certainties of the data used this agreement must be considered remarkable.

The formation of the "wrong" methylcyclopentadiene arises because step 2 yields a molecule which contains the energy of activation of this step and the large contribution due to the high value of ΔH for this reaction. (This was estimated[6] to be 36 kcal mol^{-1}, but calculations using values of 35 and 36.5 kcal mol^{-1} produced insignificant changes in A/B). The methylcyclopentadiene initially contains more than 63 kcal mol^{-1} of excess energy; the energy of activation for step 4 (and, of course, 6) is about 26 kcal mol^{-1}, so this process takes place very rapidly in the absence of collisional stabilization. Thus, although the interconversion between methylcyclopentadienes (and, similarly, 5-deuteriocyclopentadiene and its isomers) is relatively slow at 50°, because they are produced by what is essentially a process of chemical activation, this interconversion is of considerable importance, under the experimental conditions employed.

The calculated values of A/B depend only on the validity of RRKM theory and the energetics of the reaction; they do not depend on the detailed nature of the transition state. Thus, while the results are *consistent* with a biradical mechanism they do not *require* such a mechanism; the results do, however, require that by whatever process (biradical or concerted), 1-methylcyclopentadiene is formed directly from 1-methylbicyclo[2.1.0]pent-2-ene. The fact that the ratio of A/B is close to the experimental value means that it is probable that the mechanism presented represents the system completely, and hence it is unnecessary to postulate the *direct* formation of any 2-methylcyclopentadiene. Even if a small fraction of the yield of 2-methylcyclopentadiene did arise directly, this could not be determined on the basis of the gas-phase experiments reported, nor indeed from any gas-phase experiments that could be carried out at reasonable pressures.

(6) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **21** (1970).

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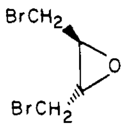
Spiro[4.4]nonatetraene and Spiro[4.4]nona-1,3,7-triene

Sir:

Spiro[4.4]nonatetraene (**1**) has been the subject of discussion concerning the overlap of orthogonal ribbons of p orbitals[1] (spiro conjugation) and experimentally accessible examples of planar tetracoordinate carbon.[2] It has also been the subject of at least two attempted syntheses,[3] both of which failed to provide detectable quantities of **1**. Highly substituted derivatives, such as 1,2,3,4-tetramethyl-6,7,8,9-tetrachlorospiro[4.4]nonatetraene, have been prepared[4] but are not useful in testing the relevant bonding theories because of electronic and/or steric perturbations by the substituents. We wish to report direct and simple syntheses of spiro[4.4]nonatetraene and spiro[4.4]nona-1,-3,7-triene (**2**).[5]

Originally, an efficient route to **2** was sought as a potential pathway to **1**, and cyclopentadiene (**3**) was chosen as an obvious synthon. Treatment of *trans*-2,3-epoxy-1,4-dibromobutane (**4**) with acetone in the presence of stannic chloride produced a mixture of *cis*- and *trans*-2,2-dimethyl-4,5-bis(bromomethyl)dioxolanes (**5a** and **5b**) in the ratio of 10:1, respectively.[6] Condensation of cyclopentadiene with **5a** using excess sodium hydride in tetrahydrofuran gave the spirodioxolane **6** in 50–60% yield (bp 80–84° (3.0 Torr)). Hydrolysis of **6** (dilute hydrochloric acid in aqueous methyl alcohol under conditions of slow distillation) produced the diol **7** which was converted to the bis-*p*-toluenesulfonate ester **8** (mp 124–126°, 40% overall for **6** → **8**). All attempts to convert the diol **7** to spiro[4.4]nonatetraene (**1**) *via* pyrolysis of the diacetate **9** or dixanthate **10** gave low (*ca.* 20%) yields of indene as the only C_9H_8 product. Similarly, attempted base-promoted elimination of *p*-toluenesulfonic acid from **8** failed to produce **1**.



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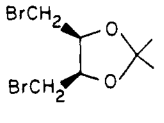
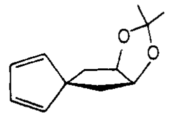
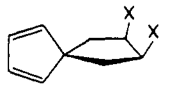


5a



6



7, X = OH
8, X = OSO_2-*p*-tolyl
9, X = $OCOCH_3$
10, X = OCS_2CH_3

The reaction of excess sodium iodide with **8** in acetone at 100° in a closed system for 20 hr gave spiro[4.4]nona-1,3,7-triene (**2**) in 70% yield, after short-path distillation. The triene **2** is obviously an attractive precursor of **1**, but all attempts to introduce a substituent such as halide at C-6 failed. For example, reaction of **2** with *N*-bromosuccinimide under the usual conditions for allylic bromination led to indene in 23% yield; no monobromide of **2** was isolated. The failure of the above approaches to **1** is not surprising, considering the reactivity of **1** (see below).

A very simple, low-temperature approach to **1** proved successful. The diacid chloride **11** (bp 57° (1.0 Torr)) of diallylmalonic acid was prepared from the diacid using thionyl chloride in carbon tetrachloride at reflux for 15 hr (88% yield). In methylene chloride solution containing several mole equivalents of nitromethane, the diacid chloride **11** reacted with aluminum

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(1) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); (c) R. Boschi, A. Dreiding, and E. Heilbronner, *ibid.*, **92**, 123 (1970).

(2) R. Hoffmann, R. W. Alder, and C. F. Wilcox, *ibid.*, **92**, 4992 (1970).

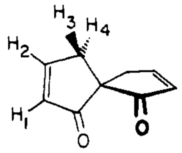
(3) (a) D. J. Cram and B. L. van Dauren, *ibid.*, 77, 3576 (1955); (b) D. Schonleber, *Chem. Ber.*, **102**, 1789 (1969).

(4) (a) E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, **31**, 4260 (1966); see also (b) G. Haas and V. Prelog, *Helv. Chim. Acta*, **52**, 1202 (1969).

(5) Spiro[4.4]nona-1,3,7-triene (**2**) is observed as a minor product during condensation of sodium cyclopentadienide with *cis*-1,4-dichlorobut-2-ene: (a) M. F. Semmelhack and J. Foos, unpublished observations; (b) ref 3b.

(6) M. S. Malinovskii, V. G. Dryak, A. G. Yudasina, and N. N. Maksimenko, *Zh. Org. Khim.*, **2**, 2086 (1966).

chloride during 1 hr at 25° to give, after hydrolysis with aqueous ammonium chloride, spiro[4.4]nona-2,6-diene-1,5-dione (**12**) in 51% yield:[7,8] mp 110.5–112° (crystals from benzene and sublimed); ^{1}H nmr ($CDCl_3$) each proton appeared as a doublet of triplets, δ 6.13 (H_1, J_{12} = 6.0 Hz, J_{13} = 2.5 Hz, J_{14} = 2.5 Hz), 7.85 (H_2, J_{23} = 2.6 Hz, J_{24} = 2.6 Hz), 3.09 (H_3, J_{34} = 18 Hz), and 2.58 (H_4); ir ($CHCl_3$) 1724 (s), 1696 (s), 1601 (m) cm^{-1}; uv max (ethanol) 220 nm (ϵ 20,100), 313 (103); mass spectral molecular weight, 148. Reduction of **12** with aluminum hydride[9] afforded the diol **13** (30%, mp 127–129°)[10] which was treated with thionyl chloride and pyridine in tetrahydrofuran at 0° for 15 min to produce (short-path distillation) a mixture of dichlorides (*e.g.*, **14**) which was used directly. To a solution of the dichloride mixture in tetraethylene glycol dimethyl ether at 25° was added potassium *tert*-butoxide (solid, 100% excess). The system was immediately evacuated (0.1 Torr) with a trap cooled to −196° between the reaction mixture and the pump. Over a period of 2.0 hr, a mixture of spiro[4.4]nonatetraene (**1**) and *tert*-butyl alcohol collected in the trap. The hydrocarbon was isolated by glpc (3 ft × 0.375 in. column, 10% DC 200 on Chromosorb Z at 75°) in an overall yield from **13** of *ca.* 15%. The ^{1}H nmr spectrum ($CDCl_3$) showed a pair of symmetrical, mirror-image related multiplets of equal area (δ 5.75 and 6.56): mass spectral molecular weight 116 (the fragmentation pattern is superimposable with that of indene); ir (neat) 3.24 (w), 5.43 (w), 6.01 (m), 6.55 (s), 7.82 (m), 9.38 (s), 9.60 (s), 10.30 (s), 12.21 (s) cm^{-1}.



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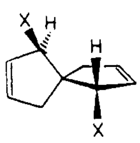
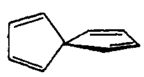


13, X = OH
14, X = Cl

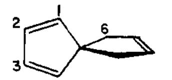
The most interesting spectral data for **1** are the uv maxima and extinction coefficients compared with those of **2** and spiro[4.4]nona-1,3-diene (**15**).[11] Both of the latter compounds show uv max 254 nm (ϵ 2750 for **2**, 2250 for **15**),[3b,11] whereas tetraene **1** has uv max 276 nm (ϵ 1120) and 218 (5350). The red shift and low extinction coefficient for the lowest energy transition of **1** compared to **2** and **15** is in accord with predictions of spiroconjugative effects in **1**.[1] The difference in energy for the transitions giving rise to the 276- and 218-nm bands may indicate the energy separation (*ca.* 27 kcal/mol) of the highest bonding levels in **1** due to interaction across the spiro carbon atom;[1] photoelectron spectroscopy should provide a definitive measure.

With excess tetracyanoethylene at 25° in chloroform, tetraene **1** reacts rapidly to form a monoadduct **16**; under similar conditions, dimethyl azodicarboxylate leads to a monoadduct **17**, and, at higher temperature, the diadduct **18**. Monoadduct **17** has been prepared independently by reaction of dimethyl azodicarboxylate and **2** followed by allylic bromination (*N*-bromosuccinimide) and base-promoted dehydrohalogenation.



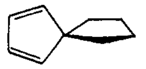
1

276 nm (1120),
218 nm (5350)



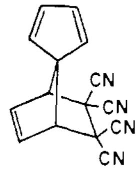
2

254 nm
(2750)

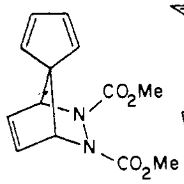


15

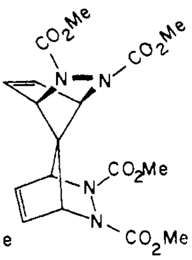
254 nm
(2250)



16



17



18

Preliminary studies of the thermal stability of **1** indicate that rearrangement occurs (half-life: 66 min at 65°, in carbon tetrachloride) to give indene (67%) and a mixture of high molecular weight products. In contrast, the triene **2** shows no change after 8 hr at 67° in solution and rearranges only at elevated temperatures (>280°) in the gas phase.[12,13]

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[7] Most new compounds reported here (**1**, **6**, **8**, **11**, **12**, **13**, **16**, **17**, and **18**) show analytical and spectral data completely in accord with the proposed structures; intermediates **7**, **9**, **10**, and **14** have been obtained in *ca.* 95% purity and are identified from spectral data.

[8] We wish to acknowledge the valuable suggestions of Professor C. A. Brown (Cornell University) concerning this reaction.

[9] H. C. Brown and H. M. Hess, *J. Org. Chem.*, **34**, 2206 (1969).

[10] The single isomer which was obtained is assigned structure **13** based on the ^{1}H nmr spectrum. The assignment is tentative and will be discussed more fully in the article describing this work.

[11] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

[12] M. Jones, Jr., R. N. Hochman, and J. D. Walton, *Tetrahedron Lett.*, 2617 (1970).

[13] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Sun Oil Company for financial support of this work. We also thank Mr. J. Nunberg for technical assistance.

[14] National Science Foundation Undergraduate Research Participant, 1971.

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Photosolvation of Benzene. Mechanism of Formation of Bicyclo[3.1.0]hex-3-en-2-yl and of Bicyclo[3.1.0]hex-2-en-6-yl Derivatives[1]

Sir:

Photolysis of benzene in acidic hydroxylic solvents is known to yield *exo*- and *endo*-bicyclo[3.1.0]hex-3-en-2-yl derivatives **1** and **2** and -bicyclo[3.1.0]hex-2-en-6-yl derivatives **3** and **4**, respectively. Trifluoroethyl ethers[2] **1a** and **4a**, methyl ethers[2,3] **1b**, **3b**, and **4b**, acetates[4,5] **1c**–**4c**, and alcohols[4,5] **1d** and **2d** have been reported. Permissive evidence for formation of **1d**,[5,6]

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **88**, 2881 (1966).

[3] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967); **90**, 2732 (1968).

[4] E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966).

[5] (a) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971); (b) N. M. Hasty, Jr., Ph.D. Thesis, University of Wisconsin, 1970.

[6] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971).