terium exchange—a result of the experimental difficulty of creating an absolutely proton-free environment and of protium generation during olefin formation. The amount of exchange is reduced when diazotization is effected in excess hexanol-*d* (system 5) as a result of swamping the reaction with exchangeable deuterium (*i.e.*, dilution of protium).

The intermediacy of a carbene can be eliminated or restricted to a maximum level of involvement of *ca.* 0.1%. However, considering the wide range of experimental conditions and the excellent internal consistency in relative deuterium content of the methylcyclopropane and 1-butene, a better explanation for the differences observed is the *limited* involvement of an equilibrating deuterated (or protonated) methylcyclopropane.[10]

(10) (a) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964). (b) An equilibrating protonated cyclopropane was postulated by these authors to account for the extensive retention of deuterium in the cyclopropane isolated. These conflicting data may be a result of the difference in (1) reaction conditions (35% aqueous perchloric acid[10a] would more effectively stabilize the cation) and (2) the nature of the cation(s) produced. Unpublished work in these laboratories show that there are only minor changes in deuterium content with wide variation of protic reaction conditions.

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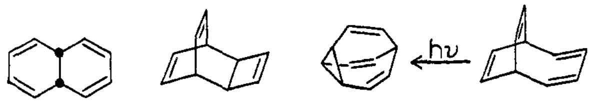
The Synthesis of Bicyclo[4.2.2]deca-2,4,7,9-tetraene. New Sources of *cis*- and *trans*-9,10-Dihydronaphthalene and Bullvalene[1]

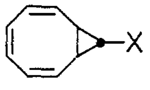
Sir:

The energy surface on which several $C_{10}H_{10}$ hydrocarbons exist features a number of paths between the isomers accessible either photochemically or thermally. The interconversion of bullvalene (I) and *cis*-9,10-dihydronaphthalene (II) and the thermal conversion of Nenitzescu's hydrocarbon, tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (III), to II have been described by Doering and Rosenthal.[2] We have previously added the photochemical conversion of I to III and a second hydrocarbon, as yet of unknown structure.[3] We wish to further enrich the known minima on this energy surface by adding the hitherto unknown bicyclo[4.2.2]deca-2,4,7,9-tetraene (IV). In addition, a new source of *cis*- and *trans*-9,10-dihydronaphthalene has been found. Finally, although we plan to report at length on the properties of IV later, we cannot resist describing its facile conversion to bullvalene.

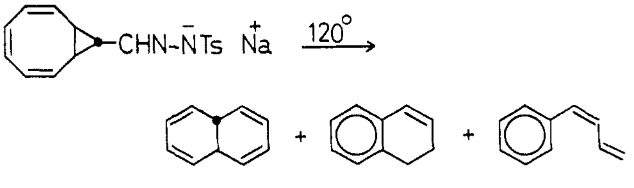


II III I IV

In a procedure previously described by Boekelheide[4,5] and others,[6,7] diazoacetic ester was decomposed thermally in the presence of cyclooctatetraene[8] and a small amount of cupric sulfate. This procedure led to methyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (Va). Nuclear magnetic resonance (nmr) spectroscopy showed that the rearrangements noted in this system[4-7] had been avoided. Conversion of Va to the salt of the tosylhydrazone Ve was accomplished *via* the acid Vb, the acid chloride Vc, and the aldehyde Vd by unexceptional steps. Decomposition of the dry salt of Ve at 90–120° led not to the conventional[9] product bicyclo[6.2.0]deca-2,4,6,9-tetraene (VI) but to a complex mixture of $C_{10}H_{10}$ products. These compounds, in order of their elution from a 2-m, 20% Dow-Corning 710 silicone oil column, are: *trans*-9,10-dihydronaphthalene (20.0%),[10] II (11.6%),[10] *cis*-1-phenylbuta-1,3-diene (4.6%),[10] IV (37.8%), and 1,2-dihydronaphthalene (13.3%). Cyclooctatetraene (12.7%) and small, variable amounts of naphthalene were also formed. All compounds save IV were identified by comparison of spectra with those of authentic samples.



Va, X = $COOCH_3$
b, X = COOH
c, X = COCl
d, X = CHO
e, X = CHN-NH-Ts



II + IV

The structure of IV remains to be proved. In particular, it must be carefully differentiated from the isomeric VI. The 100-Mcps nmr spectrum[11] of IV shows two multiplets integrating for two protons each at 604 and 565 cps from tetramethylsilane, a symmetrical four-line pattern centered at 546 cps integrating for four protons, and a two-proton multiplet centered at 312 cps. On irradiation of the 312-cps signal, the four-line pattern at 546 cps collapses to a sharp singlet. Thus this signal can be assigned to the four protons on the ethylene bridges of IV. Norbornadiene shows a similar four-line pattern and identical behavior on decoupling of the bridgehead protons.[11] It is most difficult to reconcile this behavior with structure VI.

The ultraviolet spectrum showed maxima at λ_{max}^{EtOH} 280, 268, and 258 $m\mu$ (ϵ 2900, 4200, and 4200, re-

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(1) We wish to express our gratitude to the Lilly Research Laboratories for their generous support of this work.

(2) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966).

(3) M. Jones, Jr., unpublished work.

(4) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

(5) K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 1159 (1964).

(6) S. Akiyoshi and T. Matsuda, *ibid.*, 77, 2476 (1955).

(7) D. D. Phillips, *ibid.*, 77, 5179 (1955).

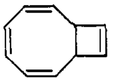
(8) We thank the Badische Anilin und Soda Fabrik for a sample of cyclooctatetraene.

(9) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

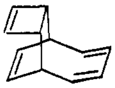
(10) We thank Professor W. von E. Doering and Mr. J. W. Rosenthal for spectra of *cis*-9,10-dihydronaphthalene, Professor E. E. van Tamelen for spectra of *trans*-9,10-dihydronaphthalene, Professor M. Pomerantz for spectra of *cis*-1-phenybuta-1,3-diene, and Dr. W. Grimme for spectra of bicyclo[4.2.1]nona-2,4,7-triene.

(11) We are most grateful to Professor M. Robert Willcott of the University of Houston who determined the 100-Mcps nmr spectra.

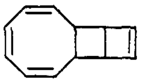
spectively). Both the nmr and ultraviolet spectra are very similar to the corresponding spectra of bicyclo-[4.2.1]nona-2,4,6-triene.[10] Further analogies exist. The structures VII and VIII were assigned by Schröder[12] to two $C_{12}H_{12}$ products. The ultraviolet spectrum of VII showed maxima at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



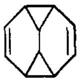
VI



VII

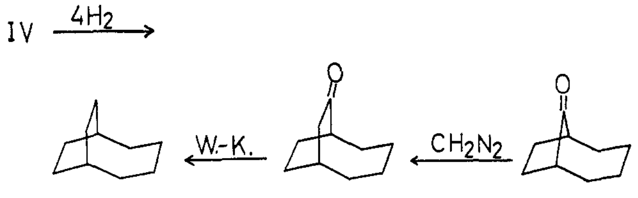


VIII



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).

[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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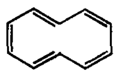
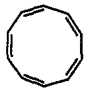
Cyclodecapentaene

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.



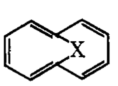
I



II

[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 [*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).



i

[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.