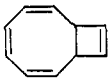
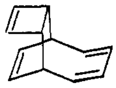
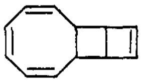
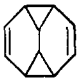
spectively). Both the nmr and ultraviolet spectra are very similar to the corresponding spectra of bicyclo-[4.2.1]nona-2,4,6-triene.[10] Further analogies exist. The structures VII and VIII were assigned by Schröder[12] to two $C_{12}H_{12}$ products. The ultraviolet spectrum of VII showed maxima at $\lambda_{\max}^{\text{hexane}}$ 280, 268.5, and 258.5 mμ (ε 2700, 5000, and 4600, respectively), while VIII exhibited only a single maximum at $\lambda_{\max}^{\text{hexane}}$ 258 mμ (ε 1300).

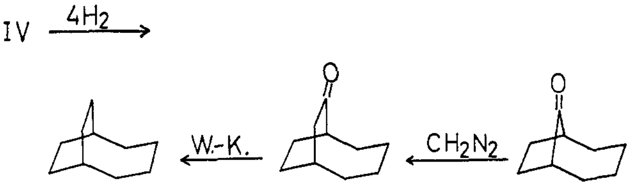

VI


VII


VIII


IX

Ozonolysis of IV, followed by acid work-up and esterification with diazomethane, led to methyl malonate with no ethanetetracarboxylic ester being isolable. This is compatible with the postulated structure of IV but not with the alternative VI. Finally, IV absorbed exactly 4 moles of hydrogen on catalytic hydrogenation to give a single product. This product was shown to be identical with the hydrocarbon obtained from Wolff–Kischner reduction of the ketone produced from bicyclo[4.2.1]nonan-9-one[13] by ring expansion with diazomethane. Proof of identity is based on comparison of infrared spectra and retention times on gas–liquid partition chromatography.[14]



Accordingly, the structure of IV seems secure. The question now arises as to its origin. Analysis of the nmr spectra of all of the precursors of IV reveals that they retain the bicyclo[6.1.0] skeleton. In the tosylhydrazone Ve the two allylic cyclopropyl hydrogens appear as a doublet centered at τ 8.25 ppm, $J = 5$ cps. The lone other cyclopropyl hydrogen appears as a triplet at τ 8.66 ppm, $J = 5$ cps. Were the structure of Ve to have the bicyclo[4.2.1] skeleton, the allylic cyclopropyl hydrogens noted above would appear at substantially lower field. For instance, in bicyclo-[4.2.1]nona-2,4,7-triene these appear at τ 6.9 ppm.[10] Three possibilities remain: either rearrangement takes place in the tosylhydrazone salt before decomposition, the carbenoid species rearranges, or VI is unstable relative to all or some of the observed products at 120°. The first of these possibilities seems remote, as in our hands the compounds retaining the bicyclo-[6.1.0] skeleton are stable at 120°. The products thus arise either from the carbenoid species or VI (IV is stable for hours at 120°). Although rearrangement of VI to IV *via* a suprafacial sigmatropic rearrangement of the order [1,5][18] seems attractive, mechanisms can be written in either case, and we would prefer at this point to defer comment.

When IV is irradiated with ultraviolet light, it is converted slowly in Pyrex, but rapidly in quartz, to bullvalene and a few very minor products. In one experiment involving only a few milligrams, bullvalene was isolated in 64% yield. Mechanistic speculation inevitably centers on the oft-cited[2,19,20] but never isolated tetracyclo[4.4.0.0^{5,7}.0^{2,10}]deca-3,8-diene (IX).

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(12) G. Schröder and W. Martin, *Angew. Chem.*, **78**, 117 (1966).

(13) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

(14) A referee has suggested that the structure of Gutsche's ketone, bicyclo[4.2.1]nonan-9-one,[13] requires some verification. In particular it must be differentiated from bicyclo[5.2.0]nonan-2-one, another possible product of Gutsche's double ring expansion.[13] Gutsche noted the carbonyl stretching frequency in the infrared at 1737 cm^{-1} and converted his ketone *via* a Haller–Bauer reaction to an unspecified amount of cyclooctanecarboxamide. More recent work has involved reduction of Gutsche's ketone to bicyclo[4.2.1]nonane identical with material prepared independently.[15,16] We have also hydrogenated bicyclo[4.2.1]-nonatriene to bicyclo[4.2.1]nonane identical with a sample prepared from Gutsche's compound.[17]

(15) D. I. Schuster and F.-T. Lee, *Tetrahedron Letters*, 4119 (1965).

(16) M. Hartmann, *Z. Chem.*, **4**, 457 (1964).

(17) M. Jones, Jr., and S. D. Reich, unpublished work.

(18) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(19) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

(20) G. Schröder, "Cyclooctatetraen," Verlag Chemie, GmbH, Weinheim, 1965.

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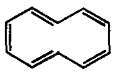
Received September 22, 1966

Cyclodecapentaene

Sir:

Despite unabated interest in the theoretical and practical aspects of the next highest Hückel homolog of benzene, cyclodeca-1,3,5,7,9-pentaene (I or II),[1] neither the hydrocarbon itself nor any substituted monocyclic case[2] has been isolated or directly identified.[3] Herein we described (a) a simple synthesis designed to give a new $C_{10}H_{10}$ valence-bond isomer, *trans*-9,10-dihydronaphthalene,[4] and (b) the low-temperature photochemical formation of a highly unstable product, shown to be a long-sought parent of the cyclodecapentaene type.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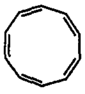
II

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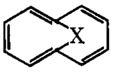
(1) (a) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952); (b) W. Baker in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 39; (c) V. Prelog in ref 1a, p 127; (d) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 477; (e) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963); (f) W. Baker, *Chem. Brit.*, **1**, 250 (1965).

(2) Various bicyclic carbon-, nitrogen-, and oxygen-bridged species (i) have been prepared and identified by (a) E. Vogel and co-workers



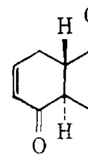
i

[*e.g.*, E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *ibid.*, **76**, 785 (1964), and succeeding papers] and by (b) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964).

(3) The conversion of 9,10-disubstituted to isomeric disubstituted 9,10-dihydronaphthalenes suggests the intermediacy of cyclodecapentaene types: (a) R. Cookson, J. Hudec, and M. Marsden, *Chem. Ind.* (London), 21 (1961); (b) B. C. T. Pappas, Ph.D. Thesis, University of Wisconsin, 1963; (c) E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem.*, **76**, 786 (1964).

(4) *cis*-9,10-Dihydronaphthalene (E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963)) has shown no promise as a cyclodecapentaene precursor.

Entry into the desired $C_{10}H_{10}$ series was managed by utilizing the hexalindione III[5] as starting material. Reduction of the diketone was carried out by soxhlet extraction into a suspension of a 100-fold molar excess of lithium aluminum hydride in refluxing ether. The desired dienediol IV (X = OH),[6] a white solid (mp 212–14°) obtained in quantitative yield, was converted back to starting material with Jones reagent. The diol was directly converted with 48% aqueous hydrobromic acid–petroleum ether to two (tlc) unrearranged diene dibromides IV (X = Br)[6] in 70% yield.[7] Through the action of N-bromosuccinimide in carbon tetrachloride, the dibromide was transformed into the allylic tetrabromide V, a mixture of various undefined racemates.[6] Dehalogenation of V was brought about by 0.5% lithium-amalgam in ether.[8] A hydrocarbon (VI) was isolated by preparative vpc (10 ft × 0.25 in., 5% DC550 on Chromosorb G) and was found to be at room temperature a liquid which decomposed with exceeding ease to naphthalene. The new polyene exhibited maximal ultraviolet absorption in methanol at 231 mμ and revealed surprisingly simple nmr behavior in that two virtually unsplit signals appeared at τ 4.1 and 7.2 (4:1 proton ratio, 60 Mc in $CDCl_3$).[9] On the basis of its chemical and spectral behavior, VI is best regarded as *trans*-9,10-dihydronaphthalene (VII).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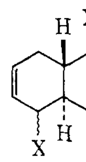
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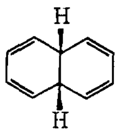
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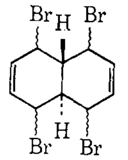
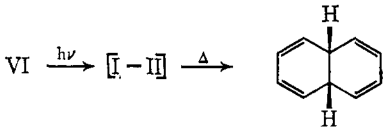

V

On being photolyzed in pentane at room temperature for 2 min by means of unfiltered light (2537 A) from a Rayonet photochemical reactor, hydrocarbon VI gave rise to a large number of products, among which the following were identified by vpc and ultraviolet methods: deca-1,3,5,7,9-pentaene, *trans*-1-phenylbuta-1,3-diene, naphthalene, 1,2-dihydronaphthalene, *cis*-9,10-dihydronaphthalene, bicyclo[4.2.2]deca-2,3,7,9-tetraene,[10] and bullvalene.[11] The appearance of *cis*-9,10-dihydronaphthalene (and its photoproducts[11]) in comparatively major amount suggested its formation by a thermal, disrotatory process from transient cyclodecapentaene, itself formed in a conrotatory[12] event from excited-state *trans*-9,10-dihydronaphthalene. On the strength of this surmise, and with the aim of preserving the unstable isomer under modified conditions, low-temperature photolysis experiments were initiated. At −190°, no *cis*-9,10-dihydronaphthalene was detected after irradiation of the *trans* isomer in ethyl ether–isopentane–ethanol; however, after being warmed to *ca.* room temperature and recooled to −190°, the photolysis mixture exhibited the characteristic ultraviolet absorption (λ_{max} 247 mμ) of the *cis* isomer.[4] Diimide reduction,[13] carried out at the lowest possible temperature, converted the elusive cyclodecapentaene to cyclodecane, which was isolated and purified by preparative vpc, then identified and compared with authentic material by appropriate vpc and mass spectral means. In the low-temperature photolysis–reduction sequence, the final product was composed of *ca.* 40% cyclodecane (vpc); after room-temperature irradiation, only traces of cyclodecane are apparently formed by diimide reduction of total product. Although the trapping and identification of cyclodecapentaene seem unequivocal, questions concerning the geometry, conformation, and electronic character of the hydrocarbon remain open and await future answers. However, it appears that a central issue, namely the nature of the balance between stabilizing, 10-π-electron aromaticity, on the one hand, and destabilizing strain and/or steric effects, on the other, has been largely resolved.



Acknowledgment. The authors are indebted to ARO(D) for grant support (Project No. CRD-AA-5227-C).

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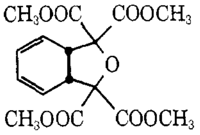
(5) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

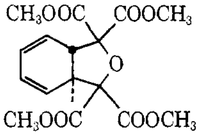
(6) Infrared and nmr spectral characteristics of this intermediate were completely consistent with the assigned structure.

(7) The two compounds were shown to be closely related isomers by separation employing column chromatography on Florisil, then generation of the same product mixture (tlc) from each in the succeeding reaction with NBS.

(8) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

(9) A satisfying nmr parallel is found in the *cis* and *trans* isomeric pair ii (R. E. Benson, W. J. Linn, and O. W. Webster, *J. Am. Chem. Soc.*, **85**, 2032 (1963)) and iii (obtained by Dr. G. V. Parry in this laboratory by ultraviolet irradiation of ii). Whereas tetraester ii, like *cis*-9,10-dihydronaphthalene,[4] exhibits extensive splitting in the vinyl and methine proton regions (τ 3.9–4.1, 4.2–4.5, and 5.98–6.02, all multiplets in the integrated ratio 2:2:2), isomer iii revealed singlets in the vinyl (τ 3.9) and methine (τ 6.50) regions.


ii


iii

(10) M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967), also detected VI as a secondary product in their synthetic route to this isomer. We are grateful to these investigators for supplying information in advance of publication.

(11) W. von E. Doering and J. W. Rosenthal, *ibid.*, **88**, 2078 (1966).

(12) R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395 (1965), and references cited therein.

(13) The reagent was generated by addition of cold acetic acid to disodium azodicarboxylate in methanol at acetone–Dry Ice temperature, both before and after addition of cold irradiation product (see E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961), for close precedents). Reduction presumably occurred at −70° and/or during the warming to room temperature.

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Received October 28, 1966

Synthesis of a Triquinocyclopropane

Sir:

Recently there has been a great deal of interest in derivatives of trimethylenecyclopropane.[1] We wish to report the synthesis of the triquinocyclopropane **2**,

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(1) (a) E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5518 (1965); (b) G. Köbrich and H. Heinemann, *Angew. Chem. Intern. Ed. Eng.*, **4**, 594 (1965);(c) P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 181 (1966).