Table III. Hyperfine Coupling Constants of Some Typical Radicals and Normalized Rates of Hydrogen Abstraction

radical	$a(\alpha\text{-H})$, G	temp, K	ref	$10^4 k_x/(\text{H})$,[b] $M^{-1}\ s^{-1}$
α-tetrahydropyranyl (IX – H·)	−15.8	300	32	65
cyclohexyl	−21.3	193	33	13.3[a]
α-tetrahydrofuranyl (I – H·)	−12.4	300	34	206
cyclopentyl	−21.5	300	35	8.8
oxiranyl (IV – H·)	+24.5	243	36	27.5
cyclopropyl	−6.66	179	37	$\leqslant 0.17$

[a] J. A. Howard, private communication. [b] At 27 °C.

expected to be more reactive than the more rigid four- and six-membered-ring systems.

Ethylene oxide (XVI) is a rather interesting case, and its relatively low rate constant tends to mask the true magnitude of the stereoelectronic effect. We know for example that cyclopentane ($k_x = 8.8 \times 10^5$) is far more reactive than cyclopropane, which is frequently regarded as a good "inert" solvent for alkoxy radical reactions. The value of k_x for cyclopropane is no doubt lower than $\sim 10^4$ $M^{-1}\ s^{-1}$, a limit that reflects hybridization differences between five- and three-membered rings. When we compare the hydrocarbons and heterocycles, we find a reactivity enhancement of a factor of ca. 5 for the six-membered ring, of ca. 24 for the five-membered ring, and of over 160 for the three-membered ring (Table III).

This behavior seems to suggest that stabilizing interactions, i.e., conjugative delocalization and back-hyperconjugation[38] in the oxacycloalk-2-yl radical, which are expected to be more effective because of conformational requirements in the three- and five-membered rings, are responsible for the larger reactivity enhancement in the case of ethylene oxide and tetrahydrofuran. An inspection of the relative values of the hfcc's for the α-H of the oxacycloalk-2-yl radical (Table III) shows that the radical formed upon H atom abstraction from ethylene oxide has a much larger (and positive) hfcc than the tetrahydropyran-2-yl radical.

It is well established[14,38] that this indicates a more pyramidal geometry at the radical center and therefore a more effective conjugative delocalization and back-hyperconjugation. For the tetrahydropyran-2-yl radical formed by abstraction of the axial H atom, only a weak conjugative delocalization is expected; furthermore, this stabilizing interaction and back-hyperconjugation cannot occur in the radical formed by abstraction of the equatorial H atom. Therefore, for the six-membered ring, no substantial reactivity difference is expected between the cycloalkane and the corresponding oxacycloalkane.

Experimental Section

Materials. Di-*tert*-butyl peroxide (MC&B) was treated on an alumina column in order to eliminate traces of *tert*-butyl hydroperoxide. Diphenylmethanol (Aldrich) was sublimed twice, and special care was taken to eliminate any traces of benzophenone. The ethers, orthoformates, and acetals used in this study were either commercial materials or were prepared according to literature procedures.[11] They were purified by preparative gas chromatography (Varian 920) on a 12 ft × $^3/_8$ in., 12% Carbowax 20M on 60/80 Chromosorb WHP column at 120 °C or on a 12 ft × $^3/_8$ in., 20% OV-101 on 45/60 HP Chromosorb W column at 95–110 °C. *cis*-1,4,5,8-Tetraoxadecalin was crystallized twice from diethyl ether. 1,3,5-Trioxane was sublimed and then crystallized from a mixture of ethanol/ether (1:1). The liquid materials were stored in the dark over K_2CO_3.

Laser Flash Photolysis. The samples, usually 1 mL, were contained in Suprasil cells made from 3 × 7 mm² rectangular tubing (Vitro Dynamics) and were deaerated by using oxygen-free nitrogen. A Molectron UV-24 nitrogen laser was used for excitation. The signals were received in a Tektronix R-7912 transient digitizer; our facility has been fully interfaced with a PDP 11/03L computer which controls the experiment, averages and processes data, and provides suitable storage and hard-copy facilities. Further details have been published elsewhere.[26]

Acknowledgment. We express our thanks to Dr. K. U. Ingold for continuous interest in this work and for his encouragement. The trioxaadamantane was a generous gift of Professor P. Lamaty, Universitê de Montepellier, France. Thanks are also due to Mr. S. E. Sugamori for his technical assistance.

Registry No. I, 109-99-9; I-H·, 19426-60-9; II, 497-26-7; III, 646-06-0; IV, 592-90-5; V, 503-30-0; VI, 60-29-7; VII, 6921-35-3; VIII, 13405-83-9; IX, 142-68-7; IX-H·, 25088-30-6; X, 534-15-6; XI, 110-88-3; XII, 123-91-1; XIII, 67-63-0; XIV, 108-20-3; XV, 75-21-8; XI-H·, 31586-84-2; XVI, 19693-75-5; XVII, 109-87-5; XVIII, 149-73-5; XIX, 279-49-2; XX, 281-32-3; di-*tert*-butyl peroxide, 110-05-4; diphenylmethanol, 91-01-0; cyclopentyl radical, 3889-74-5; cyclopropyl radical, 2417-82-5.

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[38] Brunton, G.; Ingold, K. U.; Roberts, B. P.; Beckwith, A. L. J.; Krusic, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 3177.

Contamination of 4-Substituted 1,2,4-Triazoline-3,5-diones with Urazolyl Radicals

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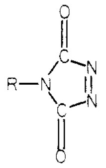
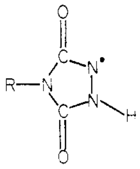
Received April 29, 1981

4-Substituted 1,2,4-triazoline-3,5-diones as normally prepared are contaminated with free radicals, which cannot be removed by sublimation or recrystallization. Solutions of these compounds contain urazolyl radicals in equilibrium with a dimer. On standing at room temperature for a few days, the urazolyl radical rearranges to a new radical, which is also in equilibrium with a dimer. The ESR spectra of these radicals are discussed and structures proposed. The presence of these free-radical initiators may have important consequences on the mechanisms of some of the thermal and photochemical reactions of triazolinediones.

In 1968, we had an occasion to prepare 4-phenyl-1,2,4-triazoline-3,5-dione (**1a**) with the expectation of using it in some cycloaddition reactions. In the course of those investigations we made some observations that led us to



1a, R = C_6H_5
b, R = C_2H_5
c, R = n-C_4H_9
d, R = H
e, R = CH_3



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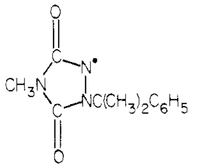

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suspect that solutions of this compound contained free radicals. When **1a** was dissolved in methylene chloride, the ESR spectrum given in Figure 1 was obtained. The spectrum appeared to have some overlapping lines, and at the time we did not have the required computer program for analysis of the spectrum. Our interest in the project was rekindled with the report of similar observations by Wamhoff and Wald,[1] who assigned the radical structure **2a**. They reported that the ESR spectra in anisole, dioxane, and tetrahydrofuran were identical. We were quite surprised to find that their published ESR spectrum was quite different from that which we had observed in methylene chloride (Figure 1). Structure **2a** proposed by Wamhoff and Wald is analogous to that of the stable radical **3** reported by Pirkle and Gravel.[2]

In order to try to understand the difference between our spectrum and that reported by Wamhoff and Wald, we undertook a study of the effect of solvent on the ESR spectra of radicals derived from 1,2,4-triazoline-3,5-diones. Carefully degassed solutions of **1a** (0.1–0.01 M) were prepared in various solvents and the ESR spectra recorded. In the course of obtaining these spctra, it was found that if the spectrum of the sample was run immediately after preparation, a different spectrum was obtained from that reported by Wamhoff and Wald. However, when the sample was allowed to stand 3–7 days, the original spectrum disappeared and was replaced by the spectrum of another radical. The appearance of the spectrum of this second radical was similar to that reported by Wamhoff and Wald. The spectrum of this second radical in benzene is given in Figure 2.

Both spectra could be reproduced by computer simulation[3] by assuming the radicals to be **1a** plus a hydrogen atom. The presence of the hydrogen atom was further suggested by the fact that the 4-ethyl compound (**1b**) gave a radical whose ESR spectrum contained an even number of lines. Since an even number of lines can only be observed when there is an odd number of spin $^1/_2$ atoms,[4] the presence of the hydrogen is indicated.

The calculated hyperfine splittings are listed in Table I. As can be seen in Table I and in Figures 1 and 2, the lines of the initial radical are somewhat broader than those of the final radical. The N-1 and N-2 hyperfine splittings of the initial radical are in a ratio of ca. 1:1.25. These hyperfine splitting constants are very similar to those reported by Pirkle and Gravel for radical **3** (7.70 and 6.25 G).[2] On this basis the initial radical should be assigned the hydrazyl structure **2**.

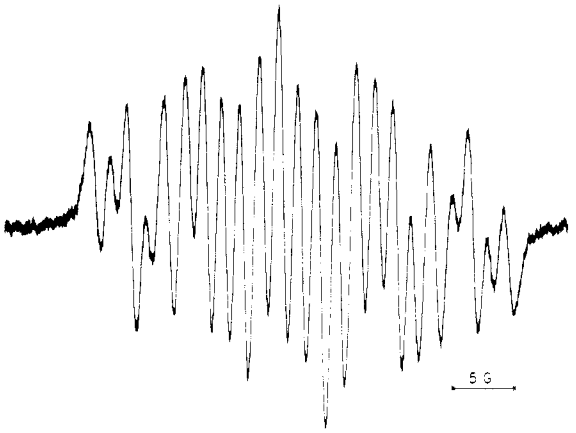

Figure 1. ESR spectrum of initial radical **2** in CH_2Cl_2.

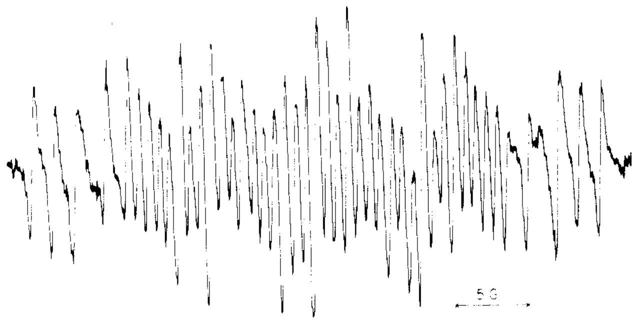

Figure 2. ESR spectrum of final radical **6** in C_6H_6.

Table I. ESR Parameters of Radicals Derived from 1a

		hyperfine splitting constants, G				
solvent	notes	a_H	$a_{N\text{-}1}$	$a_{N\text{-}2}$	$a_{N\text{-}4}$	half-width
		Initial Radical (**2**)				
$CDCl_3$	*a*	3.07	7.82	6.28	1.33	0.55
C_6H_6	*b*	2.94	7.93	6.49	1.47	0.80
CH_2Cl_2	*c*	3.01	7.64	6.21	1.50	0.60
$(C_2H_5)_2O$	*d*	2.84	7.90	6.20	1.42	0.50
		Final Radical (**6**)				
$CDCl_3$	*a*	7.20	9.19	4.87	1.48	0.18
C_6H_6	*b*	7.09	9.20	4.87	1.41	0.20
$(C_2H_5)_2O$	*d*	7.24	8.78	4.84	1.48	0.20
e	*e*	7.2	8.4	4.85	1.4	0.5

[a] Initial ESR spectrum disappeared after 18 h. After the sample was warmed to 55 °C, 7 days later, the final radical appeared. [b] The final radical was observed at room temperature after 7 days. When the sample was heated to 100 °C, the intensity was much enhanced. [c] Analysis of the spectrum originally obtained by Bigard and Fargher in 1968. [d] Spectrum of final radical obtained at room temperature after 3 days. [e] See ref 1. The solvent was dioxane, tetrahydrofuran, or anisole. The coupling constants have been estimated from the published spectrum.

The coupling constants for the final radical are quite different. The ratio of ca. 1:1.83 for the N-1 and N-2 splittings is surprisingly high. Also the proton splitting is more than double that of the initial radical. The hyperfine splittings listed in Table I for the final radical are quite different from those reported by Wamhoff and Wald.[5] We were unable to interpret our spectra for the final radical using coupling constants similar to those reported.[1,5] However, we were able to reproduce our spectra as well as the Wamhoff and Wald spectrum using the coupling constants in Table I.

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(1) H. Wamhoff and K. Wald, *Chem. Ber.*, **110**, 1699 (1977).

(2) W. H. Pirkle and P. L. Gravel, *J. Am. Chem. Soc.*, **96**, 3335 (1974).

(3) P. J. Krusic, "ESRSPEC2", Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, Program No. 210.

(4) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, 1972, pp 73–74.

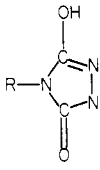
(5) Wamhoff and Wald[1] reported $a_{N\text{-}1}$ = 8.4 G, $a_{N\text{-}2}$ = 6.8 G, $a_{N\text{-}4}$ = 1.4 G, and a_H = 4.8 G.

Table II. INDO Calculated Coupling Constants and Total Spin Densities[a]

	2d (R = H)		2a (R = C_6H_5)		4d (R = H)	
atom no.	a_i, G	ρ_i	a_i, G	ρ_i	a_i, G	ρ_i
1	4.0	0.218	4.7	0.221	7.1	0.535
2	9.3	0.691	9.4	0.690	−0.3	−0.090
3	−12.2	−0.198	−12.3	−0.196	13.3	0.310
4	−1.3	−0.049	−1.1	−0.045	−0.8	−0.002
5	−3.3	−0.052	−3.2	−0.051	−13.4	−0.197
6	1.7	0.092	1.7	0.090	7.4	0.394
7	5.7	0.308	5.7	0.304	1.5	0.053
8	−5.8	−0.011	−5.8	−0.011	−1.1	−0.002
9	0.0	0.000			−0.6	−0.001

[a] Geometry optimized by using MNDO. For the following compounds are given the energy (AU), heat of formation (kcal/mol), and dipole moment (D): **2d**, −83.774, 31.3, 1.40; **2a**, −127.939, no heat of formation obtained, 1.34; **4d**, −83.742, −35.1, 4.93

One possibility for the structure of the final radical is **4**, the tautomer of **2**. To see if this was reasonable, molecular orbital calculations were undertaken on **2a**, **2d**, and **4d**. The geometry in each case was optimized by using the MNDO program.[6] The coupling constants were calculated by using the INDO program.[7] The coupling constants and total spin densities of these radicals are listed in Table II. The calculations show little or no coupling to either N-2 or to the OH proton in **4**, and so this possibility can be eliminated.



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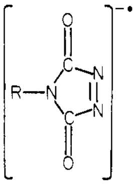

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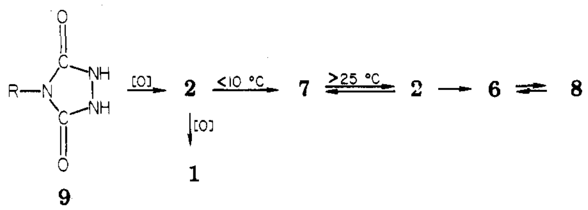
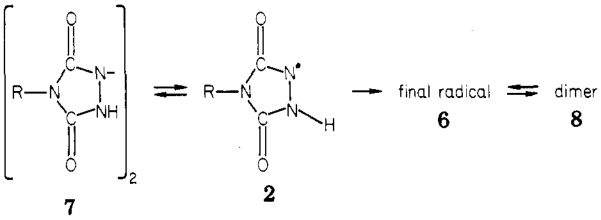
The possibility that the ESR spectrum of the final radical might in fact be the superposition of two radicals with identical *g* factors was considered, but rejected. It should be noted that **2** is the conjugate acid of the radical anion **5**. The ESR spectrum of the *N*-methyl radical anion **5e** was reported by Russell and co-workers.[8] It was generated by reduction of **1e** with potassium *tert*-butoxide. Similarly, we generated the *N*-phenyl radical anion **5a** by reduction of **1a** with potassium *tert*-butoxide in dimethylformamide–*tert*-butyl alcohol: $a_{N\text{-}1,2} = 5.08$; $a_{N\text{-}4} = 1.81$. This compares to $a_{N\text{-}1,2} = 4.87$ and $a_{N\text{-}4} = 1.85$ for the *N*-methyl radical anion.[6] Comparison of the ESR spectrum of the final radical with that of the radical anion showed the absence of the radical anion.

The structure of the final radical is still unknown. On examination of the spectral data for the final radical in Table I, the most notable features are the large values of $a_{N\text{-}1}$ and a_H. The very large a_H suggests that the hydrogen is on N-1 and that the principal structural feature of the final radical is the H–$\dot{N}$-N unit. Further, the fact that the coupling $a_{N\text{-}2}$ is almost half of $a_{N\text{-}1}$ indicates that N-2 is substituted with a substituent capable of withdrawing spin density from N-2. Finally, the value of $a_{N\text{-}3}$ is the same in the final radical as in the initial radical, suggesting that the R–N unit is still intact and still attached to carbonyl groups. Further work on the identity of this radical is in progress.

Scheme I



During the course of these investigations it was noted that the intensity of the ESR spectrum of the initial radical **2a** in methylene chloride was enhanced on warming to +60 °C and decreased to a very low level at −60 °C. This result suggests that it is in equilibrium with a diimer (**7**). Pirkle and Gravel[2] reported the isolation of the dimer of **3** as a tan solid which dissociated in solution. Similarly, the intensity of the final radical **6a** was enhanced considerably by warming to 50 °C or higher, suggesting that it also is in equilibrium with a dimer (**8**).



Several attempts were made to prepare 4-substituted 1,2,4-triazoline-3,5-diones (**1**) free from the radical contaminant. Various reagents were used to oxidize the corresponding urazole, including chlorine, lead tetraacetate, nitrogen dioxide, bromine, and *N*-bromosuccinimide. In all cases, the product contained the urazolyl radical as shown by ESR. The use of a large excess of reagent did not eliminate the radical. The standard method of purification for these azo compounds is sublimation. However, triple sublimation of **1a** did not remove the radical signal. Likewise, recrystallizations of **1a** from a concentrated methylene chloride solution at −20 °C failed to remove the radical. In one case (**1b**), the radical concentration was estimated as 10^{-6} M in a 10^{-2} M solution of the azo compound at 25 °C in a glyme–THF solution.

A proposal which can account for these observations is outlined in Scheme I. All of the oxidizing agents used would be expected to abstract hydrogen from the urazole **9** to give the urazolyl radical **2**. Further oxidation gives the triazolinedione **1**, but some of the radicals may dimerize to 1,1-biurazolyl **7**. The biurazolyl **7** would be expected to be stable to further oxidation since these oxidations are carried out at low temperatures to prevent decomposition of the azo compounds by nucleophilic

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(6) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).

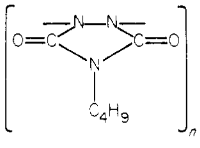
(7) The CNINDO version by Paul A. Dobosh was used (Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, Program No. 141).

(8) G. A. Russell, R. L. Blankespoor, J. Mattox, P. R. Whittle, D. Symalla, and J. R. Dodd, *J. Am. Chem. Soc.*, **96**, 7249 (1974).

products of the oxidation, conditions under which dimer **7** dissociates very little. Workup of the reaction gives solid **1** contaminated with dimer **7**. When **1** is purified by sublimation it dissociates at the higher temperatures (40–50 °C) into **2** which sublimes along with **1**. The azo compound **1** is so soluble in organic solvents it must be crystallized at low temperatures, and as a result the higher molecular weight (and presumably less soluble) dimer cocrystallizes with the azo compound. When this mixture of **1** and **7** is in solution at room temperature and above, **7** dissociates into **2**, which slowly changes to the thermodynamically more stable final radical **6**. This radical is itself in equilibrium with dimer **8** as shown by the enhancement of the ESR signal as the temperature is raised.

In two cases, samples of triazolinediones were obtained which were free of detectable radical. The first was a degassed ESR sample of **1a** in ether that stood at room temperature for 18 h. This sample on warming to 55 °C gave the final radical **6**. Apparently the dissociation of the dimer **8** into **6** is not as favorable in ether. Pirkle and Gravel[2] reported that the dimer of **3** was much less dissociated in nonpolar solvents than in polar solvents.

The second sample was a degassed ESR sample of **1b** in glyme–THF which had been stored in the dark for 6 months. On photolysis of this sample in the ESR cavity with an ultraviolet lamp, the ESR signal reappeared almost instantly and then disappeared within about 1 h as the color of the azo compound disappeared. When this same sample stood at room temperature for 2 days, the color of the azo compound was regenerated. These results are consistant with the spectroscopic observations of Pirkle and Stickler,[9,10] who studied the photopolymerization of **1c** to give a nitrogen backbone polymer (**10**) with about 20 monomer units. Our results suggest that this polymerization may be initiated by radical **2**, produced by dissociation of a dimer **7**; i.e., the polymerization may not involve photolytically activated azo compound **1c** at all.



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Finally, it has been reported that 4-substituted 1,2,4-triazoline-3,5-diones add ethers photolytically to give 1-substituted urazoles. However, THF and dioxane give even better yields of the addition product thermally.[1] It seems quite clear that these thermal addition reactions are being initiated by the radical impurities in the triazolinedione.

Experimental Section

All ESR work was performed on an X-band Varian 4500 spectrometer using a single cavity or single cavity equipped with a variable-temperature Dewar container. All ESR samples were prepared on a high-vacuum line and carefully degassed to less than 10^{-4} torr by the standard freeze–thaw technique. The 4-substituted 1,2,4-triazoline-3,5-diones were prepared by standard methods using a variety of oxidizing agents.[11] They were purified by either sublimation and/or recrystallization from concentrated solutions in methylene chloride at −20 °C. All solvents were spectral grade and were used directly, except for the ethers, which were distilled from lithium aluminum hydride prior to use.

The spectra were analyzed by comparison of the line shapes, positions and intensities with those calculated by using ESRSPEC2.[3]

Registry No. 1a, 4233-33-4; **2a**, 80540-38-1; **2d**, 80540-39-2; **4d**, 80540-40-5.

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(9) W. H. Pirkle and J. C. Stickler, *J. Am. Chem. Soc.*, **92**, 7497 (1970).

(10) J. C. Stickler, *Diss. Abstr. Int. B*, **32**, 4501 (1972).

(11) (a) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Lett.*,, 615 (1962); (b) J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 344 (1966); (c) H. Wamhoff and K. Wald, *Org. Prep. Proced. Int.*, 7 (5), 251 (1975).

α-Silicon-Substituted Vinyl Cations. A Theoretical ab Initio Investigation

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Ab initio calculations with the STO-3G, 3-21G, and 6-31G* basis sets were used to investigate several silyl- and alkyl-substituted vinyl cations, i.e., $H_2C{=}C^+{-}XR_3$ and $H_2C{=}C^+{-}C{\equiv}CXR_3$ where X = C, Si and R = H, CH_3. α-Silyl and α-methyl substituents stabilize $H_2C{=}CH^+$ by 25 and 24 kcal mol^{-1}, respectively (6-31G*), so that $H_2C{=}CSiH_3^+$ and $H_2C{=}CCH_3^+$ [or $H_2C{=}CSi(CH_3)_3^+$ and $H_2C{=}CBu\text{-}t^+$] have comparable stabilities in a hydride-transfer process (eq 5 and 6). $H_2C{=}C(OH)SiH_3$ is destabilized by 4.5 kcal mol^{-1} (6-31G*) relative to $H_2C{=}C(OH)CH_3$, so that the equation [$H_2C{=}C(OH)SiH_3 + H_2C{=}CCH_3^+ \rightarrow H_2C{=}CSiH_3^+ + H_2C{=}C(OH)CH_3$] that models the solvolysis reactions of the corresponding triflates is exothermic by 5.6 kcal mol^{-1} (6-31G*). $H_2C{=}CC{\equiv}CH^+$ is less stable than $H_2C{=}CCH_3^+$ by 2.0 kcal mol^{-1} (6-31G*). A triple bond transmits the electronic effects of alkyl substituents more effectively than that of silyl substituents. Thus, $H_2C{=}CC{\equiv}CR^+$ where R = CH_3 and SiH_3 are more stable than the parent cation (R = H) by 15.5 and 8.7 kcal mol^{-1}, respectively (3-21G). Consequently, $H_2C{=}CCCR^+$ cations with R = alkyl are more stable than with R = silyl. The close agreement between the results of the calculations and the solvolysis rates suggests that the solvation energies of the alkyl- and silyl-substituted vinyl cations are comparable.

The effect of silicon substitution on the stability of carbenium ions is much less investigated and understood than simple alkyl substitution. The limited solvolytic data available indicates that β-silicon substitution stabilizes alkyl carbenium ions while α-substitution causes destabilization.[1] Recently Schiavelli, Stang, and co-workers

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