(t, 2 H, J = 7.5 Hz, $-OCH_2CH_2-$), 4.39 (t, 2 H, J = 7.5 Hz, $-OCH_2CH-$); IR ν_{max} (CS_2) 980, 965 cm^{-1}. Anal. Calcd for $C_9H_{14}O$: C, 78.12; H, 10.21. Found: C, 77.99; H, 10.10.

Ethyl *exo*-(2′-Hydroxyspiro[cyclopropane-1,7′-norbornan]-2′-yl)acetate (16). To a solution of 0.0367 mol of ethyl lithioacetate in tetrahydrofuran at −78 °C was added a solution of 5.0 g of spiro[cyclopropane-1,7′-norbornan]-2′-one (**K2**) in 5 mL of tetrahydrofuran over a 15-min period, and the mixture was stirred for 30 min in the cold. Following hydrolysis of the lithium salt and workup as described above, the product was distilled, bp 94–96 °C (0.8 mm), to give 6.5 g (80%) of a colorless liquid. Analysis by GLC (6 ft × $^1/_4$ in. 20% Apiezon L on base-washed Chromosorb P, CT = 165 °C) indicated a purity of ~98% **16**: NMR (Me_4Si internal standard, CCl_4) δ 0.5 (m, 4 H, cyclopropyl), 1.25 (t, J = 7.0 Hz, $-COOCH_2CH_3$), 2.63 (s, 2 H, $(CH_3)_2C(OH)CH_2COOEt$), 3.45 (s, 1 H, OH), 4.15 (q, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$); IR ν_{max} (CCl_4) 3390, 2990, 1710, 1185 cm^{-1}.

***exo*-2′-(2-Hydroxyethyl)spiro[cyclopropane-1,7′-norbornan]-2′-ol (17).** Reduction of 6.0 g of ester **16** with $LiAlH_4$ in ether under the conditions described above afforded on workup 4.25 g (88%) of **17** as a thick oil: bp 120–122 °C (0.7 mm); NMR (Me_4Si internal standard, $CDCl_3$) δ 0.5 (m, 4 H, cyclopropyl), 1.95 (t, J = 5.5 Hz, $(CH_3)_2C(OH)CH_2-$), 3.0 (position concentration dependent, bs, 2 H, OH), 3.90 (t, 2 H, J = 5.5 Hz, $-CH_2OH$); IR ν_{max} (CCl_4) 3450 (sh), 3250, 3010, 1065 cm^{-1}.

Dispiro[cyclopropane-1,7′-norbornane-2′,2″-oxetane] (OX(11)). Formation of the monobrosylate ester of **17** from 3.8 g of the diol and 5.5 g of *p*-bromobenzenesulfonyl chloride followed by ring closure with potassium *tert*-butoxide in *tert*-butyl alcohol was carried out as described for **15**. Distillation of the resulting residue afforded 2.8 g of a clear liquid, bp 95–96 °C (0.5 mm), which was analyzed by GLC and found to consist of approximately 90% pure oxetane **OX(11)**. A pure sample was isolated by GLC (10 ft × $^1/_4$ in. 2% Carbowax 20M on base-washed Chromosorb G): NMR (Me_4Si internal standard standard) δ 0.4 (m, 4 H, cyclopropyl), 2.09 (2 q, 1 H, major splitting J = 13.0 Hz, H_3^x), 2.57 (t, 2 H, J = 7.5 Hz, $-O-CH_2CH_2-$), 4.40 (t, 2 H, J = 7.5 Hz, $-O-CH_2-$); IR ν_{max} (CS_2) 3030, 1005, 980, 965, 955 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.30; H, 9.89.

Ethyl *endo*-(7,7-Dimethyl-2-hydroxynorbornan-2-yl)acetate (18). To a solution of 0.0289 mol of ethyl lithioacetate in tetrahydrofuran at −78 °C was added a solution of 4.0 g of 7,7-dimethylnorcamphor in tetrahydrofuran over a 15-min period, and the mixture allowed to stir for 4 h in the cold. Following workup in the usual manner distillation of the residue gave, in addition to 2.2 g of starting ketone, 1.7 g of **18** as a clear liquid: bp 130–134 °C (6 mm); NMR (Me_4Si internal standard, CCl_4) δ 0.97 and 1.32 (2 s, each 3 H, 7-CH_3's), 1.25 (t, 3 H, J = 7.0 Hz; $-COOCH_2CH_3$), 2.51 (s , 2 H, $(CH_3)_2C(CH_2-)OH$), 3.43 (3, 1 H, OH), 4.15 (q, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$); IR ν_{max} (CCl_4) 3355, 1725, 1380, 1360 cm^{-1}.

***endo*-2-(2-Hydroxyethyl)-7,7-dimethylnorbornan-2-ol (19).** Reduction of 2 g of ester **18** with $LiAlH_4$ in ether afforded after workup 1.5 g of **19** as a thick oil: bp 125–127 °C (0.5 mm); NMR (Me_4Si internal standard $CDCl_3$) δ 1.02 and 1.33 (2 s, each 3 H, 7-CH_3's), 1.83 (t, J = 5.5 Hz, $(CH_3)_2C(CH_2-)OH$), 3.4 (bs, 2 H, OH), 3.85 (t, 2 H, J = 5.5 Hz, $-CH_2OH$); IR ν_{max} (film) 3330 (broad), 1380, 1360 cm^{-1}.

7,7-Dimethylspiro[norbornane-2,2′-oxetane] (OX(12)). Formation of the monobrosylate ester of **19** from 1.2 g of diol and 1.75 g of *p*-bromobenzenesulfonyl chloride and subsequent ring closure with potassium *tert*-butoxide in *tert*-butyl alchohol resulted in the formation of 510 mg of a clear liquid, bp 82–85 °C (2 mm), which was purified by preparative GLC (6 ft × $^1/_4$ in. 20% Apiezon L on base-washed Chromosorb P, CT = 165 °C): NMR (Me_4Si internal standard, CCl_4, 100 MHz) δ 0.95, 1.07 (2 s, each 3 H, 7-CH_3's), 0.9–2.3 (m, 8 H, norbornane), 2.5 (m, 2 H, oxetane $-CH_2CH_2O-$), 4.23 (m, 2 H, oxetane $-CH_2O$); IR ν_{max} (CS_2) 1380, 1365, 990, 965 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.33; H, 10.88.

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Studies on the Spiro[2.5]octadienyl Radical and the 2-Phenylethyl Rearrangement[1]

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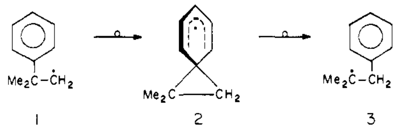
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6, and the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. Received June 9, 1980

Abstract: The title radical, **5**, has been generated by hydrogen atom abstraction from spiro[2.5]octa-4,6-diene (**4**). The radical could not be observed by EPR spectroscopy even at temperatures as low as 100 K. Instead, the EPR spectrum of the cyclopropyl ring-opened product was obtained, 2-phenylethyl (**6**). However, **5** was identified by using optical detection methods by means of its absorption and fluorescence at ca. 560 nm, which is a characteristic of cyclohexadienyls. The rate constant for H atom abstraction from **4** by *tert*-butoxyl was measured at 295 K, and approximate Arrhenius parameters for the **5** to **6** rearrangement have been estimated. The hydrocarbon **4** is remarkably resistant to the thermodynamically favored, radical induced rearrangement to ethyl benzene.

The rearrangement of neophyl (**1**) to 1-phenyl-2-methylprop-2-yl (**3**) (eq 1), which was the first free-radical rearrangement



(1)

to be discovered,[5] continues to intrigue organic chemists.[6] Abundant evidence exists that this rearrangement is intramolecular,[6] and this implies that it must proceed via a 1,1-dimethylspiro[2.5]octadienyl radical (**2**). This might be either an intermediate or merely a transition state. Attempts to detect **2**,[7-10] and related spiro radicals,[7-9,11] by EPR spectroscopy at low tem-

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[2] N.R.C.C. Research Associate, 1978–1979.

[3] N.R.C.C.

[4] Radiation Laboratory.

[5] Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438.

[6] For reviews of this and related rearrangements see: (a) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 8; (b) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, in press.

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[10] Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224, 4692.

[11] Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447.

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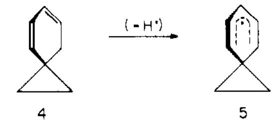
peratures have been unsuccessful. This is not too surprising as the cyclopropane ring is expected to undergo a rapid ring opening if **2** is a true intermediate. That is, although the rearrangement of cyclopropylcarbinyl to yield 3-butenyl is a rapid process ($k^{298\text{K}} = 1.3 \times 10^8$ s^{-1}),[12] the cyclopropylcarbinyl radical can at least be observed by EPR at temperatures below ca. 153 K.[12-14] In contrast, when cyclopropylcarbinyls having one[15] or two[14,16] methyl groups at the 2-position are generated the EPR spectra of only the ring-opened allylcarbinyls can be observed even at much lower temperatures. That is, methyl substitution on the cyclopropane ring enhances the rate of ring opening of cyclopropylcarbinyls.

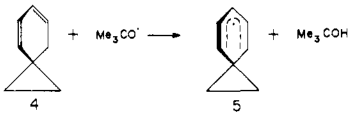
For the above reasons, the recent synthesis by de Meijere[17] of spiro[2.5]octa-4,6-diene (**4**) was of great interest to us since this compound might serve as a "direct" precursor of the parent spiro[2.5]octadienyl[18] (**5**) (eq 2), which should be more resistant to ring opening than **2** and so should be easier to detect. Professor de Meijere very generously provided samples of **4** and preliminary experiments were sufficiently encouraging that we prepared additional material by a somewhat improved route (see Experimental Section).



(2)

Results

Attempt to Observe 5 by EPR Spectroscopy. Mixtures of di-*tert*-butyl peroxide and **4** in hydrocarbon solvents were subject to continuous UV photolysis (500-W high-pressure Hg lamp) directly in the cavity of a Varian E-104 EPR spectrometer (see eq 3 and 4). Excellent spectra of the 2-phenylethyl radical[7,8,19] (**6**) were obtained in fluid propane solutions from room temperature down to 100 K.



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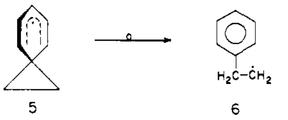


(4)

The same procedure applied to a propane matrix at 77 K also gave **6**. At 4 K a broad, anisotropic, EPR spectrum was obtained which could not be assigned to any specific radical. These experiments showed that if **5** was a discrete intermediate, it must be very short-lived.

The minimum value of the rate constant for the rearrangement of **5** to form **6** (k_4) was estimated in propane at 123 K by measuring the rate constant for the bimolecular self-reaction of **6** (k^{66}) under these conditions by the usual kinetic EPR technique.[10-12] Provided **5** is a discrete intermediate, then, under steady illumination, the overall reaction scheme can be represented by reactions 3 and 4 followed by eq 5. The usual assumptions[10-12]

$$\begin{aligned} \mathbf{5} + \mathbf{5} &\xrightarrow{k^{55}} \text{nonradical products} \\ \mathbf{5} + \mathbf{6} &\xrightarrow{k^{56}} \text{nonradical products} \qquad (5) \\ \mathbf{6} + \mathbf{6} &\xrightarrow{k^{66}} \text{nonradical products} \end{aligned}$$

lead to the kinetic expression (6). The measured value of $2k^{66}$

$$k_4 = 2k^{66}\left\{\frac{[\mathbf{6}]^2}{[\mathbf{5}]} + [\mathbf{6}]\right\} \qquad (6)$$

was 1.0×10^9 M^{-1} s^{-1}, and the concentration of **6** was 1×10^{-7} M. We assume that **5** could have been detected if it had been present at the same concentration. Since it was not observed, we estimate that $k_4 \geq 2 \times 10^2$ s^{-1} at 123 K.

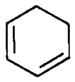
Table I. Rate Constants for H Atom Abstraction by *tert*-Butoxyl at 295 K[a]

RH	k_3 or k_8, M^{-1} s^{-1}
4	11×10^7
7	4.2×10^7
8	5.3×10^7
cyclopentane[b]	8.8×10^5

[a] The solvent is a 1:2 (v/v) mixture of benzene and di-*tert*-butyl peroxide. [b] See reference 20b.

In order to obtain a more direct measure of k_4 using EPR spectroscopy, we subjected samples of **4** and di-*tert*-butyl peroxide in propane to pulses from a nitrogen laser (337.1 nm, ~8 ns, ~10 mJ), the frequency of this irradiation being well suited for the photolysis of the peroxide. At 50 Hz a well-resolved spectrum of **6** was observed at 108 K and above. The buildup and decay of **6** after a laser pulse was monitored by using a Nicolet 1170 signal averager. At temperatures above 208 K, the formation of **6** showed a half-life of 45 μs, which we take to be the time constant of the system. At lower temperatures the half-life increased to 96, 108, 125, and 155 μs at 148, 138, 125, and 108 K, respectively. Since the measured half-lives were independent of the concentration of **4** (which was varied by a factor of 5), their increase at low temperatures cannot be due to the slowness of reaction 3. Instead, it must be attributed to a decrease in the rate of reaction 4. Although the measured half-lives cannot be very accurate since they cover a time scale which is only around thrice the response time of the system, they do yield approximate rate constants for the decay of the spirocyclooctadienyl radical at low temperatures.

Generation and Decay of 5 Studied by Laser Flash Photolysis Using Optical Detection. The rate constants for reaction 3 and for the reactions of *tert*-butoxyl with 1,3- and 1,4-cyclohexadiene, **7** and **8**, respectively, were measured at 295 K by a technique described previously.[20,21] In this technique diphenylmethanol (**9**) is used as a probe because it yields diphenylhydroxymethyl radicals (**10**), which can be easily detected by their characteristic transient absorption spectrum.[20,22] This technique has proved satisfactory for a variety of substrates,[20,21] including several containing allylic hydrogens.[21]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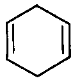
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Samples containing different amounts of the substrate RH and a constant amount of **9** in a 1:2 benzene/di-*tert*-butyl peroxide mixture were excited at 337.1 nm, and the resulting transient absorptions were monitored with a detection system having na-

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(12) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

(13) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877.

(14) Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036.

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(16) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1879.

(17) de Meijere, A. *Chem. Ber.* **1974**, *107*, 1684.

(18) The origin of this idea can be traced to the study by M. Julia and B. Malassinê (*Tetrahedron Lett.* **1971**, 987) of the products formed from spiro[4.5]deca-1,4-diene on its reaction with *tert*-butoxyl.

(19) (a) Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 2635. (b) There is some selective line broadening at low temperatures due to restricted rotation about the C_6H_5–C bond, cf. ref 8.

(20) (a) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 296. (b) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1978**, *100*, 4520.

(21) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49.

(22) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144.

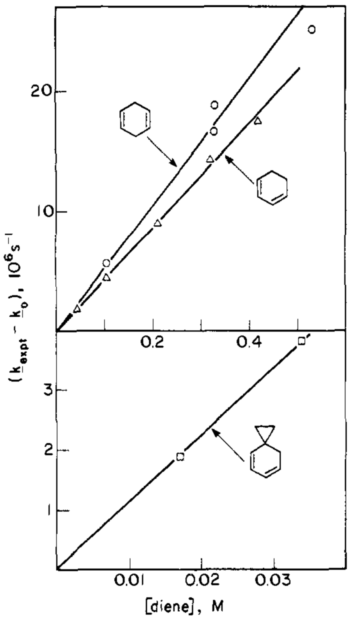


Figure 1. Kinetic data for reaction of *tert*-butoxyl with the three cyclohexadienes plotted according to eq II.

nosecond response. The overall reaction system can be represented by eq 7–9. The kinetics for the formation of the ketyl radical

$$\mathrm{Me_3COOCMe_3} \xrightarrow{h\nu} \mathrm{2Me_3CO\cdot}$$

$$\mathrm{Me_3CO\cdot} + \underset{\mathbf{9}}{\mathrm{(C_6H_5)_2CHOH}} \rightarrow \mathrm{Me_3COH} + \underset{\mathbf{10}}{\mathrm{(C_6H_5)_2\dot{C}OH}} \quad (7)$$

$$\mathrm{Me_3CO\cdot} + \mathrm{RH} \rightarrow \mathrm{Me_3COH} + \mathrm{R\cdot} \quad (8)$$

$$\mathrm{Me_3CO\cdot} \rightarrow \text{first-order decay} \quad (9)$$

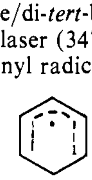
10 are given by eq I and II[20] where k_{exptl} is the experimentally

$$k_{\mathrm{exptl}} = (k_9 + k_7[\mathbf{9}]) + k_8[\mathrm{RH}] \quad (\mathrm{I})$$

$$k_{\mathrm{exptl}} = k_0 + k_8[\mathrm{RH}] \quad (\mathrm{II})$$

measured rate constant obtained from the first-order treatment of the traces for the buildup of **10**. Plots according to eq II for **4**, **7**, and **8** are shown in Figure 1, and the corresponding values of k_3 and k_8 at 295 K are given in Table I. The value of k_0 is based on rate constants reported previously.[20]

Cyclohexadienyl radicals show weak absorptions in the visible region of the spectrum, usually around 560 nm.[23] Excitation of solutions of **7** or **8** in benzene/di-*tert*-butyl peroxide mixtures using a frequency doubled ruby laser (347.1 nm) allowed characterization of the cyclohexadienyl radical **11**. The same transient



11

spectrum is observed from both **7** and **8** (see Figure 2), as would be expected. On the time scale of our experiments (usually 1 μs or less) **11** does not decay. On a longer time scale decay occurred with second-order kinetics, but this process was not examined further.

The transient spectrum observed when the spirocyclooctadiene **4** is used as the substrate is also shown in Figure 2. This only differs from that due to **11** in that there is a small red shift and the band is somewhat broader—an effect which may be due more to underlying absorptions (vide infra) than to any real change in bandwidth. In view of its spectroscopic similarity with **11**, we assign this transient absorption to the spirocyclooctadienyl radical **5**. This assignment is further supported by the results of laser fluorescence experiments at 4 K (vide infra).

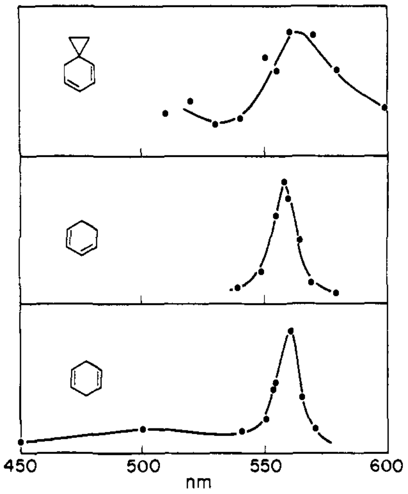


Figure 2. Transient spectra observed after reaction of cyclohexadienes with *tert*-butoxyl.

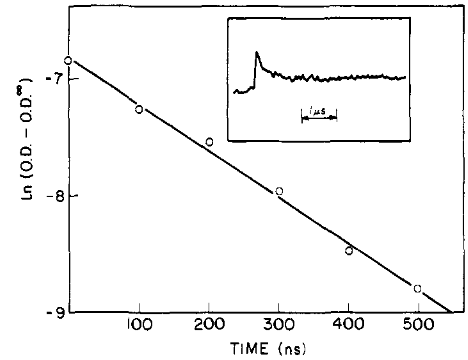


Figure 3. First-order plot for decay of **5** (monitored at 570 nm) at 243 K. Insert: typical decay trace.

It should be noted that transient absorptions in the 560-nm region are not very common in aliphatic radicals and would not be expected for any of the other radicals likely to be generated here, e.g., $\mathrm{PhCH_2CH_2\cdot}$ or $\mathrm{Me_3CO\cdot}$.[24] Also worth mentioning is the reason for using the frequency doubled ruby laser (347.1 nm) rather than the nitrogen laser (337.1 nm) used in other experiments. The absorption spectrum of **4** has a UV cutoff at ca. 325 nm, and though its absorption at 337 nm is fairly weak, it nevertheless competes with the di-*tert*-butyl peroxide (for which $\epsilon_{337} \approx 0.46\ \mathrm{M^{-1}\ cm^{-1}}$). Light absorbtion by **4** causes several problems: (i) **4** is rapidly and efficiently converted to ethylbenzene[25] which unnecessarily destroys the sample. (ii) **4** yields trace amounts[25] of an as yet uncharacterized yellow product that behaves as an efficient UV filter. (iii) **4** luminesces, which interferes with the monitoring of the transient absorptions. (We initially thought this was due to an impurity, but double preparative VPC had no effect on this emission or its intensity.) This luminescence peaks at 405 nm but tails well into the 500-nm region. The above problems are reduced by using 347.1-nm excitation because the extinction coefficient of **4** decreases with increasing wavelength more rapidly than that of the peroxide.

In contrast with the relatively long-lived cyclohexadienyl **11**, the signals from the spirocyclooctadienyl **5** decay in the nanosecond time scale. This rapid disappearance of **5** is attributed to opening of the cyclopropane ring and the formation of **6** (reaction 4). At

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[23] Shida, T.; Hanazaki, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 646. Jordan, J. E.; Pratt, D. W.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 5588.

[24] Blank experiments with benzene and di-*tert*-butyl peroxide did not give a transient absorption in this region.

[25] A 1 M solution of **4** in c-$\mathrm{C_6D_{12}}$ was degassed, sealed under vacuum, and then photolyzed in a 5-mm NMR tube with the unfiltered light from a 500-W Hg high-pressure lamp. In less than 1 h all **4** was destroyed and only the ethylbenzene could be observed by NMR, although the solution had a strong yellow color.

room temperature decay of the transient does not follow simple kinetics. At lower temperatures,[26] e.g., ca. 243 K, there was a simple first-order decay but the final signal level was different from the prepulse baseline. This can be seen in Figure 3 which shows a typical 243 K[26] trace monitored at 570 nm together with a first-order plot which gives $k_2 = 4 \times 10^6\ s^{-1}$, corresponding to a half-life for **5** of 170 ns. At ca. 198 K[26] k_2 is ca. $1.5 \times 10^6\ s^{-1}$. These experiments were carried out in a sample containing 7.5% v/v of **4** and 20% v/v of di-*tert*-butyl peroxide in isopentane. The identity of the species giving the long-lived signal (i.e., the baseline shift) is not known; apparently this species is not stable at room temperature and its decay overlaps in time with that of **5**, which makes kinetic analysis difficult. Perhaps this species is the precursor of the yellow coloration mentioned above.

Finally, although the formation and decay of **11** could be monitored at ca. 320 nm (where the extinction coefficient is substantially greater than that at 560 nm), similar experiments with **5** were not too successful. The difficulties arose because of absorbance by the parent hydrocarbon **4** in that spectral region. There was also some indication that **5** may have a smaller extinction coefficient than that of **4** since the laser pulse led to a weak transient bleaching rather than transient absorption.

Laser Fluorescence of 5 at 4 K. The fluorescence spectrum of the cyclohexadienyl radical in a benzene matrix has been observed previously by using selective excitation by a dye laser.[27] The fluorescence spectrum obtained by the same technique after γ irradiation (2 h in a cobalt cave containing 12 000 Ci of Co-60) of **4** in isobutane and octane[27] matrices at liquid-helium temperature showed an origin at 558 nm. This value is in excellent agreement with the 558.6-nm visible transition found for the unsubstituted cyclohexadienyl.[27] For this reason we attribute the fluorescence to the spirooctadienyl radical **5**, which must be rather persistent at 4 K.

An unsuccessful attempt to improve spectral quality was made by using crystals of neat **4** under the same conditions, but only Raman scattering from **4** could be detected. There were 5 prominent Raman lines: 3032 and 2992 cm^{-1}, attributable to C—H stretching; 1571 cm^{-1}, attributable to the symmetric C=C stretch of the 1,3-cyclohexadiene skeleton; 1175 cm^{-1}, attributable to the ring-breathing vibration of the cyclopropane skeleton, and 1419 cm^{-1}. The last mentioned line is of particular interest since it appears in both the infrared and Raman spectra of 1,3-cyclohexadiene[29] and is also a vibrational mode which appears in the fluorescence spectrum of **5**.

Attempts to carry out similar experiments at 77 K were unsuccessful. This is consistent with the half-lives for **5** measured by the EPR laser technique.

Resistance of 4 to Free-Radical-Induced Decomposition. The spirooctadiene **4** shows remarkable thermal stability since it is purified by preparative VPC at 373 K (see Experimental Section). We nevertheless anticipated that **4** would undergo an induced decomposition with considerable facility if a chain reaction were initiated, i.e., eq 10–12. Reaction 11 would presumably be the

Initiation

$$R\cdot + \mathbf{4} \rightarrow RH + \mathbf{5} \qquad (10)$$

Propagation

$$\mathbf{5} \xrightarrow{\ell} \mathbf{6}$$

$$\mathbf{6} + \mathbf{4} \rightarrow C_6H_5CH_2CH_3 + \mathbf{5} \qquad (11)$$

Termination

$$\mathbf{6} + \mathbf{6} \rightarrow \text{nonradical products} \qquad (12)$$

"slow" step of chain propagation, but since it should be exothermic by ca. 27 kcal/mol,[30] it was expected to be fast enough to carry the chain. This did not appear to be the case.

Experiment 1. A degassed solution of α,α-azobis(isobutyronitrile) (AIBN, 0.5 M) and **4** (0.36 M) in C_6D_6 was heated to 303 K and monitored by NMR spectroscopy. Under these conditions the rate of generation of radicals by the thermal decomposition of AIBN, R_i, is ca. $5 \times 10^{-8}\ M\ s^{-1}$. After 8 h the decrease in the concentration of **4** was less than 5%, and no ethylbenzene could be detected.

Experiment 2. In case the isobutyronitrile radicals were too unreactive to abstract from **4**, a reaction was carried out under the same conditions but with the AIBN replaced by 0.13 M (initial $R_i \approx 5 \times 10^{-7}\ M\ s^{-1}$) di-*tert*-butyl hyponitrite—an initiator which yields *tert*-butoxyls. However, even after 3 days the decrease in **4** was insignificant, and NMR peaks due to the ethylbenzene could not be observed.

Experiment 3. A similar experiment at 373 K using 0.1 M ($R_i \approx 10^{-7}\ M\ s^{-1}$) di-*tert*-butyl peroxide as the initiator gave a 20 ± 5% decrease in **4**. The yield of ethylbenzene was 8 ± 5%. If we assume that there is no direct thermal isomerization of **4** to ethylbenzene, then ca. 0.36 M × 8% = 0.023 M **4** was caused to react to yield ethylbenzene by ca. 5.8×10^{-3} M *tert*-butoxyl. Even at 373 K the chain length was, therefore, only about four. Since the difference between the amount of **4** reacted and the ethylbenzene formed is probably real, it seems possible that **6** can *add* to the cyclohexadiene ring of **4**.

The 2-Phenylethyl Rearrangement. The 1,2-migration of vinyl has been observed by EPR spectroscopy using deuterium-labeled 3-butenyl.[33] An attempt to observe a 1,2-migration of phenyl using deuterium-labeled 2-phenylethyl has been reported,[8] but the highest temperature reached appears to have been only 248 K. For this reason 1,1-dideuterio-2-phenylethyl (**12**) was generated photochemically from its bromide in hexadecane as solvent (eq 13). The unrearranged radical could be observed up to 423K without any sign of the rearranged species.

$$(n\text{-Bu})_3SnSn(n\text{-Bu})_3 \xrightarrow[Me_3COOCMe_3]{h\nu} 2(n\text{-Bu})_3Sn\cdot$$

$$(n\text{-Bu})_3Sn\cdot + C_6H_5CH_2CD_2Br \rightarrow (n\text{-Bu})_3SnBr + \underset{\mathbf{12}}{C_6H_5CH_2\dot{C}D_2}$$

$$C_6H_5CH_2CD_2\cdot \overset{k_{13}}{\not\xrightarrow{\ell}} C_6H_5CD_2\dot{C}H_2 \qquad (13)$$

Discussion

There can be no doubt that the spiro[2.5]octadienyl radical **5** is a genuine, though short-lived, intermediate which can be formed by H atom abstraction from the parent hydrocarbon **4**. This follows from the observation in both the laser flash photolysis and laser fluorescence experiments of a band at ca. 560 nm—which is a characteristic of cyclohexadienyl radicals.

Hydrogen atom abstraction from cyclohexadienes by *tert*-butoxyl is a very rapid process (Table I). These three compounds are more reactive than any other hydrocarbons so far examined.[20,21] The rate of abstraction from the spirooctadiene is about twice that for abstraction from 1,3- or 1,4-cyclohexadiene which implies that the cyclopropane ring assists the reaction. This is not unreasonable since the primary C–H bond in methylcyclopropane has been found to be ca. 0.8 kcal/mol weaker than the primary C–H bonds in alkanes.[34] The bond weakening induced by the cyclopropyl ring can probably be attributed to the fact that cyclopropyl-

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[26] Temperature control on the instrument was poor and for instrumental reasons could not be improved. The temperatures quoted could be in error as much as ±10 °C.

[27] Sheng, S. J. *J. Phys. Chem.* **1978**, *82*, 442.

[28] The emission line width was narrower in this matrix.

[29] At 1435, 1426, and 1428 cm^{-1} for IR (gas), IR (liquid), and Raman (liquid), respectively: Di Lauro, C.; Neto, N.; Califano, S. *J. Mol. Struct.* **1969**, *3*, 219.

[30] Based on carbon–hydrogen bond dissociation energies of 98 kcal/mol for $C_6H_5CH_2CH_2{-}H$[31] and 71 kcal/mol for $\overline{CH{=}CHCH{=}CHCH_2CH}{-}H$.[32] We note here that the O–H bond strength in *tert*-butyl alcohol is ca. 103 kcal/mol.

[31] Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

[32] Egger, K. W.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 241. James, D. G. L.; Stuart, R. D. *Chem. Commun.* **1966**, 484.

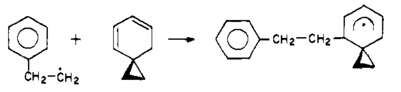
[33] Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Seralis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

[34] On the basis of the following bond strengths[35] which were determined by the same experimental technique: $DH°[\overline{CH_2CH_2C}HCH_2{-}H] = 97.4$ kcal/mol; $DH°[CH_3CH_2{-}H] = 98.2$ kcal/mol.

[35] O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K. Ed.; Wiley: New York, 1973; Vol. 2 Chapter 17, Table 2.

carbinyl[13,36] and related radicals[16,37] preferentially adopt, and hence are presumably stabilized in, a conformation in which the cyclopropyl ring bisects the nodal plane of the semioccupied orbital. Radical **5** is, of course, forced to adopt this type of conformation.

Although *tert*-butoxyls attack **4** with great facility, our difficulties in inducing a chain decomposition of **4** might suggest that hydrogen abstraction from this compound by 2-phenylethyl radicals (reaction 11) is rather slow, despite the fact that this reaction should be strongly exothermic.[30] This seems so unlikely that we believe another explanation is in order. We suggest, therefore, that the addition of 2-phenylethyl to the 2-position of **4** competes favorably with the abstraction (and with addition to the 5-position) (see eq 14).[38] The product would be the cyclohexenyl radical



(14)

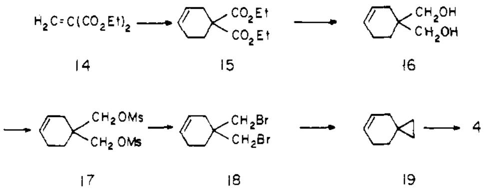
6 4 13

13, which would be incapable of undergoing a cyclopropyl ring opening and, being resonance stabilized, might well be unable to abstract from **4** and hence be unable to continue the chain. The expected induced chain decomposition would therefore be self-inhibiting. Further studies are underway to investigate this point in more detail and to try to determine the magnitude of k_{11}. In connection with the foregoing, we also tentatively suggest that the pronounced influence of the medium on the yield of **5** in the laser fluorescence experiments may be related to changes in the importance of the abstraction and addition reactions of the matrix-derived radicals.

The rate constants for the ring opening of the spirooctadienyl radical, measured by laser photolysis with optical and EPR detection methods, provide a basis for estimating the Arrhenius parameters for reaction 4. Analysis of the rather limited kinetic data suggests that $\log (A_4/\mathrm{s}^{-1}) = 9.2 \pm 1.0$ and $E_4 = 2.8 \pm 0.4$ kcal/mol. These parameters were obtained by weighting more heavily the k_4 values calculated at 198 and 108 K since for each technique the lower temperature gave the better time resolution.

Despite the obvious limitations involved in deriving Arrhenius parameters from few temperatures, it is clear that the values are quite different from those of the analogous opening of cyclopropylmethyl (viz.,[12] $\log (A/\mathrm{s}^{-1}) = 12.5$, $E = 5.9$ kcal/mol). Particularly surprising and difficult to accept is the low A factor for reaction 3. However, all our efforts to "force" a more "normal" A-factor (i.e., ca. 10^{13} s^{-1}) upon our results were unsuccessful. Depending on whether the data are "pivoted" around 198 or 108 K, certain inconsistencies with experiment will result, for example: (i) **5** should not be detectable at room temperature (see, however, Figure 2); (ii) **5** should have been detected *not* **6** upon steady irradiation at 100 K in the EPR cavity; (iii) **5** should have been observed in the fluorescence experiment at 77 K. We must therefore conclude that *either* there is something badly wrong with one (or more) of our experimental procedures *or* that our understanding of reaction 4 (and related processes) is at fault and that such processes really do have low A factors.[39] Neither conclusion is easy to accept nor should one be favored over the other at the present time.

Scheme I



Our failure to observe rearrangement of the 1,1-deuterio-2-phenylethyl radical **12** in hexadecane at 423 K is consistent with Slaugh's report[42] that [1-^{14}C]-2-phenylethyl underwent ca. 2% rearrangement at this temperature. That is, our data indicate that the rate constant for this rearrangement (k_{13}) is $\leq$ ca. 10^3 s^{-1} at 423 K and so it is not surprising that the 2-phenylethyl rearrangement is not observable at ambient temperatures.[43] If we assume that the preexponential factor for reaction 13 is the same as that for the neophyl rearrangement, viz.,[10] $10^{10.75}$ s^{-1}, then E_9 will be ≥ 16.9 kcal/mol. This value is consistent with an estimate[46] that the $\mathbf{6} \xrightarrow{\varrho} \mathbf{5}$ reaction would be endothermic by ca. 17 kcal/mol.

Although the kinetic parameters for the $\mathbf{5} \xrightarrow{\varrho} \mathbf{6}$ rearrangement and the reverse process are none too reliable, we can, nevertheless, estimate that ΔH for this equilibrium must be ≥ 13 kcal/mol and that the equilibrium constant will be $\geq 10^9$ at 298 K. For the analogous, but very much more facile, cyclopropylcarbinyl ring opening and closing,[33] ΔH is only 3.2 kcal/mol and $K^{298\mathrm{K}} = 2.6 \times 10^4$. While the intermediate cyclopropylcarbinyls involved in 1,2-vinyl migrations have occasionally been trapped in low yield,[6,47] there would seem to be little or no hope of trapping, or otherwise identifying, spiro[2.5]octadienyl radicals during the neophyl rearrangement or the 1,2-phenyl migration. That such species are involved as genuine intermediates in these reactions is, unfortunately, not proved by the fact that one such species (**5**) is a genuine intermediate in another reaction.[48]

Experimental Section

Materials. Preparation of Spiro[2.5]octa-4,6-diene (4). This compound was prepared by the general route first described by de Meijere[17] (see Scheme I). Only improvements and a few notes on this preparation are described herein. Diethyl methylenemalonate[50] (**14**) [^{1}H NMR in $\mathrm{CDCl_3}$: δ 1.33 (6 H, t, $\mathrm{CH_3}$), 4.30 (4 H, q, $\mathrm{CH_2}$), 6.53 (2 H, s, $=\mathrm{CH_2}$)] should be used immediately as it polymerizes readily even at low temperatures. Diethyl 1-cycohexene-4,4-dicarboxylate[50] (**15**) [^{1}H NMR in $\mathrm{CDCl_3}$: δ 1.23 (6 H, t, $\mathrm{CH_3}$), 2.13 (4 H, br, $\mathrm{CH_2}$), 2.55 (2 H, br, $\mathrm{CH_2}$), 4.18 (4 H, q, $\mathrm{CH_2}$), 5.67 (2 H, br, $\mathrm{CH{=}CH}$)] was prepared from **14** and butadiene without solvent at room temperature. 4,4-Bis(hydroxymethyl)-1-cyclohexene (**16**) [^{1}H NMR in $\mathrm{CDCl_3}$: δ 1.53 (2 H, t, $\mathrm{CH_2}$), 1.65–2.15 (4 H, br, $\mathrm{CH_2}$), 2.85 (2 H, br, OH), 3.55 (4 H, s, $\mathrm{CH_2O}$), 5.58 (2 H, br, $\mathrm{CH{=}CH}$)] was prepared in 96% yield from **15** by a standard procedure[51] that is somewhat simpler than that originally used. 4,4-Bis[(mesyloxy)methyl]-1-cyclohexene (**17**) [^{1}H NMR in $\mathrm{CDCl_3}$: δ 1.60

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(36) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1979**, *101*, 4958.

(37) See, e.g.: Russell, G. A.; Malkus, H. *J. Am. Chem. Soc.* **1967**, *89*, 160. Stock, L. M.; Young, P. E. *Ibid.* **1972**, *94*, 7686. Davies, A. G.; Muggleton, B.; Godet, J.-Y.; Pereyre, M.; Pommier, J.-C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1719. Blum, P.; Davies, A. G.; Pereyre, M.; Ratier, M. *J. Chem. Soc., Chem. Commun.* **1976**, 814. Blum, P. M.; Davies, A. G.; Henderson, R. A. *Ibid.* **1978**, 569. Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1978**, *155*, 25. Blum, P. M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 217 and references cited.

(38) The allyl radical produced by addition to the 5-position should be capable of undergoing ring opening and the product radical, viz., $\mathrm{C_6H_5CH_2CH_2\overline{CHCH{=}CHCH{=}C(CH_2\dot{C}H_2)C}H_2}$, should continue the chain.

(39) As factors which *might* reduce A_2 below a "normal" value we note: (i) the freezing out in the transition state of the cyclohexadienyl ring vibrations, particularly the out-of-plane wagging of $\mathrm{C_1}$;[40] (ii) a possible requirement for localization of the unpaired electron at position 2 or 6; (iii) stereoelectronic effects arising from the specific orientational requirements of the bond to be cleaved and the semioccupied orbital[6b,41] in **5** which are due to the nonplanarity[40] of cyclohexadienyls.

(40) See, e.g.: Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 3892 and references cited.

(41) Suzuki, M.; Murahashi, S.-I.; Sonoda, A.; Moritani, I. *Chem. Lett.* **1974**, 267.

(42) Slaugh, L. H. *J. Am. Chem. Soc.* **1959**, *81*, 2262.

(43) An early claim for extensive rearrangement[44] has been shown[45] to be in error.

(44) Smith, W. B.; Anderson, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 656.

(45) Thornhill, D. P.; Lee, C. C. *Can. J. Chem.* **1963**, *41*, 2861.

(46) Walsh, R., private communication.

(47) Montgomery, L. K.; Matt, J. W.; Webster, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 923.

(48) It should not be forgotten that the 1,2-acyloxy migration involved in the rearrangement, $\mathrm{Me_2C(OAc)\dot{C}H_2} \xrightarrow{\varrho} \mathrm{Me_2\dot{C}CH_2OAc}$, does not occur via the cyclized radical, $\mathrm{\overline{OCH_2CMe_2O\dot{C}}Me}$.[49]

(49) Beckwith, A. L. J.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 2* **1973**, 861.

(50) Bachman, G. B.; Tanner, H. A. *J. Org. Chem.* **1939**, *4*, 493.

(51) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967, p 584.

(2 H, t, CH_2), 1.96 (4 H, br, CH_2), 3.03 (6 H, s, SCH_3), 4.63 (4 H, s, OCH_2), 5.63 (2 H, br, CH=CH)] was prepared by a modified (longer reaction time, products poured into ice/HCl) literature procedure[52] in 95% yield after recrystallization from MeOH/water (mp 77.5 °C). The reported[17] synthesis of the ditosylate gave only a 35% yield of pure product. 4,4-Bis(bromomethyl)-1-cyclohexene (**18**) [^{1}H NMR][17] was prepared in 90% yield according to a literature method.[53] Anal. Calcd for $C_8H_{12}Br_2$: C, 35.82, H, 4.47; Br, 59.70. Found; C, 35.61; H, 4.69; Br, 59.38. Spiro[2.5]oct-5-ene (**17**) and spiro[2.5]octa-4,6-diene (**4**) were prepared by de Meijere's route[17] and in similar yields. The diene **4** was purified by preparative VPC (with considerable loss) at 100 °C on a 10 ft × $^3/_8$ in. aluminum column packed with 30% carbowax 20 M on chromosorb "W" (40–60 mesh), high performance, acid washed, and dimethylchlorosilane treated.

1,1-Dideuterio-2-phenylethyl bromide was prepared from phenylacetic acid by a literature procedure.[54] All other materials were commercial products.

EPR Spectroscopy. All work was carried out on a Varian E-104 EPR spectrometer with degassed samples. In the laser experiments the light from a Molectron UV-24 nitrogen laser was concentrated but not focussed on the cavity with a quartz lens. Since the beam issuing from the laser has a rectangular cross section with the long axis horizontal, it was first rotated through 90° with two mirrors, so as to put the long axis vertical, thus lighting the sample uniformily. The buildup and decay of **6** after a laser pulse was monitored by terminating the unfiltered but modulated (standard 100-KHz EPR modulation) EPR output into 5000 Ω and into a Nicolet 1170 signal averager. Typically, the signals from 500 laser shots were averaged, giving virtually noise-free traces. The lifetimes could be reproduced to better than ±2%.

Laser Flash Photolysis. To measure the rates of H atoms abstraction, we used a Molectron UV-400 nitrogen laser providing pulses (8 ns, ~3 mJ) at 337.1 nm. The experimental system has been described previously.[55]

The experiments leading to the data in Figures 2 and 3 were carried out by using a frequency doubled ruby laser for excitation. The instrument has been described.[20,21] The monitoring system consists of a pulsed xenon lamp, a monochromator, and an RCA-4840 photomultiplier tube. All samples were deoxygenated by bubbling with oxygen-free argon.

Laser Fluorescence. The experimental system, which has been previously described,[27] makes use of a Molectron DL-300 dye laser pumped by a UV-1000 nitrogen laser for excitation.

Acknowledgments. We are extremely grateful to Professor A. de Meijere for the samples of his spiro[2.5]octa-4,6-diene which got the present work underway. We should also like to thank Dr. R. D. Small, Jr., for his involvement in some of the preliminary laser flash experiments, Dr. J. K. Thomas for the use of his ruby laser system, and Dr. R. Walsh for communicating to us the results of his calculations and for acting as liaison officer.

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(52) Buchta, E.; Kröniger, A. *Chimia* **1968**, *22*, 430.

(53) Buchta, E.; Kröniger, A. *Chimia* **1969**, *23*, 225.

(54) Schmid, P.; Bourns, A. N. *Can. J. Chem.* **1975**, *53*, 3513.

(55) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146.

Low-Lying Electronically Excited States of Cycl[3.3.3]azine, a Bridged 12π-Perimeter[1]

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Contribution from the Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland. *Received March 17, 1980*

Abstract: The previously unnoticed, symmetry-forbidden transition to the lowest excited singlet state S_1 of cycl[3.3.3]azine (**1**) occurs in the near infrared (0.78 μm^{-1}) and the position of this absorption band is very sensitive to inductive perturbations. In a series of aza-substituted derivatives of **1** this band is progressively shifted throughout the visible into the ultraviolet region. The energy difference between the lowest excited singlet and triplet states, S_1 (**1**) and T_1 (**1**), is small and probably negative in violation of Hund's rule. Excitation of **1** to upper excited singlet states gives rise to a moderately intense fluorescence from the degenerate second excited state S_2 ($\phi_f = 3 \times 10^{-3}$). The low-lying electronic states of **1** are described in terms of a simple MO model. Since the frontier orbitals of **1** are localized on two different, alternantly connected sets of atoms, the electronic excitation of **1** is accompanied by a profound redistribution of charge. The concomitant changes in electronic repulsion need to be considered explicitly, at least in a qualitative manner, in order to account for the unusual energetic spacing of the lower electronic states.

Introduction

The synthesis of cycl[3.3.3]azine[2] (**1**) was achieved over 10 years ago by Farquhar and Leaver[3] after a series of unsuccessful attempts by various groups.[2b] In contrast to previous theoretical predictions,[2a,4] **1** was found to be a highly reactive compound, exhibiting a strong paratropic shift in the ^{1}H NMR signals[3,5] and a high propensity toward both oxidation[3,6,7] and reduction.[6] Such properties are characteristic for compounds with a small energy gap between the frontier orbitals (i.e., biradicaloids[8]). Indeed, Dewar and Trinajstić[9] have advanced a simple and convincing

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* Dedicated to the memory of Professor Dr. E. Hueckel.

(1) Presented in part at the Swiss Chemical Society Meeting, Bern, Oct 19, 1979, and at the Pacific Conference on Chemistry and Spectroscopy, Pasadena, Calif., Oct 12, 1979 (W. Leupin and J. Wirz, Proceedings of the Pacific Conference on Chemistry and Spectroscopy, Pasadena, Calif., 1979, Abstract No. 235).

(2) (a) IUPAC nomenclature: pyrido[2,1,6-*de*]quinolizine. The cyclazine nomenclature was introduced by R. J. Windgassen, Jr., W. H. Saunders, and V. Boekelheide, *J. Am. Chem. Soc.*, **81**, 1459–1465 (1959). (b) For recent reviews on cyclazine chemistry see A. Taurin, *Chem. Heterocycl. Compd.*, **30**, 245–270 (1977); W. Flitsch and U. Krämer, *Adv. Heterocycl. Chem.*, **22**, 321–365 (1978).

(3) D. Farquhar and D. Leaver, *Chem. Commun.*, 24–25 (1969); D. Farquhar, T. T. Gough, and D. Leaver, *J. Chem. Soc., Perkin Trans. 1*, 341–355 (1976).

(4) R. D. Brown and B. A. W. Coller, *Mol. Phys.*, **2**, 158–168 (1959).

(5) R. C. Haddon, *Tetrahedron*, **28**, 3613–3633, 3635–3655 (1972).

(6) F. Gerson, J. Jachimowicz, and D. Leaver, *J. Am. Chem. Soc.*, **95**, 6702–6708 (1973).

(7) M. H. Palmer, D. Leaver, J. D. Nesbet, R. W. Millar, and R. Egdell, *J. Mol. Struct.*, **42**, 85–101 (1977).

(8) The designation *biradicaloid* asserts that a given molecular structure has, in the MO description, two approximately nonbonding orbitals occupied by a total of two electrons, regardless of the prevailing electronic configuration(s) in the ground state. J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **95**, 7391–7401 (1973).

(9) M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. A*, 1754–1755 (1969).

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