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.

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

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

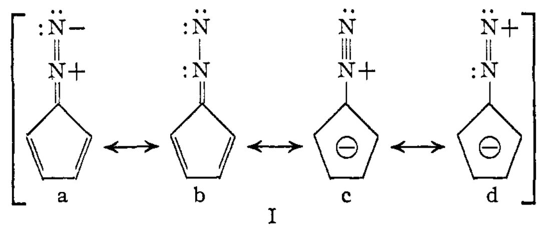
Diazocyclopentadiene[1]

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

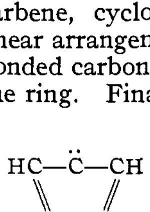
RECEIVED MAY 8, 1953

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

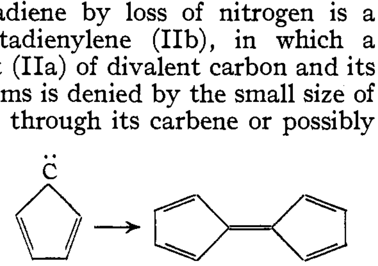
Among various points of interest associated with the unknown diazocyclopentadiene (I), three are noteworthy. The arrangement of π-orbitals is such that withdrawal of electrons from the diazo grouping to carbon leads to an aromatic resonance system of six electrons (Ic and Id).[2] This situation should 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 nonbenzenoid hydrocarbon of considerable resonance energy.[3]



I



IIa



IIb III

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 Thiele[4] 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 C_1 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-

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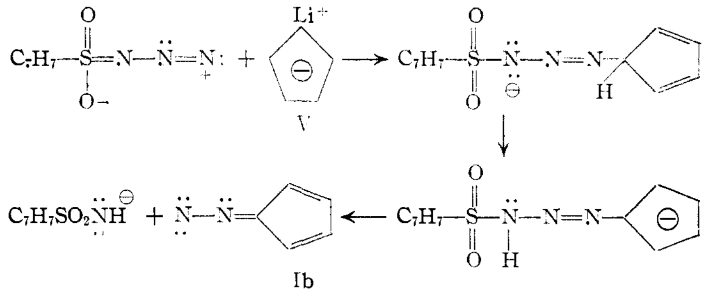
[1] Taken from a thesis submitted by C. H. DePuy to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. This work was supported in part by Contract DA-; 9-059-ORD-950 between the Office of Ordnance Research, U. S. Army, and Yale University.

[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).

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

[5] Stimulus for this conception was the work of M. Beringer and coworkers 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)].



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 μ) 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.

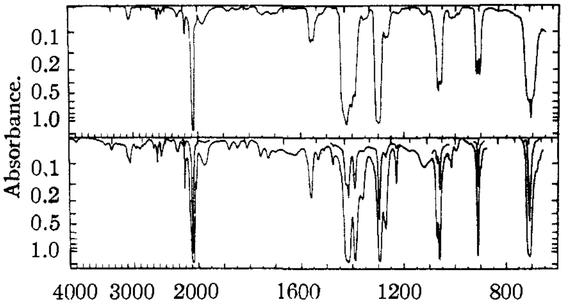


Fig. 1.—Lower curve, infrared absorption spectrum of diazocyclopentadiene in carbon tetrachloride (1.0 and 0.2 *M* in a 0.104-mm. cell) measured with a Perkin-Elmer Model 21 spectrophotometer, sodium chloride prism; upper curve, spectrum of the vapor (*ca.* 17 mm.) in an 8 cm. cell.

The ultraviolet spectrum (Fig. 2) of I has a maximum at 298 mμ (log ε 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.

Experimental[7]

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. 178–180° (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. 208–209° as reported by Thiele.

In 95% ethanol the ultraviolet absorption spectrum of (IV) had a maximum at 261.5 mμ (log ε 3.40).

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

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: 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. 148–149°, λ_{max} 261.5 mμ, log ε 3.38 (95% ethanol).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.5; H, 5.1; N, 8.0. Found: C, 68.4; H, 5.0; N, 8.0.

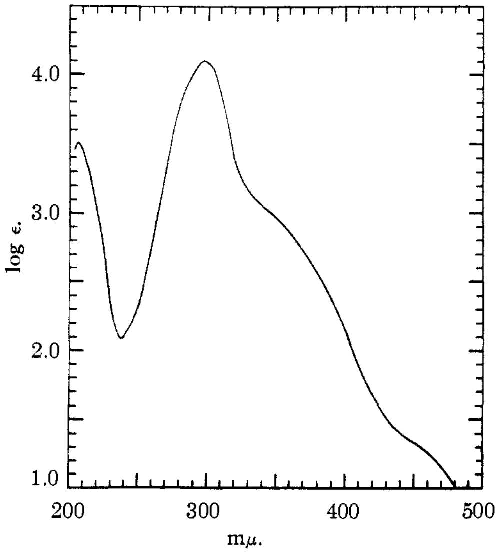


Fig. 2.—Ultraviolet absorption spectrum of diazocyclopentadiene in isoöctane solution measured with a Beckman Model DU spectrophotometer (with photomultiplier tube).

Diazocyclopentadiene (I).—*p*-Toluenesulfonyl azide was prepared in a modification of the procedure of Curtius and Kraemer[8] 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 Miller[9] and filtered by forcing through a tube containing glass wool by

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

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

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

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

means of pressure from a tank of prepurified nitrogen), a solution of 33 g. of freshly distilled cyclopentadiene in 150 cc. of dry ether was added dropwise with stirring over a period of 30 min.

After being stirred another hour at room temperature, the suspension of cyclopentadienyllithium (V) was forced under nitrogen pressure in a slow, steady stream into a cooled, stirred solution of 100 g. of *p*-toluenesulfonyl azide in 300 cc. of dry ether. The reaction became deep yellow almost immediately and gradually turned reddish-brown. A precipitate appeared during the addition which required one hr. Rapid filtration separated the mixture into a solid phase (A) and a red ether solution which was extracted twice with 100-cc. portions of water, dried over anhydrous sodium sulfate and concentrated. Distillation of the residue through a short Vigreux column gave 16 g. (35% of theory) of red diazocyclopentadiene, b.p. 52–53° at 50 mm. The material was best purified by crystallization first from alcohol and then from pentane, both at −70°. The heavy yellow needles melted at −23 to −22° to a red liquid, n^{25}D 1.6150, d^{29}_{25} 1.059.

Anal. Calcd. for $C_5H_4N_2$: mol. wt., 92.1. Found: mol. wt. (cryoscopic in benzene), 93.1.

Anal. Calcd. for $C_5H_4N_2$: C, 65.2; H, 4.4; N, 30.4. Found: C, 65.2; H, 4.3; N, 30.5.

The solid (A) was dissolved in water, treated with activated charcoal, filtered and acidified with hydrochloric acid. The colorless precipitate was filtered and dried to give 25.3 g. of *p*-toluenesulfonamide, m.p. 135–136° after one recrystallization and infrared spectroscopically identical with an authentic sample.

Catalytic Reduction of Diazocyclopentadiene.—Diazocyclopentadiene (2.0 g.) in 50 cc. of ether rapidly absorbed 3.0 molar equivalents of hydrogen over Adams platinum catalyst. Removal of the ether and distillation of the residue gave 1 cc. of colorless material; b.p. 42–43° at 2 mm., n^{26}D 1.5058.

Authentic **cyclopentanone hydrazone** was prepared from 50 g. of 85% hydrazine hydrate in 100 cc. of 95% ethanol, to which 30 g. of cyclopentanone was added with shaking. The mixture was refluxed for 30 min. and, after standing at 4° overnight, was concentrated on the steam-bath and distilled at 2 mm. There was obtained 9 g. of hydrazone; b.p. 45–45.5° at 1 mm., $n^{25.5}$D 1.5083.

Anal. Calcd. for $C_5H_{10}N_2$: C, 61.2; H, 10.2; N, 28.6. Found: C, 61.0; H, 10.5; N, 28.5.

The infrared spectrum of the reduction product was identical with that of the authentic cyclopentanone hydrazone. Furthermore, when treated with 2,4-dinitrophenylhydrazine, a derivative, m.p. 137–139°, was obtained which melted at 139–140° in admixture with authentic cyclopentanone 2,4-dinitrophenylhydrazone of m.p. 140–141°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Preparation and Condensation of Polymethylol Compounds

BY CHARLES A. BURKHARD, JOHN V. SCHMITZ AND ROBERT E. BURNETT

RECEIVED AUGUST 12, 1953

Several polymethylol compounds were prepared and their relative rates of condensation and thermal decomposition were compared.

Introduction

Sprung and Gladstone[1] have reported that the initial uncatalyzed rate of reaction of saligenin with phenol at 99° is 10 mole % per hour. In a continuation of this study it was of interest to compare reactivities of several other methylol compounds. It has now been found that the rate of reaction of 1-allyloxy-2,4,6-trimethylolbenzene with phenol is very nearly equal to that of saligenin while 2,4,6-trimethylolphenol reacts at a much greater rate. The rates of condensation were derived from measurements of changes in the concentrations of methylol groups determined by means of analytical acetylation.[2] In the absence of catalyst and at 99° a mixture of 1-allyloxy-2,4,6-trimethylolbenzene and three equivalents of phenol gave an initial rate of reaction of about 9 mole % per hour whereas the rate of a similar mixture of 2,4,6-trimethylolphenol and phenol was about 60 mole % per hour. At 60° in the presence of 1% (by weight) of *d*-camphorsulfonic acid, 1-allyloxy-2,4,6-trimethylolbenzene and phenol reacted at an initial rate of about 50 mole % per hour whereas the reaction of 2,4,6-trimethylolphenol was exceedingly rapid under the same conditions.

The decreasing order of thermal stability of the pure compounds is: 1-allyloxy-2-methylolbenzene, 1-allyloxy-2,4,6-trimethylolbenzene, saligenin, 2,4,-6-trimethylolphenol. After two hours at 120° a pure sample of 1-allyloxy-2-methylolbenzene lost 3% of its methylol groups, 1-allyloxy-2,4,6-trimethylolbenzene lost 9%, saligenin lost 81%, and 2,4,6-trimethylolphenol polymerized to an insoluble gel. In thermal decompositions both 2,4,6-trimethylolphenol and 1-allyloxy-2,4,6-trimethylolbenzene evolved formaldehyde.

1-Allyloxy-2,4,6-trimethylolbenzene was reported by Martin[3] to be a light tan liquid (*n* 1.575–1.579, *d* 1.20–1.21). In the course of the present investigation the 1-allyloxy-2,4,6-trimethylolbenzene of Martin was further purified and isolated as a colorless crystalline solid (m.p. 86.0–86.2°). In addition the following three compounds were prepared: 1-allyloxy-2-methylolbenzene, 1-allyloxy - 2,4,6 - tristrimethylsiloxymethylbenzene and 1-allyloxy-2,4-bistrimethylsiloxymethylbenzene.

2,4,6-Trimethylolphenol was prepared from sodium 2,4,6-trimethylolphenate by two methods: partial acidification[4] and by isolation and hydrolysis of the trimethylsilyl ether.[5] It was found that 2,4,6-trimethylolphenol exists in two polymorphic forms (m.p. 76 and 82°; mixed m.p. 82°). Previous workers have reported a diversity of melting points, 74–75°,[4] 76–78°[6] and 84°,[5] for this compound. Freeman[4] found that 2,6-dimethylolphenol also exhibits polymorphism.

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[1] M. M. Sprung and M. T. Gladstone, THIS JOURNAL, **71**, 2907 (1949).

[2] R. E. Burnett, *Anal. Chem.*, in press.

[3] R. W. Martin, U. S. Patent 2,579,330 (December 18, 1951).

[4] J. H. Freeman, THIS JOURNAL, **74**, 6257 (1952).

[5] R. W. Martin, *ibid.*, **74**, 3024 (1952).

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