benzene (an impurity in the phenyllithium reagent) eluted with Ib under these conditions, Ib was rechromatographed on a similar column packed with 20% w./w. of the diglyceride of ω-trifluorohexanoic acid supported on 40–60 mesh Columpak (Fisher Scientific Co.) maintained at 82° with the vaporizer at 140° and a helium flow rate of 92 cc./min.

Additional studies of these and related systems will be published at a later date.

Acknowledgment.—The author wishes to express appreciation to Dr. W. D. Phillips for helpful discussion and to Mrs. A. B. Richmond and Mr. J. W. Robson for the vapor phase chromatographic separations.

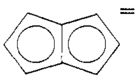
CONTRIBUTION NO. 736
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION S. ANDREADES
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE

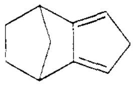
RECEIVED JANUARY 5, 1962

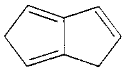
THE PENTALENYL DIANION

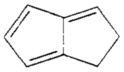
Sir:

We wish to report the synthesis of dilithium pentalenide, the first derivative of the pentalenyl dianion (I), the pure reduction product of the unknown pentalene and the lower homolog of naphthalene. Since the pentalenyl dianion and the cyclopentadienyl anion are related in the same way as naphthalene and benzene, the preparation of this dianion seemed a natural entry into the elusive pentalene series.[1] Previous success in the preparation of salts of the cycloöctatetraenyl dianion[2] strengthened our faith in this supposition.


I


II


III


IV

Dilithium pentalenide forms readily on treatment of dihydropentalene in tetrahydrofuran solution with somewhat more than two moles of n-butyllithium in n-heptane. The salt, which is white, crystallizes beautifully from solution on cooling, or precipitates on addition of n-pentane. Solutions in tetrahydrofuran are slightly yellow but appear to be perfectly stable at room temperature. The presence of the dianion in these solutions and in the crude reaction mixtures is signalled in the nuclear magnetic resonance spectrum (Fig. 1) by the replacement of the intricate dihydropentalene spectrum by one consisting of two bands, a triplet centered at $\tau = 4.27$ and a doublet centered at $\tau = 5.02$. The spin-spin splittings are identical ($J = 3.0$ cps.), and the ratio of intensities is exactly 1:2.

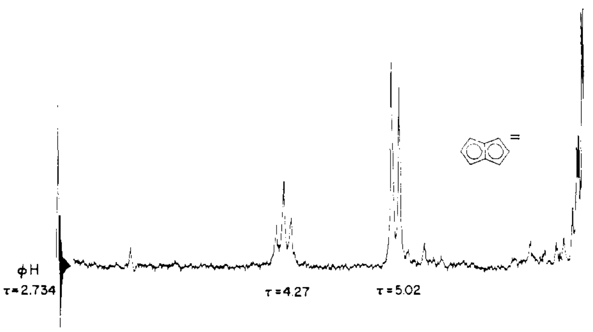
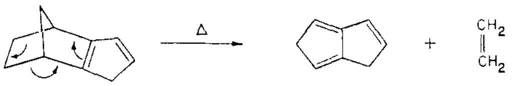


Fig. 1.—N.m.r. spectrum of dilithium pentalenide in tetrahydrofuran (containing pentane) with benzene and tetramethylsilane as internal reference standards. Spectra were determined on the Varian A-60 spectrometer.

Dihydropentalene was prepared pyrolytically from isodicyclopentadiene (II)[3] by passing the vapor in a nitrogen stream at 20 mm. pressure through a quartz tube packed with quartz chips at 575°.[4] Distillation of the pyrolysate resulted in a 30% yield of a yellow liquid, b.p. 52.5–53° at 18 mm., which was shown to be homogeneous by vapor phase chromatography. Addition of hydroquinone prevented its otherwise ready polymerization. That this was dihydropentalene was proven by analysis (Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.81) and by hydrogenation over platinum in ether, a reaction which proceeded with the absorption of three moles of hydrogen and yielded a hydrocarbon shown to be *cis*-bicyclo[3.3.0]octane. The identity of the latter with an authentic sample[5] was demonstrated by comparison of the n.m.r. spectra, the infrared spectra, and the retention times characteristic of vapor phase chromatography on an Aerograph 5% SE-30 column. If dihydropentalene is not a mixture of double bond isomers, the location of the double bonds is indicated by the n.m.r. spectrum, which consists of four multiplets of equal intensity centered at $\tau = 3.67$, 4.2, 6.77, and 7.02. Thus, two structures for dihydropentalene, of sufficient symmetry that only one methylene peak can be anticipated, are eliminated by the observation of two high field resonances, while of the remaining structures III and IV, only III seems consistent with the observed chemical shifts.[7,8]



(1)

---

[1] The pentalene system has attracted considerable theoretical and experimental interest. References to the field may be found (a) in the chapters by E. D. Bergmann and D. Craig in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Editor, Interscience Publishers, Inc., New York, N. Y. 1959, and (b) in H. J. Dauben, Jr. and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).

[2] T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

[3] K. Alder, F. H. Flock, and P. Janssen, *Chem. Ber.*, **89**, 2689 (1956).

[4] P. Janssen, Dissertation, Köln, 1959; R. Reimschneider and K. Heymans, *Monatsh.*, **92**, 1080 (1961).

[5] We are grateful to J. D. Roberts, W. F. Gorham, and M. Caserio for a gift of this compound.[6]

[6] J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952).

[7] This latter observation is that of Professor Ronald Breslow.

[8] The methylene protons in cyclopentadiene appear at $\tau = 7.10$,[9] while the allylic methylenes of cyclopentadiene appear at $\tau = 7.7$.[10]

[9] G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) 'Shielding Values' (Spectral Positions) for Hydrogen in Organic Molecules," Central Research Lab., Minnesota Mining and Manufacturing Co., St. Paul, Minnesota, 1958.

[10] "A Catalogue of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and their Derivatives," Humble Oil and Refining Co., Research Division, Baytown, Texas, 1959.

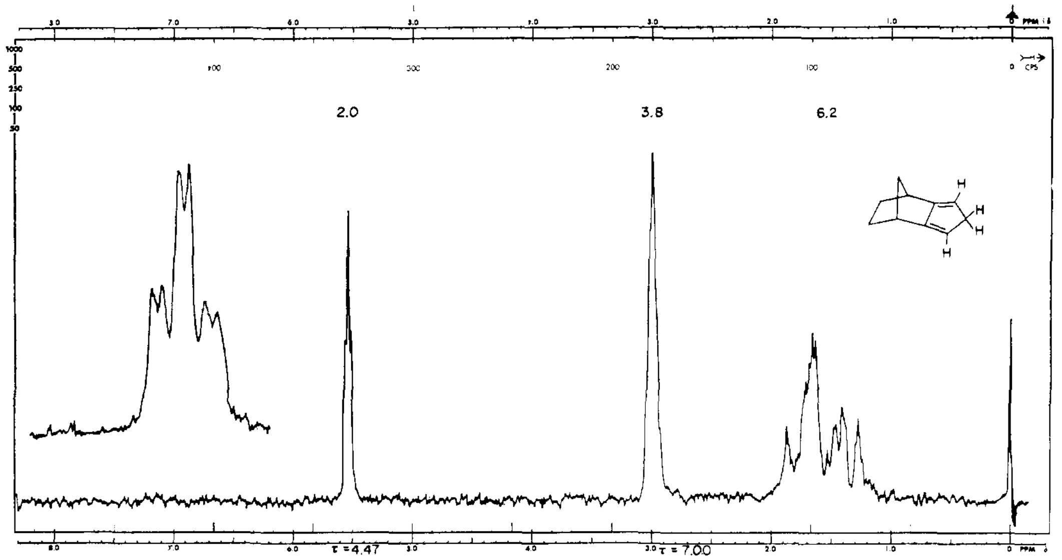


Fig. 2.—N.m.r. spectrum of isodicyclopentadiene in CCl_4 with tetramethylsilane as an internal reference. The spectrum integrals are given above each major band. The insert is a ten-fold expansion of the olefin resonance.

Structures III and IV both appear consistent with the observed ultraviolet spectrum, λ_{max} (n-pentane) 268 mμ (log $\epsilon = 3.64$).[11]

That the double bonds in isodicyclopentadiene are located as shown in II is indicated by the appearance of the n.m.r. spin–spin splitting pattern of the olefinic protons (Fig. 2). The cracking reaction which leads to dihydropentalene must, therefore, proceed by initial isomerization of isodicyclopentadiene to V, which then undergoes a reverse Diels–Alder reaction (eq. 1). The facility of double bond isomerization in the cyclopentadiene series is expected on the basis of known precedents.[14]

Acknowledgments.—We are grateful to Larry Parker and Barbara Wirth for assisting in the organic syntheses, and to the National Science Foundation (NSF G-15561) and the Socony Mobil Oil Co. for financial support.

---

[11] For cyclopentadiene in n-heptane λ_{max} = 244 mμ (log ϵ = 3.40),[12] while for dimethylfulvene in isoöctane λ_{max} = 265 mμ (log ϵ = 3.9).[13]

[12] R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1803 (1958).

[13] M. T. Murphy and A. C. Duggan, *J. Am. Chem. Soc.*, **71**, 3347 (1949).

[14] For example, the reaction of indene with maleic anhydride which yields a normal Diels–Alder adduct of isoindene[15]; the reverse Diels–Alder reactions of dicyclopentadienol-1[16] and its acetate[17] which yield mixtures of double bond isomers.

[15] K. Alder, F. Pascher and H. Vagt, *Chem. Ber.*, **75**, 1501 (1942).

[16] M. Rosenblum, *J. Am. Chem. Soc.*, **79**, 3179 (1957); K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

[17] R. E. Vanelli, Dissertation (Harvard, 1950); C. J. Norten, Dissertation (Harvard, 1955).

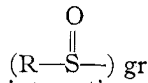
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

THOMAS J. KATZ
MICHAEL ROSENBERGER

RECEIVED JANUARY 26, 1962

METHYLSULFINYLCARBANION

Sir:

Little is known about the chemical reactivity of carbanions substituted by a single alkylsulfinyl  $(R-\overset{O}{\overset{\|}{S}}-)$ group although there is evidence that the interaction of this function with adjacent negative charge produces appreciable stabilization, intermediate in degree between that associated with nitro, carbonyl, sulfonyl, *etc.*, on the one hand and hydrogen (*vs.* alkyl) on the other.[1] We have found that the parent member of this class, methylsulfinyl carbanion (I), the conjugate base of dimethyl sulfoxide, is simply generated, highly reactive and sufficiently promising in a wide variety of applications to warrant preliminary mention here. For various reasons including the great reactivity of the anion no attempt has been made as yet to obtain it in the form of crystalline salts. The present investigations were carried out with freshly prepared solutions of sodium methylsulfinylcarbanion in dimethyl sulfoxide which were formed from reaction of powdered sodium hydride with excess dry dimethyl sulfoxide (500–600 ml. per mole of sodium hydride) at 65–70° under nitrogen with stirring until evolution of hydrogen is complete (*ca.* 45 minutes).[2] The formation of anion was verified by reaction with an equimolar amount of benzophenone to give the hydroxy sulfoxide II, m.p. 148–148.5°, in 86% yield; analogous reaction with benzaldehyde afforded III as a mixture of diastereomers, m.p. 78–123°.[3]

---

[1] See, for example, (a) H. H. Szmant in "Organic Sulfur Compounds," Vol. I, edited by N. Kharasch, Pergamon Press, New York 22, N. Y., 1961, pp. 154–169; (b) A. Schöberl and A. Wagner in "Methoden der Organischen Chemie (Houben-Weyl)," 4th Ed., Georg Thieme Verlag, Stuttgart, Vol. IX, p. 211 (1955); (c) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).

[2] The sodium salt also can be made using sodium amide; the lithium salt is available starting from lithium hydride. Dimethylsulfoxide was dried by distillation from calcium hydride under reduced pressure (*ca.* 1 mm.).

[3] Acceptable elemental analyses have been obtained for all new compounds reported herein along with sufficient physical data (infrared, ultraviolet, and nuclear magnetic resonance spectra) to define structure.