[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Pentalenyl Dianion[1]

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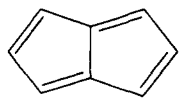
The synthesis of dilithium pentalenide, the reduction product of pentalene, by the reaction of dihydropentalene with *n*-butyllithium is described. Spectral properties of the pentalenyl dianion are presented.

Introduction

Despite its theoretical interest the hydrocarbon pentalene[2] (I) has defied synthesis. The Hückel molecular orbital theory is not completely consistent in its application to a nonalternant system such as this,[3] but implies that the molecule should be easily reduced, and that the related anions $C_8H_6^-$ and $C_8H_6^{-2}$ (II) should be readily accessible. This follows from the energy distribution of the one electron L.C.A.O. molecular orbitals, which for the hydrocarbon in its electronic ground state leaves a nonbonding orbital empty. Since the reduction potential of the molecule should be proportional to the energy of its first unfilled molecular orbital,[4] and inasmuch as better known hydrocarbon molecules (*e.g.*, derivatives of triphenylmethyl,[5] perinaphthenyl,[6] and cyclooctatetraene[7]) can be oxidized and reduced by common reagents to oxidation states that have nonbonding molecular orbitals filled to varying degrees and that are stable in at least some chemical environments, so the lower oxidation states of pentalene, the related anions, should be preparable.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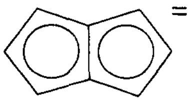
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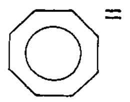
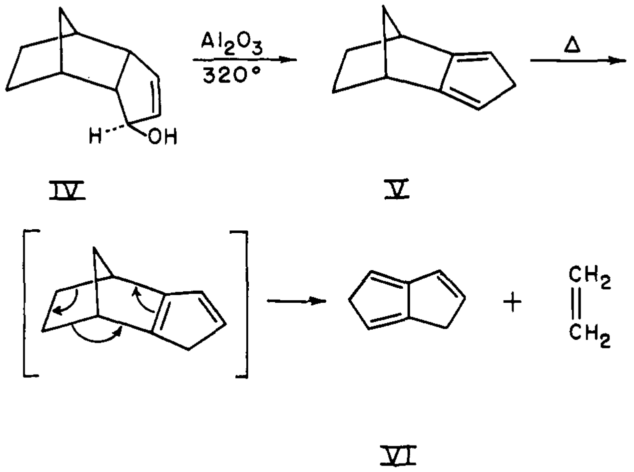

III

The pentalenyl dianion is related to the cyclopentadienyl anion as naphthalene is to benzene in that a common double bond fuses two like fundamental aromatic moieties. The pentalenyl dianion is also related to the cyclooctatetraenyl dianion[7a] (III) if the ring fusion only slightly perturbs the π-electronic structure of the monocyclic system.[8]

The synthesis of the pentalenyl dianion is described below.[9]

Results

Hydrogenation of dicyclopentadiene in ethanol in the presence of a palladium-on-charcoal catalyst selectively saturates the strained double bond of the bicyclic ring system.[10] The resultant dihydrodicyclopentadiene, on oxidation with selenium dioxide in acetic anhydride–acetic acid and subsequent saponification of the acetate so formed, yields 1-hydroxy-5,6-dihydrodicyclopentadiene (IV).[11,12] On dehydration over alumina[13] at 320°, this yields the hydrocarbon isodicyclopentadiene (V).



IV V VI

Pyrolysis of isodicyclopentadiene,[14] in a nitrogen stream at 575°, gives ethylene, identified as the bromine adduct, and in 33% yield, dihydropentalene (VI),[15] a pale yellow liquid that boils at 50–54° at 6 mm. pressure. At higher temperatures less dihydropentalene is found in the pyrolysate, but the isomeric hydrocarbon styrene is readily isolated. Dihydropentalene, styrene, and isodicyclopentadiene are distinguishable by gas chromatography, and the efficiency of the pyrolysis reaction can, therefore, be easily monitored. The dihydropentalene prepared in our laboratory usually contained a small amount (*ca.* 1%) of styrene. Dihydropentalene polymerizes readily, but can be stored for months at Dry Ice temperature in the presence of a trace of hydroquinone. Hydrogenation of dihydropentalene over platinum in ether yields *cis*-bicyclo[3.3.0]octane, identified by comparison of its n.m.r. and infrared spectra and its gas chromatographic behavior with an authentic sample.[16]

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(1) Preliminary communication: T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

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(3) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

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(7) (a) T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960); (b) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); (c) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

(8) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

(9) The preparation of a dibenztetraaza analog of the pentalenyl dianion was recently described: R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962).

(10) K. Alder and G. Stein, *Ann. Chem.*, **485**, 223 (1931).

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

(12) The hydroxyl group is probably *syn* to the adjacent hydrogens and *anti* to the fusion with the bridged ring system (*cf.* R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959)).

(13) AGS alumina from Gebr. Giulini GmbH., Ludwigshafen a. Rhein, Germany, was used (*Cf.* ref. 11 and K. Alder and H. V. Brachel, *Ann. Chem.*, **608**, 198 (1957)).

(14) (a) P. Janssen, Dissertation, Köln, 1959; (b) R. Riemschneider, *Z. Naturforsch.*, **16b**, 759 (1961).

(15) Some substituted dihydropentalenes have recently been synthesized: ref. 2d; E. Cioranescu, A. Bucur, G. Mihai, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **95**, 2325 (1962); L. Horner, H.-G. Schmeltzer, H. U. von der Eltz, and K. Habig, *Ann. Chem.*, **661**, 44 (1963).

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

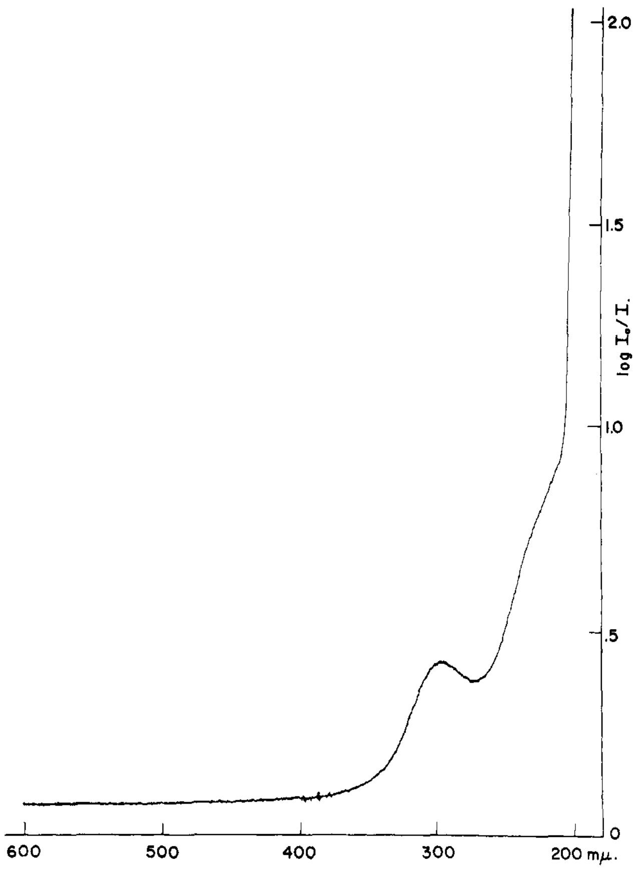


Fig. 1.—Ultraviolet spectrum of dilithium pentalenide in THF.

Treatment of dihydropentalene in a tetrahydrofuran (THF) solution with *n*-butyllithium in *n*-hexane furnishes a pale yellow solution, which on cooling precipitates a white crystalline solid. This appears to be dilithium pentalenide, the lithium salt of the pentalenyl dianion. It is insoluble in *n*-pentane, only slightly soluble in 1,2-dimethoxyethane (DME), and moderately soluble in THF. In THF solution, its n.m.r. spectrum[1] below 6.3 τ (the position of the low-field THF peak) consists only of a triplet at 4.27 τ and a doublet at 5.02 τ, with identical splittings of 3.0 c.p.s. This is the pattern that would be expected of the pentalenyl dianion. As required, the doublet is twice as intense as the triplet.

Quenching the solution with a neutral phosphate buffer, rapidly extracting the reaction mixture with *n*-pentane, and then hydrogenating over platinum gives *cis*-bicyclo[3.3.0]octane in 28% yield. Thus, the *n*-butyllithium treatment has not changed the carbon skeleton. The reagent has not added to one of the double bonds of dihydropentalene.

The ultraviolet spectrum of dilithium pentalenide (Fig. 1) was measured in THF and was found to have a maximum at 296 mμ (log ε 3.7) and a slight shoulder at 210 mμ. In DME the maximum appeared at 295 mμ (log ε 3.8).

Discussion

Isodicyclopentadiene was previously assigned the structure V on the basis of its reaction with dienophiles.[11] Since a rearrangement might have occurred in the course of this reaction, the assignment can be regarded as only tentative. It appears however to be correct, for the n.m.r. spectrum[1] of isodicyclopentadiene in the olefinic region consists of a triplet ($J = 1.35$ c.p.s.), each line of which is further split into a doublet ($J = 0.5$ c.p.s.). The equivalent olefinic protons in V should produce only a single resonance, split into a triplet by the adjacent methylene hydrogens and further into doublets by the allylic bridgehead hydrogen.[17]

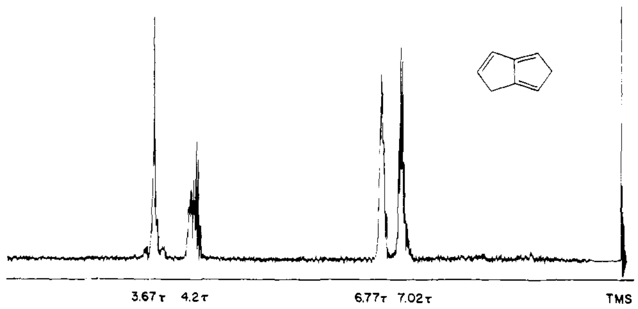
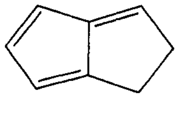


Fig. 2.—Nuclear magnetic resonance spectrum of dihydropentalene in CCl_4.

The structure of dihydropentalene, except for the position of the double bonds, is proved by its hydrogenation to *cis*-bicyclo[3.3.0]octane. The position of the double bonds is suggested by the n.m.r. spectrum of the hydrocarbon, which consists of four groups of bands at 3.67, 4.2, 6.77, and 7.02 τ, all of equal intensity (Fig. 2). There are only six structures that can be drawn for dihydropentalene. Of these, two, because of their high symmetry, have only one kind of methylene hydrogen, and are thus excluded by the observation of two high-field resonances. Two that have different kinds of nonolefinic protons are excluded by the observed intensity ratios. And of the two structures remaining that can account for the gross appearance of the spectrum, structure VI for dihydropentalene is favored over structure VII because the chemical shifts of the high-field peaks are more similar to the shift of the allylic protons in cyclopentadiene (7.10 τ)[19] than to the shift of the allylic protons in cyclopentene (7.7 τ).[20] While in VI the nonolefinic hydrogens are each double allylic, in VII they are each only singly allylic.



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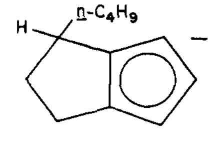

VIII

The structure VI does not appear to be excluded by the ultraviolet spectrum of dihydropentalene, although the position of the maximum ($\lambda_{\max}^{n\text{-pentane}}$ 268 mμ, log ε 3.64) is very similar to that of dimethylfulvene ($\lambda_{\max}^{\text{isooctane}}$ 265 mμ, log ε 3.9),[21] for the conjugation of another double bond with cyclopentadiene ($\lambda_{\max}^{n\text{-heptane}}$ 244 mμ, log ε 3.40)[22] might also place the VI chromophore in the observed wave length region.

If the *n*-butyllithium had added to dihydropentalene (as it might have to VII) rather than abstracted two hydrogen atoms, then VIII rather than the pentalenyl dianion II might have formed. Although the n.m.r. spectra of both VIII and II should be expected to exhibit A_2B patterns, the spectra should be very different.

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(17) The methylene–olefin splitting is, as expected, small (*cf.* ref. 18).

(18) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

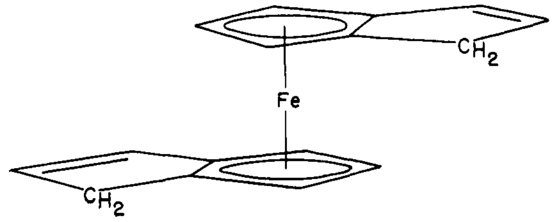
(19) G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) 'Shielding Values' (Spectral Positions) for Hydrogen in Organic Molecules," Central Research Lab., Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

(20) "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.

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

(22) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1803 (1953).

While the large observed chemical shift between the A and B protons is a natural consequence of the structure of the pentalenyl dianion, it is not expected of VIII. The inductive effect of the alkyl substituents in VIII should not produce such a shift; the two kinds of ring protons in methylcyclopentadienide, for example, are immeasurably shifted.[23] Nor should alkyl substituents have moved the cyclopentadienide resonance to lower fields than the resonance[18] of the unsubstituted anion. A ring fusion (Mills-Nixon[24]) effect might possibly account for even these observations. But the reisolation of bicyclo[3.3.0]octane after the anion was quenched with water and hydrogenated (as described in the Results section above) is not in accord with this formulation. Neither is the observed formation of dihydrodipentalenyl iron[25] (IX and its double bond isomer) when dihydropentalene is treated with one mole of *n*-butyllithium and then ferrous chloride, for X or an isomer should then have been expected to result.[26]



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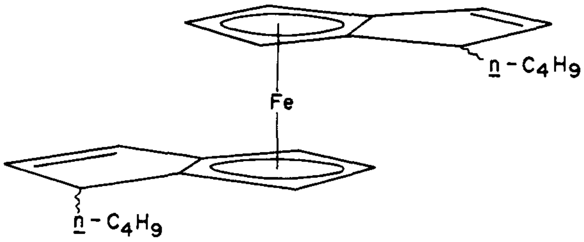

X

The chemical shifts observed in the n.m.r. spectrum of the pentalenyl dianion are in reasonable accord[27] with expectation based on a ring-current deshielding effect of the π-electrons[28] and a shielding effect associated with the negative charge on the carbon atoms to which the protons are attached,[18] if charge densities calculated by the Hückel molecular orbital method are used. If charge densities calculated by an A.S.M.O.C.I. calculation[29] are used to derive the expected chemical shift, the agreement with the relative line positions is excellent. If densities calculated by an S.C.F.[30] method are used, the agreement is poor; the doublet should then have been displaced 1.0 p.p.m. to higher fields than was observed. The S.C.F. calculations would indicate that charge is less uniformly distributed about the molecule than even the Hückel theory predicts, while the n.m.r. data show that in this, as in other ions,[27,31] the charge distribution is much more uniform. Both the molecular orbital calculations and expectation based on considerations of valence bond structures would suggest that the negative charge in the dianion is more concentrated at the α- than the β-positions, which is borne out by the observation that the doublet of relative intensity two appears at higher, and not lower, applied magnetic field than the triplet of relative intensity one.

The longest wave length maximum in the ultraviolet spectrum of dilithium pentalenide (Fig. 1) appears at 295 mμ. The values calculated for the position of this maximum, assuming a regular pentagonal geometry for the rings, and bond lengths equal to those in benzene, are 271 mμ by the Pariser-Parr method,[29] 250 mμ by the Pople S.C.F. method,[32] and 268 mμ by the split p-orbital method.[32,33] The ultraviolet spectrum of lithium cyclopentadienide in THF, in contrast, has no high intensity maximum above 205 mμ.[34]

Experimental

Tetrahydrofuran was stored over KOH and freshly distilled from $LiAlH_4$ before use. 1,2-Dimethoxyethane (DME) was freshly distilled from $LiAlH_4$. Pentane was distilled from CaH_2.

Nuclear magnetic resonance spectra were determined on the Varian A-60 instrument, infrared spectra on the Perkin-Elmer 421.

Dihydrodicyclopentadiene.[10]—Dicyclopentadiene (Matheson Coleman and Bell technical grade) was hydrogenated in a Parr shaker in 80-g. lots dissolved in 165 g. of ethanol with 0.25 g. of 10% Pd-on-charcoal catalyst. Cooling and filtering yielded, from 2520 g. of dicyclopentadiene, 1900 g. of the dihydro derivative.

1-Hydroxy-5,6-dihydrodicyclopentadiene.[11]—Dihydrodicyclopentadiene (1516 g.) in acetic anhydride (3800 g.)-acetic acid (723 cc.) was stirred and slowly treated with selenium dioxide[35] (1125 g.) in water (456 ml.). The temperature was maintained at 40–50° throughout the addition. The mixture was stirred overnight, the precipitated selenium filtered, and the solvent cautiously distilled at 12 mm.

The crude residue was added to KOH (700 g.) in methanol (7970 ml.) while being stirred and cooled. After a day, the volume was quintupled with water, and the mixture extracted with ether. After drying and distilling the solvent, the product (1020 g., 60%), b.p. 77–85° (0.1 mm.), was isolated.

Isodicyclopentadiene.[11]—The above alcohol (840 g.) was added in a nitrogen stream at 18–21 mm. pressure, from a steam-heated Hershberg dropping funnel to a vertical Pyrex tube (14-in. × $1^1/_8$-in.), packed with alumina[13] and heated to 320° in a furnace, which led to a cooled (Dry Ice), 2-l., 3-necked flask connected in series with a trap. The alumina was replaced three times in the course of this experiment. The product was extracted with pentane (*ca.* 4 l.), treated with a trace of hydroquinone, dried ($MgSO_4$), and distilled. The yield of isodicyclopentadiene, b.p. 78° (20 mm.), was 546 g. (74%).

Dihydropentalene.—The apparatus consisted of a water-cooled Hershberg dropping funnel attached to a prevaporizer that led into a quartz pyrolysis tube packed with quartz chips and enclosed in a vertical furnace. The product was collected at liquid nitrogen temperature in two traps in series. The prevaporizer consisted of a short tube packed with Pyrex helices, wrapped on the outside with nichrome wire, and heated to approximately 100°. The dropping funnel was attached to a source of nitrogen, purified by passage over heated copper and then Drierite, and the traps were attached *via* a manometer and tilting manostat to a vacuum pump. The glassware was washed with hot chromic acid in nitric acid and rinsed with dilute aqueous ammonia. It was assembled, pumped to 1 mm., and heated to 500°. The pressure was raised to atmospheric, and the isodicyclopentadiene placed in the dropping funnel. The pressure was decreased to 20 mm., the furnace heated to 570°, and 3–5 drops of diene added. Vapor phase chromatographic analysis of the pyrolysate dissolved in a small amount of pentane was carried out on an Aerograph Hi-Fi instrument (flame ionization detector) using a 5% SE-30 column. In a successful experiment, the area ratios of the styrene, dihydropentalene, and isodicyclopentadiene peaks were 5:300:5.

The first trap was now replaced by a 1-l. 3-necked flask, and both it and the second trap were charged with small amounts of hydroquinone. The diene was pyrolyzed at a rate of 2–3 drops/sec.

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[23] S. McLean and P. Haynes, *Can. J. Chem.*, **41**, 1231 (1963).

[24] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p. 134.

[25] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **85**, 2026 (1963).

[26] G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 4610 (1961).

[27] T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[28] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

[29] H. E. Simmons, private communication. Dr. Simmons has informed us that his ASMO CI calculations predict that the charge densities in the dianion will be 1.32 at the α-positions and 1.23 at the β-positions.

[30] A. J. Silvestri, L. Goodman, and J. A. Dixon, *Tetrahedron*, **18**, 1329 (1962).

[31] C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

[32] M. J. S. Dewar, private communication.

[33] This should be a weak α (L_b) band, however; a strong band at 252 mμ is also expected.

[34] Observation of William Okamura in this Laboratory.

[35] N. Rabjohn, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 345.

On vapor phase chromatography, a small sample of the cold pyrolysate dissolved in pentane showed two closely-spaced peaks (areas *ca.* 7:3) with retention times near that of dihydropentalene. When the pyrolysate was warmed to room temperature, an exothermic reaction took place, and in the v.p.c., the two peaks were now in the ratio of approximately 10:1.

The product distilled at 50–54° at 16 mm. pressure. The yield of dihydropentalene from 50.5 g. (0.382 moles) of isodicyclopentadiene was 13 g. (0.125 moles, 33%). The major fraction contained about 1% styrene. The ultraviolet spectrum in *n*-pentane has λ_{max} 268 mμ (ϵ 4400). The n.m.r. spectrum in CCl_4 (internal TMS) has four groups of bands at 3.67, 4.2, 6.77, and 7.02 τ of integrated intensities 1.01:1.00:1.00:1.01.

Anal. Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.81.

The maleic anhydride adduct, prepared at room temperature and recrystallized from ethyl acetate, melted at 233°.

The ethylene formed in the pyrolysis was trapped by allowing the gases evolved when the traps were allowed to warm to room temperature to pass through bromine in CCl_4. Ethylene dibromide, b.p. 128°, 6.35 τ (n.m.r.), was isolated by distillation.

Pyrolysis at much higher temperatures yielded, after distillation, styrene, identified by the identity of its n.m.r. spectrum and its vapor phase chromatographic behavior with those of authentic styrene.

Hydrogenation of Dihydropentalene.—Redistilled dihydropentalene (151.6 mg., 1.46 mmoles) was added to a suspension of prereduced PtO_2 in ether (15 ml.). At room temperature (27°) and atmospheric pressure, 122 ml. of hydrogen was absorbed corresponding to 3.3 moles of hydrogen. The mixture was filtered and the ether distilled. The residue was purified by vapor-phase chromatography on a 10% silicone column. The v.p.c. retention time, the infrared spectrum (CCl_4), and the n.m.r. spectrum (CCl_4, internal TMS) were identical with those of an authentic sample of *cis*-bicyclo[3.3.0]octane.

The Pentalenyl Dianion.—A 50-ml. centrifuge tube containing a magnetic stirring bar and sealed with a serum bottle cap was evacuated (0.5 mm.) and filled with oxygen-free nitrogen. Dihydropentalene (100 mg.) and THF (1 ml.) were added. While being stirred at −70°, *n*-butyllithium in *n*-hexane (5 mole equivalents) was slowly added with a hypodermic syringe. After 10 min. the mixture was warmed to room temperature and stirred for 15 min. more. The solution was pale yellow. The product was precipitated as a white solid by the addition of *n*-pentane, centrifuged, the supernatant liquid withdrawn, and the precipitate washed further with pentane and dissolved in fresh THF. The n.m.r. spectrum of this solution (internal benzene and TMS) consisted of a triplet at 4.27 and a doublet at 5.02 τ, J = 3.0, relative intensity 1.01:1.98. Solutions kept at −70° for several months exhibited the same spectrum.

Recovery of *cis*-Bicyclo[3.3.0]octane from Dilithium Pentalenide.—A solution of 0.5 g. of dihydropentalene in THF (8 ml.) was treated with 2 moles of *n*-butyllithium in *n*-hexane. Dry olefin-free *n*-pentane (20 ml.) was added and the mixture was rapidly mixed with 10 ml. of neutral phosphate buffer (50 ml. of 1.0 *M* KH_2PO_4 and 30 ml. of 1.0 *M* NaOH diluted to 100 ml.). The resulting suspension was filtered, and the yellow pentane solution was separated, dried over $MgSO_4$, and added to 100 mg. of prereduced PtO_2 in *n*-pentane in an atmospheric pressure hydrogenation apparatus. After hydrogen uptake had stopped, the catalyst was filtered, the solution was carefully concentrated, and the crude product was distilled on a high-vacuum manifold. Repeated injection of small samples onto a Carbowax vapor-phase chromatographic column and collection yielded 147.5 mg. (28%) of pure *cis*-bicyclo[3.3.0]octane, identified by its n.m.r. and infrared spectra.

The Ultraviolet Spectrum of the Pentalenyl Dianion.—An improved procedure for preparing dilithium pentalenide was used in the determination of its ultraviolet spectrum. A 25-ml. centrifuge tube containing a magnetic stirring bar was sealed with a serum bottle cap and kept filled with a nitrogen atmosphere. Dihydropentalene (400 mg., 3.8 mmoles) was injected, stirred at −70° with THF (10 ml.), and treated with excess *n*-butyllithium in *n*-hexane (10 ml., 1.6 *M*, from the Foote Mineral Co., Exton, Pa.). After stirring at −70° for 15 min., the mixture was allowed to warm to room temperature. The white solid, which precipitated upon cooling to −70°, was separated by centrifugation and by withdrawal of the supernatant liquid with a syringe. The precipitate was washed twice with 15-ml. portions of DME. Then 20 ml. of DME, in which the salt is not very soluble, was added, the mixture was stirred, and the precipitate centrifuged. An aliquot of the solution was transferred to a 0.105-mm. path length quartz ultraviolet cell sealed with a serum bottle cap pierced by a nitrogen inlet; another aliquot was diluted with water, and the total base titrated. The ultraviolet spectrum was determined on the Cary Model 14 spectrophotometer. The precipitate was treated with fresh DME, and the solution examined as above. This was repeated. Finally, the salt was dissolved in THF (8 ml.), and an aliquot diluted and analyzed as above.

A base-line correction was made for the absorption of the cell filled with pure solvent. Found for the dilithium pentalenide solutions were, in DME, λ_{max} 295 mμ (log ϵ 3.8), and in THF, λ_{max} 296 mμ (log ϵ 3.7). The extinction coefficients were based on the assumption that the concentration of the pentalenyl dianion was equal to the total base titer.

Addition of a small amount of water yielded a spectrum with $\lambda\lambda_{max}$ 283 and 405 mμ.

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Concerning the Role of Protonated Cyclopropane Intermediates in Solvolytic Reactions. I. The Solvolysis of Cyclopropane in Deuteriosulfuric Acid[1]

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The solvolysis of cyclopropane in 8.4 *M* sulfuric acid solutions leads to 1-propanol (and its acid-sulfate) as the only important products. In deuteriosulfuric acid, deuterium is incorporated into all three positions of the 1-propanol carbon skeleton, although control experiments indicate that no scrambling of deuterium occurs either before or after solvolysis of the cyclopropane. The implications of this observation are discussed and a mechanism involving protonated cyclopropane intermediates is proposed to account for it.

Introduction

The role of protonated cyclopropane intermediates in aliphatic systems has recently been the subject of considerable controversy. The existence of methyl-bridged intermediate I was seriously questioned by Reutov's observation[3] that the supposed methyl migration *via* ion I in the deamination of 1-propylamine[4] did not, in fact, occur. Subsequently, other workers[5,6] verified Reutov's supposition that a 1,3-hydride shift had occurred, and an intermediate of structure II was proposed.[6]

In addition to the above observations, the observation was made that cyclopropanes were formed in the deamination of alkylamines[7,8] and in the "deoxideation" of 1-propanol.[8] Accordingly, protonated cyclopropanes of structure IIIa were suggested as possible intermediates in both the above and in Wagner–Meerwein rearrangements.[8] This hypothesis has since

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