The difference between the 9,10-cis/trans ratios of the hydrolysis products from diol epoxides **1** and **2** resists a simple explanation. Nevertheless, these reactions do provide models for the reactions of **1** and **2** with other weak nulceophiles in aqueous systems. In particular, on the basis of our results, it would be reasonable to expect both cis and trans adducts of metabolically produced *anti*-diol epoxide, **1**, with the nucleophilic sites on cellular DNA. Furthermore, while the intramolecular hydrogen bond in **2** greatly facilitates the addition of nucleophiles in the *tert*-butyl alcohol solvent system,[3a] S_N1 reactivity of the two diol epoxide stereoisomers, **1** and **2**, in aqueous solvents seems to be very similar. Also, in the naphthalene system, sulfur nucleophile addition rates in aqueous ethanol were very similar for the *syn*- and *anti*-3,4-diol 1,2-oxides.[3a] Thus, the suggestion[2d] that the observed lower mutagenic activity of **2** may be a consequence of the fact that this isomer is so "highly reactive that it hydrolyzes rapidly before it can reach and react with DNA" would appear untenable.

Finally, it should be noted that epoxide rearrangement to afford *trans*-7,8-dihydroxy-9-keto-7,8,9,10-tetrahydrobenzo[*a*]pyrene could not be detected. This is consistent with the known tendency of aryl epoxides to hydrolyze rather than rearrange in aqueous solvents.[17] The K-region arene oxides which furnish large amounts of rearranged products (i.e., phenols) during aqueous solvolysis represent a special case for the reasons discussed previously.[4]

References and Notes

(1) P. Sims, P. L. Grover, A. Swaisland, K. Pal, and A. Hewer, *Nature (London)*, **252**, 326 (1974).
(2) Anti-diol epoxide, **1**, is also named $(\pm)$-7α,8β-dihydroxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene. The syn-diol epoxide, **2**, is also named $(\pm)$7α,8β,-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene. (b) C. Malaveille, H. Bartsch, P. Grover, and P. Sims, *Biochem. Biophys. Res. Commun.*, **66**, 693 (1975). (c) P. G. Wislocki, A. W. Wood, R. L. Chang, W. Levin, H. Yagi, O. Hernandez, D. M. Jerina, and A. H. Conney, *ibid.*, **68**, 1006 (1976). (d) E. Huberman, L. Sachs, S. K. Yang, and H. V. Gelboin, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 607 (1976). (e) R. F. Newbold and P. Brookes, *Nature (London)*, **261**, 52 (1976).
(3) (a) H. Yagi, O. Hernandez, and D. M. Jerina, *J. Am. Chem. Soc.*, **97**, 6881 (1975); (b) F. A. Beland and R. G. Harvey, *J. Chem. Soc., Chem. Commun.*, 84 (1976); (c) D. J. McCaustland and J. F. Engel, *Tetrahedron Lett.*, 2549 (1975).
(4) J. W. Keller and C. Heidelberger, *J. Am. Chem. Soc.*, **98**, 2328 (1976).
(5) The acetylation procedure consisted of first removing the hydrolysis solvent under vacuum, then extracting the reaction products from the salts with THF and adding the THF solution (about 1 ml) to a mixture of 10 ml of acetic anhydride and 1 ml of pyridine, which had been previously refluxed for 10 min. After sitting overnight at room temperature under nitrogen, the mixture was mixed with equal volumes of benzene and water and was separated, and the organic phase was reduced to dryness under vacuum.
(6) Thin layer chromatography was performed on Kodak silica gel sheets with dichloromethane–1% diethyl ether as the eluting solvent. The developed chromatograms were cut into pieces and extracted with diethyl ether, and the optical density of the extracts was measured at 280 nm; 80–90% of the total OD units recovered from the sheets coincided with the tetraacetate spots.
(7) The tetraacetates showed mass spectral molecular ions at *m/e* 488 and base peaks at 488 − CH_3CO_2H. The ultraviolet spectra showed λ_{max}'s at 248, 263, 278, 310, 336, and 348 nm in 95% EtOH.
(8) We thank Professor H. W. Whitlock for performing this NMR experiment.
(9) In subsequent experiments, we were able to separate $(Ac)_4$-**3** and -**5** by thin layer chromatography. NMR(CDCl$_3$) (Ac)$_4$ -**3** (R_f 0.25) δ 2.06 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.15 (s, 3 H, OAc), 5.64 (q, 1 H, $J_{7,8}$ = 3.5, $J_{8,9}$ = 2.3 Hz, H-8), 5.95 (q, 1 H, $J_{9,10}$ = 4.9, $J_{8,9}$ = 2.3 Hz, H-9), 6.66 (d, 1 H, $J_{7,8}$ = 3.5 Hz, H-7), 7–8.5 (m, H-10 and aromatic H's); (Ac)$_4$-**5** (R_f 0.30) δ 2.03 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.16 (s, 3 H, OAc), 2.29 (s, 3 H, OAc), 5.79 (q, 1 H, $J_{8,9}$ = 2.25, $J_{7,8}$ = 8.90 Hz, H-8), 5.84 (q, 1 H, $J_{9,10}$ = 3.75, $J_{8,9}$ = 2.25 Hz, H-9), 6.80 (d, 1 H, $J_{7,8}$ = 8.9 HZ, H-7), 7–8.5 (m, 9 H, H-10 and aromatic H's).
(10) NMR (CDCl$_3$) of Ac$_4$-**4**: δ 2.04 (s, 6 H, 2 OAc's), 2.06 (s, 3 H, OAc), 2.29 (s, 3 H, OAc), 5.60 (q, 1 H, J = 3.4, 11 Hz, H-9), 6.09 (q, 1 H, J = 11,8 Hz, H-8), 6.76 (d, 1 H, J = 8 Hz, H-7), 7.47 (d, 1 H, J = 3.4 Hz, H-10), 8.0–8.5, 8 H, aromatic H's).
(11) This buffer system was made by titrating a solution of 1: dioxane–water,

0.0950 M in KCl and 0.0034 M in K_2HPO_4 with 1:1 dioxane–water, 0.0950 M in KCl and 0.50 M in HCl at 35 °C. The pK_a was 5.9. Thus, buffers with an ionic strength of 0.106 M could be made up with less than 2% difference in the ionic strength between pH 5.2 and pH 9.
(12) Both oxides **1** and **2** exhibited UV maxima at 280.0 nm which shifted to 278.6 nm during hydrolysis. Isosbestic points were observed at 279.5 nm.
(13) R. C. Williams and J. W. Taylor, *J. Chem. Educ.*, **47**, 129 (1970).
(14) General acid catalysis by dihydrogen phosphate anion in the solvolysis of **1** cannot be totally excluded by these preliminary experiments. However, $k_{H_2PO_4^-,1}$ is certainly less than 0.05 M^{-1} s^{-1}.
(15) P. Hulbert, *Nature (London)*, **256**, 146 (1975).
(16) D. L. Whalen, *J. Am. Chem. Soc.*, **95**, 3432 (1973).
(17) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

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Construction of the 1,5-Methano[10]annulene (Bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene) System

Sir:

Vogel and his associates accomplished the first synthesis of 1,6-methano[10]annulene (**1**) in 1964[1] and have built the elegantly organized chemistry of bridged cyclic π-electron systems.[2] This development has naturally aroused interest in 1,5- (instead of 1,6-)methano[10]annulene (**2**) and its chemistry, initially for the apparent structural similarity of the two systems. Indeed numerous attempts at the synthesis of **2** have been made.[3] Our own interest in **2** originated from two main experimental facts: (i) the lability exhibited by two (nonbridged) [10]annulenes[4] appears more pronounced than that intuitively conceived from the stability of **1** and (ii) the apparent existence of a nonnegligible 1,6-interaction calculated by several theoretical treatments[5] seems to be manifested in the photoelectron[5a] and ultraviolet spectra of **1**.[6,7] To further examine to what extent the transannular interaction, if it exists, perturbs the monocyclic 10 π-electron system of **1**, we have selected **2** where such an interaction would very likely vanish (cf. azulene and naphthalene[8,9]). It is obvious, however, that the evaluation of the electronic structure of **2** in comparison with **1** requires a careful examination of the geometry of the two compounds, since Allinger and Sprague[10] have recently predicted that the σ system constraints of **2** would force ring dihedral angles to differ up to 54° from planarity; thus **2** would have complete bond alternation and lack so-called aromaticity. We have now achieved the first construction of this system in a remarkably simple manner and wish to present its spectral and chemical properties in preliminary form.

1
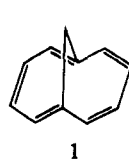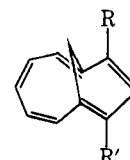
2, R = R' = H
11, R = H; R' = CO_2CH_3
14, R = H; R' = OCH_3
15, R = H; R' = $OSi(CH_3)_2t$-C_4H_9

16, R = H; R' = $OPO(OC_2H_5)_2$
17, R = OCH_3; R' = CO_2CH_3
18, R = Cl; R' = CO_2CH_3
19, R = H; R' = Cl

The present scheme owes its success to a one-step synthesis of the proper ring system containing four carbon–carbon

Table I. Spectral Properties of Selected Compounds[a]

5 UV 230 (4.01), 304 (3.74); ^{1}H NMR δ 2.10 (br d, $J_{11a,b}$ = 14.0 Hz, 1, H11), 2.66 (dd, $J_{11a,b}$ = 14.0 Hz, J = 2.4 Hz, 1, H11), 3.09 (br s, 2, two H2), 3.40 (br s, 1, H7), 3.77 (s, 3, CH_3), 5.14 (m, 1), 5.63 (m, 3), 5.89 (m, 1, H10), 7.07 (d, $J_{9,10}$ = 5.0 Hz, 1, H9); ^{13}C NMR δ 28.6 (dd, C11), 33.6 (d, C7), 39.0 (t, C2), 51.9 (q, CH_3), 119.5 (d), 124.3 (d), 124.4 (d), 125.9 (d), 127.3 (d), 131.3 (s), 135.0 (d), 145.8 (s), 168.2 (s, $COOCH_3$)

6 UV 206 (4.39), 255 (3.32); ^{1}H NMR δ 1.78 (dd, $J_{11a,b}$ = 11.0 Hz, J = 4.0 Hz, 1, H11), 2.98 (m, 3, two H10, H11), 3.77 (s, 3, CH_3), 3.84 (m, 1, H7), 5.88 (m, 5), 7.22 (m, 1, H11); ^{13}C NMR δ 30.2 (dd, C11), 37.3 (t, C10), 40.8 (d, C7), 51.7 (q, CH_3), 121.5 (d), 122.7 (d), 126.8 (d), 127.2 (d), 134.0 (d), 134.5 (s), 141.5 (d), 142.4 (s), 167.2 (s, $COOCH_3$)

10 Mp 62–63 °C; UV 204 (4.35), 235 (4.16), 336 (2.86), sh 406 (1.91), sh 430 (1.51); ^{1}H NMR δ 2.44 (dd, $J_{11a,b}$ = 12.0 Hz, J = 4.0 Hz, 1, H11), 3.38 (dd, $J_{11a,b}$ = 12.0 Hz, J = 2.5 Hz, 1, H11), 3.86 (s, 3, CH_3), 3.94 (m, 1, H7), 5.96 (m, 4), 6.59 (m, 1), 6.94 (s, 1, H9); ^{13}C NMR δ 30.5 (dd, C11), 41.4 (d, C7), 52.7 (q, CH_3), 124.9 (d), 126.8 (d), 129.1 (d), 131.1 (d), 132.9 (d), 135.7 (d), 140.1 (s), 151.1 (s), 166.5 (s, $COOCH_3$), 191.8 (s, C10)

11 UV sh 251 (4.1), 266 (4.2), 295 (4.4), 364 (3.9), 480 (2.8); ^{1}H NMR (acetone-d_6) δ –1.27 (dd, $J_{11a,b}$ = 10.0 Hz, J = 1.5 Hz, 1, H11), –0.34 (d, $J_{11a,b}$ = 10.0 Hz, 1, H11), 3.80 (s, 3, CH_3), 7.50 (m, 5), 8.14 (m, 1), 8.78 (m, 1); ^{13}C NMR (acetone-d_6) δ 35.3 (dd, C11), 51.5 (q, CH_3), 126.9 (d), 127.9 (d), 128.6 (d), 131.5 (d), 131.9 (s), 134.3 (d), 142.8 (d), 146.1 (d), 155.3 (s), 158.5 (s), 172.1 (s, $COOCH_3$)

13 Mp 72–73 °C; UV 220 (4.19), sh 252 (3.77), 318 (3.46), sh 390 (2.41); ^{1}H NMR δ 2.68 (dd, $J_{11a,b}$ = 12.0 Hz, J = 3.0 Hz, 1, H11), 3.50 (m, 2, H7, H11), 5.50 (d, $J_{9,10}$ = 10.0 Hz, 1, H9), 6.02 (m, 5), 7.38 (br d, $J_{9,10}$ = 10.0 Hz, 1, H10); ^{13}C NMR δ 30.8 (dd, C11), 52.0 (d, C7), 120.6 (d), 127.3 (d), 127.6 (d), 127.8 (d), 130.3 (d), 131.0 (d), 138.3 (s, C1), 147.5 (d), 201.3 (s, C8)

14 UV 244 (4.0), 290 (4.1), 355 (3.4), 505 (2.5); ^{1}H NMR (acetone-d_6) δ –0.34, –0.20 (ABq, $J_{11a,b}$ = 10.0 Hz, 2, two H11), 3.90 (s, 3, OCH_3), 5.85 (d, J = 7.0 Hz, 1, H9), 6.95 (m, 3), 7.20 (m, 1), 7.55 (m, 1), 8.06 (m, 1); ^{13}C NMR (acetone-d_6) δ 34.2 (dd, C11), 57.5 (q, OCH_3), 104.5 (d), 122.6 (d), 123.4 (d), 128.9 (d), 133.7 (d), 138.2 (d), 145.3 (d), 150.4 (s), 154.6 (s), 165.5 (s, C8)

17 UV 248 (4.8), 294 (4.6), 375 (4.1), sh 500 (3.1); ^{1}H NMR (acetone-d_6) δ –0.41 (d, $J_{11a,b}$ = 10.0 Hz, 1, H11), 0.36 (d, $J_{11a,b}$ = 10.0 Hz, 1, H11), 3.86 (s, 3, OCH_3), 3.93 (s, 3, $COOCH_3$), 6.41 (s, 1, H9), 7.14 (m, 3 H), 7.56 (m, 1 H), 8.86 (m, 1 H); ^{13}C NMR (acetone-d_6) δ 35.8 (dd, C11), 52.0 (q, CH_3), 56.8 (q, CH_3), 102.1 (d), 126.2 (d), 126.8 (d), 129.2 (d), 132.1 (s), 136.9 (d), 146.9 (d), 147.1 (s), 150.3 (s), 163.9 (s), 166.5 (s)

[a] UV spectra use cyclohexane as solvent. The absorption maximum and intensity are expressed in nm and (log ϵ), respectively (error: approximately 0.1 for sensitive compounds **11**, **14**, and **17**). NMR spectra use Me$_4$Si as reference and CDCl$_3$ as solvent, unless otherwise specified. The parentheses following the ^{1}H NMR chemical shift includes multiplicity, coupling constant (first order), relative intensity, and assignment whenever appropriate. The multiplicity in off-resonance decoupling ^{13}C NMR follows the chemical shift of the signal in parentheses. All compounds gave intense parent ions of satisfactory accurate mass (MS – 50).

double bonds, the application of a reaction discovered by Büchi[11a] and applied to the construction of strained systems by Dauben.[11b] Thus condensaton of cycloocta-2,4,6-trienone (**3**)[12] with the anion of methyl 4-(dimethylphosphinyl)-2-butenoate (**4**)[13] in tetrahydrofuran gave initially tetraene **5**, which underwent base-catalyzed isomerization to **6** at a rate comparable to the formation of **5**. The combined yield of **5** and **6** ranged from 30 to 40%, with **6** predominating (60–80%).[14] Upon treatment with a strong base (vide infra) both **5** and **6** provided the same dark red anion, which gave rise to **6** quantitatively

Scheme I
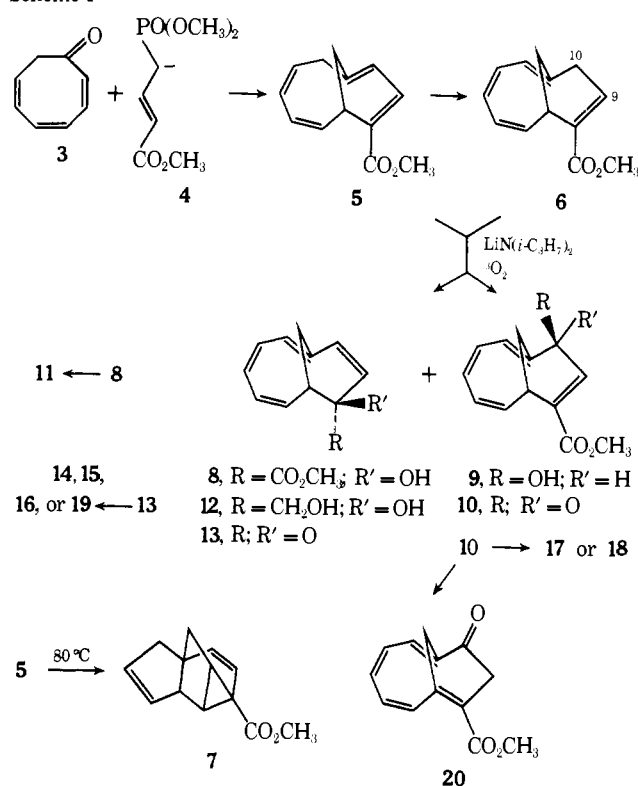
upon protonation. The assignment of the double bonds in **5** and **6** as shown in Scheme I is based on (i) the mode of formation, (ii) facile thermal conversion of **5** into **7** in boiling benzene, and (iii) the sizable spin–spin coupling between the low field vinyl proton (H9) and a methylene group (H10) of **6** as opposed to the apparently negligible interaction in **5**. The success of the above ring construction reaction is indeed remarkable in view of the known instability of **3** and the enormous amount of torsion incorporated in **5**.[15] The methoxycarbonyl group of **4** was required for the essential proton transfer in the Michael intermediate and use of the phosphonate anion rather than the corresponding triphenylphosphorane was necessitated to enhance the nucleophilicity of the reagent.

Oxygenation (using $^3O_2$)[16] of the enolate anion generated from **6**, or a mixture of **5** and **6** (vide supra), with lithium diisopropylamide at –78 °C, followed by reduction with triethyl phosphite provided an approximately 1:1 mixture of two readily separable isomeric hydroxy compounds (**8**, mp 76 °C and **9**, mp 93 °C) in 90% yield. ^{1}H NMR spectra were used to distinguish between the two compounds, and the stereochemistry of the hydroxy groups of **8** and **9** were both assigned exo on the basis of the assumed conformation of **6** and also on the size of the spin–spin coupling between H9 and H10 in the case of **9**, as compared with that of its epimer prepared through the corresponding ketone (**10**) (MnO$_2$ oxidation followed by reduction).[17] The p-nitrobenzoate of **8** lost the acid at 150 °C to give in 35–40% yield a methoxycarbonyl compound (**11**), whose spectral data are fully consistent with the structure of 8-methoxycarbonyl-1,5-methano[10]annulene (see Table I).

Several other derivatives of **2** have been obtained. LiAlH$_4$ reduced **8** to diol **12**, which was in turn converted to yellow ketone **13** with NaIO$_4$ (80%). Quenching the dark red enolate anion derived from **13** (generated with lithium diisopropylamide) led to the formation of its O-derivatives (such as 8-methoxy-[18] and 8-tert-butyldimethylsilyloxy-**2** (**14**, **15**) and diethyl phosphate (**16**)[19]). Similarly, the ketoester **10** was transformed to the corresponding enol methyl ether **17**. Phosphorus pentachloride converted both **10** and **13** into their

dichloro derivatives, which, with lithium diisopropylamide, provided monochloro derivatives of **2** (**18** and **19**). Syntheses of **2** have thus far proceeded only in low yields and difficulties encountered in purification have not allowed us to fully characterize **2**.[20] Interestingly, protonation of the **10**-enolate took place at the 9 position, producing an extremely strained compound, **20**, presumably the first example of a methano-bridged cyclodecane in which two trans double bonds are accommodated without benefit of full cyclic conjugation.

Although compound **14** is somewhat air-sensitive, other derivatives such as **11**, **17**, and **18** are stable and can be handled with routine precautions. There is no indication of polymerization even upon heating. Characteristic of the 1,5-methano[10]annulene system is the appearance of ^{1}H NMR signals due to the methano-protons H11a, 11b at high field as observed for the 1,6-methano series.[1,20] All the derivatives of **2** thus far obtained exhibit only one set of ^{1}H and ^{13}C NMR signals even at -90 °C. Therefore, if single and double bond switching is proceeding in these molecules, it is not detectable at the present time. The electronic absorption of the present system is shifted toward longer wavelengths compared with that of its 1,6-methano counterpart and extends deeply over the visible region, an observation reminding one of the comparison between azulene and naphthalene. Comments on the crucial problem concerning the transannular electronic interaction demand more information and are being deferred until we have completed an x-ray analysis and photoelectron spectral studies, as well as a theoretical treatment of the system.[21]

References and Notes

(1) E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964); H. D. Roth, *Inang. Diss.*, Köln, 1965; E. Vogel, W. Klug, and A. Breuer, *Org. Synth.*, **54**, 11 (1974).
(2) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1968).
(3) In addition to unpublished results from at least several laboratories, the following unsuccessful routes to **2** have been recorded: (a) the contraction of a methoxy[11]annulenone, E. Vogel, J. Ippen, and V. Buch, *Angew. Chem., Int. Ed. Engl.*, **14**, 566 (1975); (b) conversion of bicyclo[5.3.1] undecadiene derivatives to **2** and other routes, B. P. D. Chong, Ph. D. Thesis, *Diss. Abstr.*, **32**, 3845-B (1972); (c) ring opening of tricyclo[5.3.1.0^{1,7}] undecatrienes, R. E. Klem, Ph.D. Thesis, *ibid.*, **32**, 2072-B (1972).
(4) S. Masamune, K. Hojo, K. Hojo, G. Bigam, and D. L. Rabenstein, *J. Am. Chem. Soc.*, **93**, 4966 (1971); S. Masamune and N. Darby, *Acc. Chem. Res.*, **5**, 272 (1972).
(5) (a) R. Boschi, W. Schmidt, and J.-C. Gfeller, *Tetrahedron Lett.*, 4107 (1972); (b) G. L. Grunewald, I. M. Uwaydah, R. E. Christoffersen, and D. Spangler, *ibid.*, 933 (1975); (c) R. C. Haddon, *J. Am. Chem. Soc.*, **97**, 3608 (1975).
(6) H.-R. Blattmann, E. Heilbronner, and G. Wagnière, *J. Am. Chem. Soc.*, **90**, 4786 (1968); also see J. Kolc, J. Michl, and E. Vogel, *ibid.*, **98**, 3935 (1976), and references quoted therein.
(7) An x-ray analysis of **1**-carboxylic acid shows that the distance between C-1 and C-6 is 2.26 Å. M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965); also see R. Destro, T. Pilati, and M. Simonetta, *J. Am. Chem. Soc.*, **98**, 1999 (1976).
(8) (a) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, N.Y., 1975, Chapter 3; (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, Chapters 5 and 6.
(9) A. V. Kemp-Jones and S. Masamune, "Topics in Nonbenzonoid Aromatic Chemistry", Vol. 1, T. Nozoe, Ed., Hirokawa Publishing Company, Tokyo, 1973, pp 121–157; A. V. Kemp-Jones, A. J. Jones, M. Sakai, C. P. Beeman, and S. Masamune, *Can. J. Chem.*, **51**, 767 (1973).
(10) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973).
(11) (a) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **54**, 1767 (1971); (b) W. G. Dauben and J. Ipaktschi, *J. Am. Chem. Soc.*, **95**, 5088 (1973). A number of reactions of similar type, combining the Michael and Wittig reactions have appeared recently, e.g., P. L. Fuchs, *ibid.*, **96**, 1607 (1974).
(12) Using a procedure modified from the original one by A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).
(13) F. Bohlmann and Ch. Zdero, *Chem. Ber.*, **106**, 3779 (1973).
(14) The separation of the two compounds, **5** and **6**, was achieved on a silver nitrate impregnated TLC plate.
(15) All attempts to introduce additional double bonds into bicyclo[5.3.1]undeca-8,10-dien-5-one have failed.
(16) Some recent examples are (a) W. Adam, O. Cueto, and V. Ehrig, *J. Org. Chem.*, **41**, 370 (1976); (b) S. J. Selikson and D. S. Watt, *ibid.*, **40**, 267 (1975); (c) T. Cuvigny, P. Hullot, M. Larcheveque, and H. Normant, *C. R. Acad. Sci.*, **281**, 251 (1975); (d) E. Vedejs, *J. Am. Chem. Soc.*, **96**, 5944 (1974); (e) E. Vedejs and J. E. Telschov, *J Org. Chem.*, **41**, 740 (1976).
(17) $J_{9,10}$'s of **9** and its stereoisomer are 5 and ~0 Hz, respectively.
(18) For the 1,6-methano series, see E. Vogel, W. Schröck, and W. A. Böll,

Angew. Chem., Int. Ed. Engl., **5**, 732 (1966); W. A. Böll, *ibid.*, **5**, 733 (1966).
(19) (a) R. E. Ireland and G. Pfisten, *Tetrahedron Lett.*, 2145 (1969); (b) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).
(20) GLC-mass and ^{1}H NMR spectra (δ -0.96(dt, $J_{11a,b}$ = 10 Hz, J = 2 Hz, t, Htt) and -0.45 (d, $J_{11a,b}$ = 10 Hz, t, Htt)) of a crude mixture confirmed the formation of **2**.
(21) The authors are grateful to Dr. A. Venot for exploring other approaches prior to this work and the National Research Council of Canada for financial support.

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An Electron Spin Resonance Study on the Spiro Cyclohexadienyl Radicals[1]

Sir:

The 1,n-aryl shift is one of the important homolytic reactions and a spiro (or bridged) cyclohexadienyl radical has been postulated as an intermediate or a model of the transition state.[2]

$$(1)$$
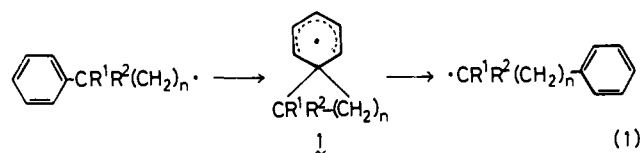
However, no evidence for the spiro radicals such as **1** was obtained by ESR even in the system suitably designed for the homolytic rearrangement,[3] although it has been demonstrated chemically that the spiro radical (**1**) can serve as an intermediate.[4] In the neophyl rearrangement, only ESR spectra of unrearranged and rearranged radicals have been observed before and after the reaction.[5,6]

Recently, we[7] have reported ESR spectra of various 2,4-di-*tert*-butyl-6,6-bis(organosilyl)cyclohexadienyl radicals (**2**) arising from the addition of a silyl radical to 3,4-di-*tert*-butylphenylsilanes[8] and have demonstrated that such a homolytic ipso substitution occurs very efficiently to give the intermediate radicals in high concentration.

$$(2)$$
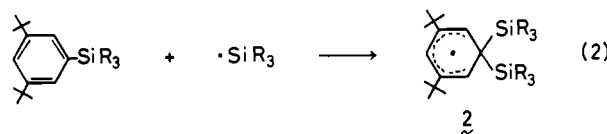
In this paper, we report the first ESR spectra of spiro radicals derived from ω-(3,5-di-*tert*-butylphenyl)-α,ω-disilaalkanes. Analysis of the spectra indicates interesting features of the radicals.

$$(3)$$

3a, n = 2	**4a**, n = 2
3b, n = 3	**4b**, n = 3
3c, n = 4	**4c**, n = 4
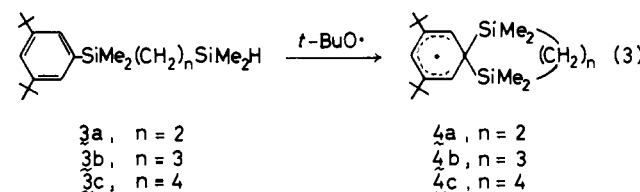
Irradiation of a mixture of 1,1,4,4-tetramethyl-4-(3,5-di-*tert*-butylphenyl)-1,4-disilabutane (**3a**)[9] and di-*tert*-butyl peroxide with a 500W super-high-pressure mercury arc lamp in the cavity of an ESR spectrometer[10] gave a well-resolved spectrum as shown in Figure 1. The spectrum is composed of a doublet (11.83 G) of triplets (7.54 G) with a g value of 2.00284 similar to the spectrum of the 2,4-di-*tert*-butyl-6,6-bis(trimethylsilyl)cyclohexadienyl radical (**2**, R = Me),[7] but each line splits further into small quintets (0.34 G). No spectral