5536 (1970).
(2) Graduate assistant on grants (G 19878 and GP 6492X) provided by the National Science Foundation.
(3) E. Vogelfanger, Ph.D. Thesis, University of California, Los Angeles, CA, 1963.
(4) S. J. Cristol, et. al., *J. Org. Chem.*, **31**, 2719, 2726, 2733 (1966); **33**, 106 (1968).
(5) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966); S. J. Cristol and J. M. Sullivan, *J. Am. Chem. Soc.*, **93**, 1967 (1971).
(6) F. K. Fong, *J. Am. Chem. Soc.*, **96**, 7638 (1974).
(7) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **97**, 600 (1975).
(8) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **97**, 2469 (1975).
(9) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969).
(10) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **92**, 201 (1970); H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970); H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971).
(11) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Am. Chem. Soc.*, **95**, 2209 (1973).
(12) Dr. Charles B. Schewene carried out independent analyses at the University of Wisconsin. Excellent agreement was realized between the two sets of analyses. We are grateful for his generous assistance.
(13) Cf. H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965).
(14) Cf. A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965).
(15) No correction was made for the 97% isotopic purity of the perdeuterioacetic acid.
(16) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **95**, 8665 (1973).
(17) Both signals are separated from others at 100 MHz. We are grateful to Professor L. M. Stock of the University of Chicago for providing the use of the Varian HA-100 spectrometer for this study and to Dr. K.-T. Liu for the spectra and interpretation.
(18) S. Winstein, et. al., *J. Am. Chem. Soc.*, **87**, 376 (1965).
(19) For a review of the question of the structure of the 2-norbornyl cation under solvolytic conditions with pertinent references, see H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973).
(20) Actually, some six different nonclassical structures for the 2-norbornyl cation, all with a plane of symmetry, have now been proposed (ref 7).
(21) Only the reaction of 7,7-dimethylnorbornene with diimide represents an exception to this generalization (ref 11).
(22) No exception to this effect of the 7,7-dimethyl substituents on the relative rates of exo addition for cyclic processes has yet been encountered.
(23) G. D. Sargent, "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., Chapter 24.
(24) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).
(25) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).
(26) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).
(27) J. K. Stille and R. D. Hughes, *J. Org. Chem.*, **36**, 340 (1971).
(28) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **92**, 1990 (1970).
(29) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **92**, 6914 (1970).
(30) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Am. Chem. Soc.*, **92**, 1760 (1970).
(31) D. G. Farnum and G. Mehta, *J. Am. Chem. Soc.*, **91**, 3256 (1969).
(32) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).
(33) M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).
(34) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973).
(35) G. Kramer, *Adv. Phys. Org. Chem.*, in press.
(36) P. v. R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).
(37) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970).

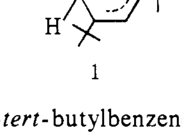
Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XIX. Persistent Cyclohexadienyls and Related Radicals[1]

D. Griller,[2] K. Dimroth,[3] T. M. Fyles,[4] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR9. *Received January 20, 1975*

Abstract: A variety of persistent radicals of the cyclohexadienyl type have been generated by the addition of certain carbon, silicon, oxygen, and phosphorus centered radicals (e.g., $\dot{C}F_3$, $Cl_3Si\cdot$, $Me_3CO\cdot$, $(CH_3CH_2O)_2\dot{P}{=}O$) to the following sterically hindered aromatic compounds: 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butyl-λ^3-phosphorin, 1,3-di-*tert*-butylbenzene, and 2,6-di-*tert*-butylpyridine. The structures of the radicals, which have been deduced from their epr spectra, should assist in the identification of more transient cyclohexadienyls. It is shown that persistence is a consequence of steric protection of the reactive sites in these radicals. Kinetics for decay of some of the radicals are reported.

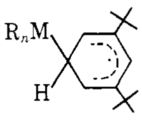
We have recently emphasized the dominant role that steric factors play in determining the persistence (i.e., the lifetime) of carbon-centered free radicals in solution.[1,5,6] Our success in generating persistent secondary and tertiary alkyls,[1,7,8] α-aminoalkyls,[9] phenyls,[10] vinyls,[1,11] and allyls,[1] together with Berndt's preparation of a persistent benzyl[12] and a persistent allyl,[13] led us to extend our experiments to cyclohexadienyls and related radicals. These species are of great interest as they are formed as intermediates in all homolytic aromatic substitutions.[14] Thermodynamically, cyclohexadienyls are strongly stabilized,[15] but simple cyclohexadienyls are nevertheless very transient radicals which normally decay by bimolecular processes at, or near, the diffusion-controlled limit.[17] It was our expectation that addition of a radical, $\cdot MR_n$, to a sterically hindered aromatic such as 1,3,5-tri-*tert*-butylbenzene would produce a persistent, stabilized,[18] cyclohexadienyl (**1**) since there would be no easy route open for this radical to decay, provided the addition of $\cdot MR_n$ was irreversible. Thus, a radical of type **1** should be too hindered to dimerize or disproportionate.



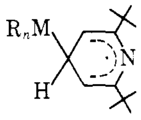
1

Unfortunately, tri-*tert*-butylbenzene is so hindered that a persistent radical (**1**) was only obtained with $MR_n = C_6F_5$. Extension of our experiments to 2,4,6-tri-*tert*-butylpyridine yielded only the 1-trichlorosilyl adduct. However, with 2,4,6-tri-*tert*-butyl-λ^3-phosphorin,[19] several persistent radicals of the cyclohexadienyl type were produced by the addition of various $\cdot MR_n$ to the phosphorus. Similar radicals were produced from 2,4,6-triphenyl-λ^3-phosphorin.[19]

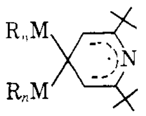
Cyclohexadienyl and cyclohexadienyl type radicals were also produced by $\cdot MR_n$ additions to 1,3-di-*tert*-butylbenzene and 2,6-di-*tert*-butylpyridine. (The corresponding phosphorin is not available.) As well as the expected adducts, viz., **2** and **3**, which are relatively short lived, some extremely persistent radicals having structures such as **4**



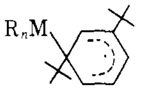
2



3



4



5

and **5** were also formed. In this paper, we report EPR parameters and some kinetic data on various radicals of the types described.

Experimental Section

Our general technique has been adequately described in previous papers.[1,5-11] The two phosphorins were prepared by literature methods.[19] All other compounds were commercial materials that, when necessary, were purified before use.

Attempts were made to add to each of the hindered aromatic compounds most of the following $\cdot MR_n$ radicals: $Me_3Si\cdot$, $Cl_3Si\cdot$, $(EtO)_2\dot{P}{=}O$, $\dot{P}(\overline{OCH_2CH_2O})_2$, $\dot{C}_6H_5$, $\dot{C}_6F_5$, $Me_3\dot{C}$, $\dot{C}F_3$, $\dot{C}Cl_3$, $Me_3CO\cdot$, $CF_3O\cdot$, and $CF_3S\cdot$. Many persistent radicals were obtained that could not be identified, frequently because there were two or more present in the solution. When the lifetimes of these various radicals were substantially different, it was often possible to obtain a "clean" spectrum of the most persistent radical by storage of the sample for a few days at room temperature. However, in many cases the lifetimes of the different radicals were sufficiently long or sufficiently similar that storage did not simplify the spectra. In this paper, we have restricted ourselves largely to radicals with structures that can be unequivocally deduced from the EPR spectrum. All spectra were recorded at room temperature.

The frequent formation of two or more radicals in these systems made kinetic studies of the decay of most of the radicals difficult or impossible. For this reason, most of the kinetic data in this paper are restricted to qualitative observations of radical lifetimes at room temperature.

Results and Discussion

Radicals from 1,3,5-Tri-*tert*-butylbenzene. The adduct with C_6F_5 persisted for days at room temperature. Its EPR spectrum was very complex, consisting of a doublet (24.3 G) of multiplets, each multiplet consisting of over 120 well-resolved lines (splitting ~0.14 G) in nine or more groups. We believe this radical probably has structure **1** ($MR_n = C_6F_5$), the small hyperfine splitting coming from the *tert*-butyl groups and/or the fluorine atoms. The 24.3 G splitting must be due to the hydrogen on the carbon to which the C_6F_5 group is attached. This splitting is considerably smaller than that from the analogous hydrogens in cyclohexadienyl (viz.,[20] 47.71 G) and in most ring-substituted cyclohexadienyls[21] (e.g.,[21a] 36.0 G for the OH adduct to benzene). Whatever the origin of these splittings,[22] it seems certain that any distortion of the cyclohexadienyl ring which brings the unique hydrogen more nearly into the plane of ring (i.e., into the nodal plane of the radical) will reduce a^H. In the present radical, such distortion is likely because of steric hindrance between the C_6F_5 group and the adjacent *tert*-butyls.[23]

The $Me_3CO\cdot$ radical removed a hydrogen from one of the *tert*-butyl groups to give the 3,5-di-*tert*-butylneophyl radical.[10]

Radicals from 2,4,6-Tri-*tert*-butylpyridine. The $\cdot SiCl_3$ radical added to the nitrogen to give a relatively short-lived azacyclohexadienyl (pyridinyl)[24] radical (**8**). The EPR parameters are similar to those reported for analogous radicals[24-29] (see Table I).

Radicals from 2,4,6-Tri-*tert*-butyl-λ^3-phosphorin. The radicals and their EPR spectral parameters are listed in Table II, together with data on two radicals from triphenylphosphorin. Despite the immense variation in a^P for these radicals, we *tentatively* suggest that they are all of the cyclohexadienyl type with the MR_n group attached to the phosphorus. Our reasons for this suggestion are outlined below.

We have shown previously[1,30] that all $(Me_3C)_2\dot{C}CH_2MR_n$ radicals have their MR_n groups in the eclipsed position with respect to the orbital occupied by the unpaired electron. Since these radicals are isostructural, the *principal* factor that determines the magnitude of a^{HCH_2} is the electronic effect of MR_n. We find that a^{HCH_2} decreases as MR_n becomes more electron withdrawing, presumably because it becomes more difficult for spin to get to the methylene hydrogens. However, if spin is removed from these hydrogens by the electronic effect of MR_n, it will also change on the methylene carbon (i.e., $a^{^{13}CCH_2}$ should be directly proportional to a^{HCH_2})[40]. A similar effect should operate in other radicals of similar structure. Figure 1 shows that the changes in a^P for the tri-*tert*-butylphosphorin adducts are linearly related to the changes in a^{HCH_2} in the $(Me_3C)_2\dot{C}CH_2MR_n$ radicals. This implies that the changes in a^P are due mainly to the varying electronic effects of MR_n and hence that all the phosphorin adducts are *isostructural.*

All the MR_n groups must be attached to the phosphorus atom since this is specifically indicated for the $SiCl_3$ adduct. This radical (i.e., **13**) can be compared with the $SiCl_3$ adduct with tri-*tert*-butylpyridine (i.e., **8**), which certainly has $SiCl_3$ on the nitrogen. The ratio $a^P/a^N = 34.34/5.04 = 6.81$, which is almost identical with the ratio of the calculated isotropic hyperfine couplings, $A_0{}^P/A_0{}^N$, viz.,[31] 10,178/1540 = 6.61. This must mean that **13** and **8** are isostructural. Therefore all the tri-*tert*-butylphosphorin adducts probably have the structures indicated with MR_n on the phosphorus. We presume that the two adducts to triphenylphosphorin (**15** and **16**) are of similar structure despite the notable difference in a^P values between **11** and **15.**

Not all the phosphacyclohexadienyl radicals listed in Table II were formed "cleanly". For example, addition of tri-*tert*-butylphosphorin to di-*tert*-butyl peroxide gave, even before photolysis, a weak signal due to a radical (**17**) with $g = 2.0025$, $a^P = 27.96$, $a^H(2H) = 3.06$ G with some partly

Table I. EPR Parameters for Some N-Substituted Azacyclohexadienyl Radicals (Hyperfine Couplings are in Gauss)

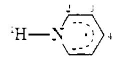
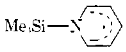
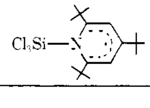
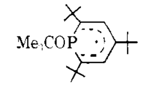
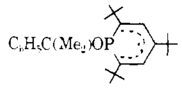
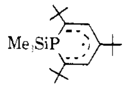
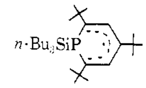
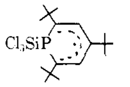
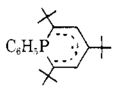
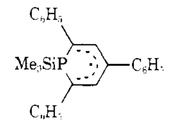
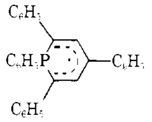
	Radical	g	a^N	a^{H_1}	a^{H_2}	a^{H_3}	a^{H_4}	Ref
(6)		2.0029	5.93	3.44	5.93	0.88	11.55	29
(7)		2.0037	4.2		6.26	1.38	11.5	27
(8)		2.0030	5.04			1.46		This work

Table II. EPR Parameters and Decay Rate Constants for Radicals Derived from Phosphorins at 24° (Hyperfine Couplings in Gauss)

	Radical	g	$a^{31}P^{a}$	a^{H}(2H)	a^{other}
(9)		2.0023	175.93	4.38	
(10)		2.0023	186.90	4.33	
(11)		2.0030	14.32	4.10	b
(12)		2.0030	16.84	4.43	$a^{29}Si = 42.32$
(13)		2.0038	34.34	c	$a^{29}Si = 62.95; d$
(14)		2.0027	70.28	2.89	$a^{13}C(1C) = 35.70$
(15)		2.0032	46.13	c	$a^{29}Si = 35.30; e$
(16)		2.0028	79.47	c	

[a] These parameters were determined using the measured line positions and the microwave frequency in conjunction with the Breit–Rabi formula. P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967, p 238. [b] Coupling due to ^{29}Si could not be identified because of the presence of other radicals in low concentration. [c] Not resolved. [d] Additional hyperfine structure with spacings of 1.94 and 0.2 G on main lines of spectrum. [e] Additional hyperfine structure with a spacing of 0.5 G on main lines of spectrum.

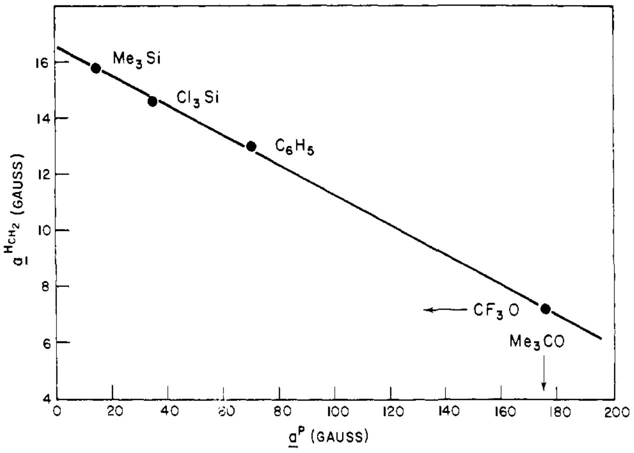
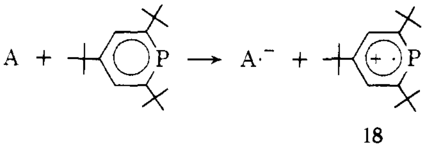


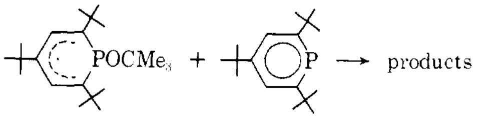
Figure 1. Plot of a^{HCH_2} for $(Me_3C)_2\dot{C}CH_2MR_n$ against a^P for **9**, **11**, **13**, and **14**. Note that $Me_3CO\cdot$ did not add to $(Me_3C)_2C{=}CH_2$ and no adduct of $CF_3O\cdot$ and the phosphorin could be obtained because of a direct thermal reaction of the phosphorin with CF_3OOCF_3.

resolved hyperfine lines (~0.40). The concentration of **17** was increased somewhat by photolysis, but the amount of **9** formed was at least ten times as great. Radical **17** does not appear to be the cation radical, **18** (a^P = 26.9, a^H(2H) = 2.9)[19,32] formed by some electron transfer since the g value for authentic **18** is 2.00218.[33] It seems unlikely that **17** is formed by the prior oxidation of some of the phosphorin in the air. Thus, no EPR signal was produced when oxygen was bubbled into a solution of the phosphorin in di-*tert*-butyl peroxide. Upon irradiation of this solution, both **9** and **17** were formed in about the same ratio as in the absence of oxygen but were rather quickly destroyed. A solution of the phosphorin in toluene containing di-*tert*-butyl hyponitrite gave somewhat more **17** than **9** without photolysis at room temperature but, on warming to 50°, the concentration of **9** increased markedly while the concentration of **17** decreased slightly. The structure of **17** remains a mystery.



18

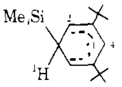
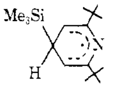
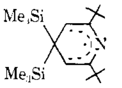
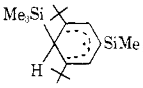
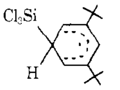
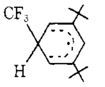
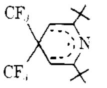
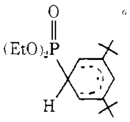
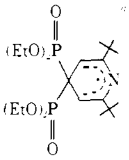
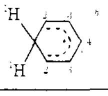
Radical **9** builds up immediately once photolysis is started. There is no sign of any induction period, and so **9** must be formed in some "primary" process as is implied by its proposed structure. Two of the more interesting features of **9** are its blue color [λ_{max} 590 nm (ϵ 7.4 × 10^2)][34] and its decay with pseudo-first-order kinetics. The first-order rate constant for decay (measured both by EPR spectroscopy and by monitoring the decrease in the 590-nm absorption band) was directly proportional to the initial concentration of the phosphorin, which indicates that decay actually occurs by the bimolecular process:



At 24° in di-*tert*-butyl peroxide, the rate constant for this reaction is 0.14 M^{-1} sec^{-1}.

Kinetic studies on the other radicals in Table II were not undertaken because of the formation of various unknown

Table III. EPR Parameters for "Symmetric" Cyclohexadienyl and Azacyclohexadienyl Radicals at 24° (Hyperfine Couplings are in Gauss)

	Radical	g	a^{H_1}	a^{H_2}	a^{H_3}	a^{H_4}	a^N	a^{other}
(19)		2.0028	34.60	8.06		12.29		
(20)		2.0033	39.83	8.08			6.90	
(21)		2.0032		7.65			6.80	a^{29Si}(2Si) = 21.3
(22)	 [a]	2.0024	6.00		2.96			
(23)		2.0032	21.62	5.12		9.20		a^{29Si} = 43.0
(24)		2.0029	42.71	8.74		13.65		
(25)		2.0024		6.75			7.85	a^H or F (many nuclei) ~0.25
(26)	 [a]	2.0029	41.73	8.65		12.84		a^P = 114.27
(27)	 [a]	2.0030		10.71			4.43	a^P(2P) = 55.6
(28)	 [b]	2.0025	47.71	8.99	2.65	13.04		

[a] Tentative identification, see text. [b] From ref 20, see also ref 21d and 21k.

radicals which build up rather quickly when photolysis was carried out for more than a minute or two. Qualitatively we may note that at least some of the radicals decay with second-order kinetics. Thus, at 24° the rate constants for decay of **12** and **13** are both ca. 10^4 M^{-1} sec^{-1} ($\tau_{1/2} \sim 1$ min under our experimental conditions). Radicals **11** and **14** were appreciably longer lived under the same conditions.

"Symmetric" Radicals from 1,3-Di-*tert*-butylbenzene and 2,6-Di-*tert*-butylpyridine. The problem with both these aromatics was that, when the $\cdot MR_n$ did add to them, there was a tendency to add to at least two positions in the ring. In some reaction systems not less than three radicals were formed, and their identification was always difficult and often impossible.

The most readily identifiable cyclohexadienyls were those in which one, or occasionally two, $\cdot MR_n$ had added to the position meta to both *tert*-butyl groups, thus producing "symmetric" cyclohexadienyl radicals, such as **2, 3,** and **4**. These radicals almost always have sharp EPR spectral lines. They show a characteristic EPR spectral pattern and have a^H values very similar to those that have been reported for cyclohexadienyl itself (**28**)[20] and for various ring-substituted cyclohexadienyls[21] (see Table III). The radicals with a single MR_n substituent (i.e., **2** and **3**) were relatively short-lived and, to be observed, the sample had to be photolyzed continuously. However, the radicals with two MR_n substituents were quite persistent. They were normally generated by prolonged photolysis but, once formed, could often be readily observed after the light was cut off. For example, radical **21** decayed with first-order kinetics and with a rate constant of ca. 3×10^{-4} sec^{-1} at 24° ($\tau_{1/2} \sim 35$ min), and radical **27** did not decay appreciably in 4 or 5 days. If photolysis of the sample was fairly brief, storage for several days to destroy "transient" radicals yielded "clean" EPR spectra of the extremely persistent "asymmetric" cyclohexadienyls that are discussed in the following section.

Some of the structural assignments in Table III raise a few questions. For instance, while the low value of a^{H_1} for **22** can be attributed to steric factors (see above discussion of **1**, $MR_n = C_6F_5$), it is not clear why **22** was formed rather than a structure analogous to **21**, nor is it obvious why a radical analogous to **22** was not formed with tri-*tert*-butylbenzene. Both **21** and **22** are presumably formed by oxidation of the mono-adduct to a trisubstituted aromatic, followed by addition of the second $Me_3Si\cdot$ radical.

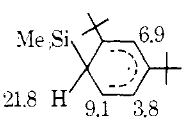
Radical **23** was the most persistent cyclohexadienyl of type **2** or **3**, decaying with first-order kinetics and with a rate constant at 24° of 1.8×10^{-3} sec^{-1}. Prolonged photolysis of the reaction mixture does not give a recognizable di-adduct.

With MR_n = CF_3, di-*tert*-butylbenzene gave the mono-adduct **24**, and di-*tert*-butyl pyridine the di-adduct **25.** All attempts to observe the mono-adduct with the pyridine were unsuccessful. However, the benzene did give an extremely persistent second radical ($\tau_{1/2}$ of several hours), the EPR spectrum of which consists of a 1:2:1 triplet of broad, overlapping lines (coupling 10.6 G) which, at low modulations, can be resolved into more than 146 lines with a hyperfine coupling of ~0.3 G.

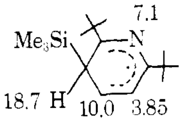
With MR_n = $(EtO)_2P{=}O$ in the benzene, radical **26** was identified in a spectrum containing at least two other radicals by the sharpness of its lines and its transience. On turning off the light, **26** decayed and there was left an extremely persistent radical, the EPR spectrum of which could be *approximately* simulated with $a^H(1H) \sim 3.8$, $a^H(2H) \sim 10.8$, and $a^P(2P) = 58.5$. However, there were unexplained features in the spectrum since the simulation required a line width some three times greater than that indicated by the experimental spectra. This radical is mentioned only because it serves to emphasize the intriguing difference between the a^P values for the mono-adduct to the benzene **26**,[35] and the di-adduct to the pyridine **27.** Since we can think of no explanation for this large change in a^P, we have listed both **26** and **27** as "tentatively" identified. The radical **27** is extremely persistent—an excellent spectrum being obtained by storing a photolyzed sample for 4 days. This allowed a more plentiful but unidentified radical (g = 2.0024, four-spin ½ nuclei with couplings of 14.68, 17.68, 23.02, and 58.07 G) to decay.

Reaction of 1,3-di-*tert*-butylbenzene with *tert*-butoxy radicals at room temperature gives the unrearranged primary alkyl radical, 3-*tert*-butylneophyl. In contrast, 2,6-di-*tert*-butylpyridine gives the rearranged tertiary alkyl radical, 2-methyl-2(6′-*tert*-butyl-2′-picolinyl)ethyl.[36]

"Asymmetric" Radicals from 1,3-Di-*tert*-butylbenzene and 2,6-Di-*tert*-butylpyridine. If the light is cut off after a few minutes photolysis of solutions of the benzene in di-*tert*-butyl peroxide containing trimethylsilane a very persistent radical (**29**) is readily observed since it takes days to decay. The same phenomenon is observed with the pyridine. The EPR spectra of the two radicals **29** and **30** are generally similar and are characterized by fairly broad lines. The radical from the benzene (g = 2.0026) can be analyzed in terms of four nonequivalent hydrogens and that from the pyridine (g = 2.0023) in terms of three nonequivalent hydrogens and a nitrogen. If we assume that the radicals retain the six-membered ring,[37] they can only be "asymmetric" cyclohexadienyls having either structure A or B (a^H and a^N values are in Gauss).

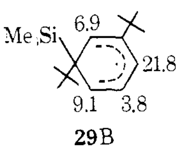


29A

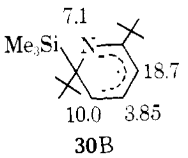


30A

There are problems with either structural assignment. We favor B since an a^N = 7.1 G is much easier to believe for **30B**[38] than for **30**A and, for **29**, an a^{H_2} = 6.9 (**29B**)[39] is easier to believe than a^{H_3} = 6.9 (**29A**). However, the B structures leave unexplained the large magnitude of a^{H_4} (which is a perfectly reasonable a^{H_1} value in the A structures). If the B structures are correct, these radicals must be distorted from the usual cyclohexadienyl geometry.



29B



30B

Summary

Radical additions to *tert*-butyl substituted aromatics have yielded a number of unequivocally identified, sterically hindered, cyclohexadienyl, azacyclohexadienyl, and phosphacyclohexadienyl radicals, some of which are extremely persistent. The EPR parameters of these radicals should prove useful in identifying quite a wide variety of transient cyclohexadienyls derived from less hindered aromatic compounds. Unfortunately, rather few systems gave "clean" EPR spectra and so meaningful kinetic studies covering a significant range of radical structures were impracticable. Our initial hopes of assisting in the solution of some of the many kinetic problems that are still unanswered in the chemistry of homolytic aromatic substitutions[14] have not been realized.[40]

References and Notes

(1) Issued as NRCC No. 1.4876. Part XVIII: D. Griller, J. W. Cooper, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 4269 (1975).

(2) NRCC Postdoctorate Fellow 1973–1975.

(3) Fachbereich Chemie der Phillipps-Universität, Marburg, West Germany.

(4) NRCC Summer Student 1974.

(5) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, in press.

(6) G. D. Mendenhall, D. Griller, and K. U. Ingold, *Chem. Br.*, **10**, 248 (1974).

(7) G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 2441 (1974).

(8) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6203 (1974).

(9) R. A. Kaba, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6202 (1974).

(10) L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 3011 (1974).

(11) J. W. Cooper, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 233 (1975).

(12) K. Schreiner and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **13**, 144 (1974).

(13) H. Regenstein and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **13**, 145 (1974).

(14) See, e.g., G. H. Williams, "Homolytic Aromatic Substitution", Pergamon Press, Oxford, 1960; Intra-Science Symposium, "Free Radical Aromatic Substitutions and other Selected Free Radical Reactions", N. Kharasch, Ed., *Intra-Sci. Chem. Rep.*, **3**, 167–301 (1969); M. J. Perkins in "Free Radicals", Vol. II., J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 16; D. C. Nonhebel and J. C. Walton, "Free Radical Chemistry", Cambridge University Press, Cambridge, 1974, Chapter 11; R. A. Jackson, *J. Chem. Soc., Chem Commun.*, 573 (1974).

(15) The stabilization energy, defined as $D[c\text{-}C_6H_{11}\text{-}H] - D[c\text{-}C_6H_7\text{-}H]$ [see: S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968; D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969)], for cyclohexadiene is ~24–25 kcal/mol.[16]

(16) See, e.g., K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966); D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **64**, 2752 (1968).

(17) See, e.g., M. C. Sauer, Jr., and B. Ward, *J. Phys. Chem.*, **71**, 3971 (1967); R. Wander, P. Neta, and L. M. Dorfman, *ibid.*, **72**, 2946 (1968).

(18) In gaining persistence, such radicals should not lose their stabilization.[5] This contrasts with the behavior of allyls[1,5] and benzyls.[5]

(19) K. Dimroth, *Fortschr. Chem. Forsch.*, **38**, 1 (1973).

(20) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963); **39**, 2147 (1963).

(21) See, e.g.; (a) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964); (b) C. R. E. Jefcoate and R. O. C. Norman, *J. Chem. Soc. B*, **48** (1968); (c) G. A. Helcké and R. Fantechi, *Mol. Phys.*, **17**, 65 (1969); **22**, 737 (1971); (d) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **75**, 1186 (1971); (e) S. DiGregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.*, **95**, 8455 (1973); (f) S. P. Mishra and M. C. R. Symons, *Tetrahedron Lett.*, 4061 (1973); (g) J. Edwards, D. J. Hills, S. P. Mishra, and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 556 (1974); (h) G. Filby and K. Gunther, *J. Phys. Chem.*, **78**, 1521 (1974); (i) T. Shiga, T. Kishimoto, and E. Tomita, *ibid.*, **77**, 330 (1973); (j) G. Filby and K. Gunther, *J. Chem. Phys.*, **60**, 3355 (1974); (k) K. Eiben and R. H. Schuler, *ibid.*, in press.

(22) For speculation on this point, see e.g., H. Fischer, *J. Chem. Phys.*, **37**, 1094 (1962); J. P. Colpa and E. DeBoer, *Mol. Phys.*, **7**, 333 (1964); C. Corvaja and G. Giacometti, *Theor. Chim. Acta*, **14**, 352 (1969).

(23) A much more pronounced example of this effect can be seen in radical **22.**

(24) E. M. Kosower and A. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963); **86**, 5515 (1964).

(25) M. Itoh and S. Nagakura, *Tetrahedron Lett.*, 417 (1965); *Bull. Chem. Soc. Jpn.*, **39**, 369 (1966).

(26) C. Chachaty and A. Forchioni, *C.R. Acad. Sci., Ser. C*, **264**, 1421 (1967).

(27) B Schroeder, W. P. Neumann, J. Hollaender, and H. P. Becker, *Angew.*

Chem., Int. Ed. Engl., **11**, 850 (1972).
(28) H. Zeldes and R. Livingston, *J. Phys. Chem.*, **76**, 3348 (1972); **77**, 2076 (1973).
(29) R. W. Fessenden and P. Neta, *Chem. Phys. Lett.*, **18**, 14 (1973).
(30) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6715 (1974).
(31) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, N.Y., 1972.
(32) The coupling constants appear to depend to a slight extent on the conditions used to prepare **18**.[33] We have prepared a radical we believe to be **18** ($g = 2.00219$, $a^{P} = 27.21$, $a^{H}(2H) = 3.01$) under conditions as close as possible to those used to produce **9**, viz., addition of a trace of Me_3COOH to a solution of the phosphorin in the peroxide and photolysis.
(33) K. Dimroth and H. Weber, unpublished results.
(34) For comparison, cyclohexadienyl itself has two "relatively weak" absorption bands at 512 and 554 nm: J. E. Jordan, D. W. Pratt, and D. E. Wood, *J. Am. Chem. Soc.*, **96**, 5588 (1974).
(35) Phosphorus couplings of ~200 and ~133 G have been reported for analogous radicals.[21f]
(36) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, in press.
(37) For an example of a rearranged adduct to pyridine, see: C. Chachaty, J. C. Ronfard-Haret, A. Lablache-Combier, J. P. Quazebeur, and H. Ofenberg, *J. Chem. Soc., Chem. Commun.*, 579 (1974).
(38) The H atom adduct to pyridine with the B structure has $a^{N} = 5.1$ G.[21e] The A structure OH adducts to three pyridinecarboxylic acids have $a^{N} = 2.8$–3.4 G.[21l]
(39) In **29**B $(a^{H_2} + a^{H_6})/2 = 8.0 = a^{H_2}$ in **19**.
(40) Note Added in Proof. $a^{^{13}CCH_2}$ is not linearly related to a^{HCH_2} in these radicals: J. C. Scaiano and K. U. Ingold, unpublished results.

Kinetics of Degenerate Solvolysis. Reaction of Covalent Amino Adducts of Heteroaromatic Compounds in Liquid Ammonia

John A. Zoltewicz* and John K. O'Halloran

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received June 26, 1975*

Abstract: Ammonium ion catalyzed solvolysis of covalent complexes formed by the addition of ammonia to quaternized heteroaromatic compounds in liquid ammonia was studied by NMR. Rates of turnover of the amino group were obtained at coalescence of the signals for the diastereotopic *N*-benzyl protons as a function of ammonium salt concentration. By means of Arrhenius plots it was possible to relate reactivities to a common temperature and to obtain relative rates. Relative rates for a series of 5-substituted 1-amino-2-benzyl-1,2-dihydroisoquinoline adducts in ammonia were correlated by linear free energy relationships.

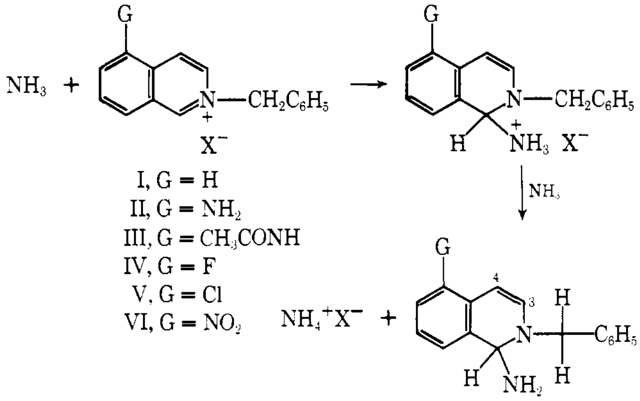
Nucleophilic addition to the annular carbon atoms of carbocyclic and heterocyclic molecules to give ionic or neutral covalent adducts is a common reaction in chemical and biochemical systems.[1-7] Such adducts may be the products of a reaction or they may be intermediates leading to new products. The aim of many current investigations is to obtain data from kinetic, equilibrium, and calorimetric studies for such reactions so that the structural factors which influence rates and equilibria may be determined.

We wish to report a study dealing with substituent effects on the rates of solvolysis of some amino adducts of heteroaromatic molecules in liquid ammonia. Our study primarily involves molecules formed by the addition of ammonia to isoquinolinium ions[4] containing a prochiral *N*-benzyl group, Scheme I. A novel application of NMR line shape analysis was employed to determine rates. The kinetic method is expected to be a useful complement to the usual spectrophotometric approaches employed in studying covalent adducts.

Results

Adducts from Isoquinolinium Ions. *N*-Benzylisoquinolinium ions react with liquid ammonia on mixing to give adducts which have the 1-amino-2-benzyl-1,2-dihydroisoquinoline structure (I–VI), Scheme I. Included in this series are the parent ion as well as those ions having at position 5 amino, acetylamino, fluoro, chloro, and nitro substituents. Conversion to adduct is complete; no evidence could be found by NMR for the presence of unreacted starting material in any case. Chemical shifts and coupling constants for these adducts are reported in Table I. The high-field shifts provide direct evidence of the change in structure associated with complex formation.[1,4] The especially interesting feature of the spectra is the nonequivalence of the *N*-methylene hydrogen atoms (diastereotopic protons[8]). Nonequivalence of these protons results because a chiral center is formed when ammonia adds to position 1.

Scheme I



The multiplicity of the *N*-benzyl protons depends on temperature and also on ammonium ion concentration. The AB pair of doublets collapses to a singlet on raising the temperature of a reaction mixture. The temperature required to bring about coalescence is lowered when the ammonium ion concentration is increased. For example, the coalescence temperature of the signal of the complex resulting from 2-benzylisoquinolinium ion decreases from 37 to 26 to 10° as the concentration of ammonium ion increases from 0.34 to 0.86 to 1.86 *M*. Moreover, when powdered KOH is added to a reaction mixture to reduce the ammonium ion concentration, coalescence is not observed even up to 88°. Therefore, the reaction which destroys the nonequivalence of the diastereotopic protons is ammonium ion catalyzed. In some