. F. Hunter, *J. Appl. Chem.*, **1**, 217 (1951).