

N_{T_1} is assumed to decay to N_{S_0} without affecting product formation. The step of energy transfer from N_{T_2} to E has been omitted. Under the experimental condition that $[B] \gg [E]$, this step is of negligible importance. Also, k_5 should be equal to k_5' with both approaching k_{diff} .¹² With these assumptions, the Stern-Volmer expression for the product formation becomes

$$\frac{1}{\phi_p} = \frac{1}{abc} \left(\frac{[E]}{[E] + [N]} \right) \left(1 + \frac{k_2}{k_1} \frac{1}{[B]} \right)$$

Preparation of samples and irradiation procedure are similar to those reported.³ To avoid singlet quenching complications, [E] was kept constant for all samples (Table I). Also, [N] was kept constant so that the

Table I. Naphthalene Sensitized Cyclization of *endo*-Dicyclopentadiene^a

[Benzene], <i>M</i>	% conversion to product ^b	[Benzene], <i>M</i>	% conversion to product ^b
10.0	3.96	2.00	1.54
5.73	3.55	1.32	1.03
4.03	2.79	0	0.46
3.57	2.08	10.0 ^c	0.46
2.45	1.65		

^a Concentration of naphthalene, 2.0×10^{-3} *M*; concentration of *endo*-dicyclopentadiene, 5.0×10^{-2} *M*. ^b Irradiated for 29 days in "M.-G.-R." quantum yield apparatus (F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969) a 550-W Hanovia Hg lamp with Corning 0-54 filters. ^c In the absence of naphthalene.

same amount of light quanta was absorbed by all samples even though only the Corning 0-54 filters were used. The omission of the long wavelength cut-off filter permits higher light intensity, necessary for this low quantum yield reaction. After irradiating samples for the same period of time relative product yield becomes relative quantum yield. Results of such a run are summarized in Table I with a corresponding Stern-Volmer plot shown in Figure 1.¹³

It is clear that benzene enhances the efficiency in T_2 sensitization and within the concentration range, there is a linear relation between $1/\phi$ (rel) and $1/[B]$ as predicted by the above Stern-Volmer equation. From the ratio of the slope and intercept, k_2/k_1 can be calculated and is equal to 9.7 *M*. If one assumes that exothermic triplet-triplet energy transfer proceeds at diffusion rate, i.e., $k_1 = 6.2 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$,¹⁴ then k_2 , the rate constant of radiationless deactivation of naphthalene T_2 , is $6.0 \times 10^{10} \text{ sec}^{-1}$. Its average lifetime ($\tau = 1/k_2 = (1.7 \pm 0.5) \times 10^{-11} \text{ sec}$) is therefore about an order of magnitude shorter than that of anthracene T_2 , consistent with the relative spacing between the two lowest triplet states in the two compounds.

With recent interest in "intermolecular intersystem

(12) For a recent discussion on this point, see N. J. Turro, N. E. Schore, H. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **96**, 1936 (1974).

(13) The last two samples in Table I are controls to show that the observed effects are not due to direct sensitization by naphthalene nor due to imperfect filtering systems resulting in direct excitation of benzene molecules.

(14) An experimental value from flash photolysis studies: W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

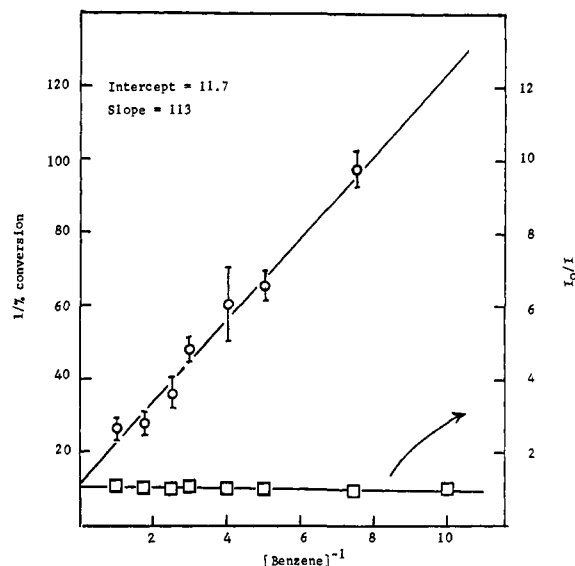


Figure 1. Stern-Volmer plots of (a) the naphthalene sensitized reaction of *endo*-dicyclopentadiene (○) and (b) the fluorescence of naphthalene in the presence of benzene (□).

crossing,"¹⁵ we carried out additional quenching experiments to show that our results are not due to energy transfer processes originating from the singlet state of naphthalene. Therefore, we showed that in the same concentration range as in the chemical study benzene has only a negligible effect on the intensity of naphthalene fluorescence (Figure 1). In fact, if anything, it shows a weak enhancement.

Acknowledgment. The work was supported by the National Science Foundation (GP-14248).

(15) (a) G. Vaubel, *Chem. Phys. Lett.*, **9**, 51 (1971); (b) H. Zimmerman, D. Stehlike, and K. H. Hausser, *ibid.*, **11**, 496 (1971); (v) G. Vaubel and H. Baessler, *ibid.*, **11**, 613 (1971); (d) V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectrosc. (USSR)*, **29**, 324 (1970).

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An Electron Spin Resonance Study of the Steric Rigidity in the Allyl and 1,1-Disubstituted Allyl Radicals

Sir:

Despite a large expenditure of effort and the application of various experimental techniques, the stabilization energy of the allyl radical continues to be a subject of controversy.¹ Estimates range from 9 to 24 kcal/mol although a value of about 10 kcal/mol is now

(1) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964); D. M. Golden, A. S. Rogers, and S. W. Benson, *ibid.*, **88**, 3196 (1966); D. Golden, N. Gac, and S. W. Benson, *ibid.*, **91**, 2136 (1969); D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); Z. B. Alfassi, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **5**, 155 (1973); J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971); D. K. S. Sharma and J. L. Franklin, *J. Amer. Chem. Soc.*, **95**, 6562 (1973); A. S. Rogers and M. C. R. Wu, *ibid.*, **95**, 6913 (1973); J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4730 (1968); R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959 (1964); A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1737 (1973); M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **18**, 237 (1950); W. v. E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973); P. S. Engel, A. I. Dalton, and L. Shen, *J. Org. Chem.*, **39**, 384 (1974); R. J. Field and P. I. Abell, *J. Amer. Chem. Soc.*, **91**, 7226 (1969).

Table I. ESR Spectral Parameters of 1-Substituted Allyl Radicals^a

R ₂ C \dot{C} H=CH ₂	Temp, °C	(g) ^c	Isotropic hyperfine coupling constants, G				
			$\alpha(H_3^{anti})$	$\alpha(H_3^{syn})$	$\alpha(H_2)$	$\alpha(R^{anti})$	$\alpha(R^{syn})$
R = H ^b	-130	2.00254 ^c	14.81	13.90	4.06	14.81	13.90
H	+230		14.82	14.00	4.53	14.82	14.00
R = CH ₃	-120	2.00259	14.06	13.33	3.56	15.35 ^d	12.22 ^d
	+90		13.83	13.14	4.04	15.31	12.44
R = OCH ₃	-68	2.00283	14.97	14.43	2.29	0.832 ^d	0.832 ^d
	+31		14.79	14.22	2.69	0.748	0.583
R = F	-82	2.00325	15.98	15.21	3.50	34.50	29.29
	-14		15.78	15.08	3.72	35.46	30.68

^a The assignments of the larger coupling to the anti substituent on each terminal carbon atom are based on internal consistency with the 1-methylallyl radicals (*cf.* ref 2a). ^b Reference 2a. ^c Reference 2b. ^d CH₃ proton hfs.

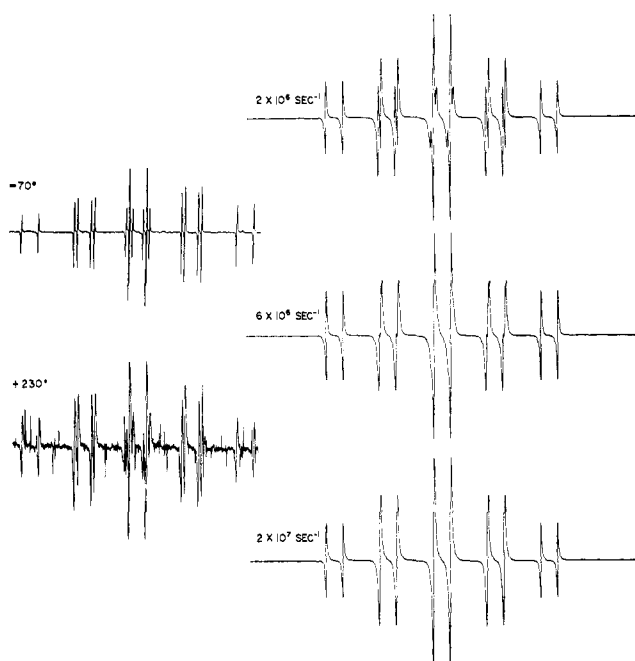


Figure 1. Experimental and calculated esr spectra of the allyl radical. The sharp spikes in the high temperature spectrum are caused by bubbling. The simulated spectra were calculated by the density matrix method using the spectral parameters at 230° ($T_2 = 1.99 \times 10^{-7}$ sec). The calculated spectrum for the slower rate of exchange shows incipient coalescence.

widely accepted. We wish to present yet another approach to this general problem which considers the allylic delocalization energy defined as the energy released when a noninteracting, orthogonal vinyl group attached to a carbon radical center rotates by 90° into the coplanar orientation allowing the delocalization of the unpaired electron.

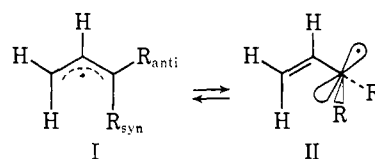
The low temperature esr spectrum of the allyl radical² (Figure 1) reveals two pairs of magnetically inequivalent syn and anti terminal protons (13.90 and 14.81 G) which give rise to a triplet-of-triplets hyperfine structure further split into doublets by the proton in the 2 position (4.06 G). This inequivalence implies that the allyl radical at these temperatures cannot exchange the terminal protons at rates approaching 1×10^7 sec⁻¹. The latter represents the difference in the hyperfine coupling constants of the terminal protons ($\Delta a = 0.91$ G) expressed in angular frequency units. The spectral changes expected to occur in the proximity

(2) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968); (b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

of this rate can be calculated by the density matrix method³ for an uncorrelated rotation of the CH₂ groups (Figure 1).

The spectrum of the allyl radical at 230° (Figure 1), obtained by photolysis of an eicosane (C₂₀H₄₂) solution containing triallylphosphine and di-*tert*-butyl peroxide,⁴ shows no indication of line width effects. Partial sweeps over one of the critical doublets failed to reveal any coalescence up to 280°. Comparison with the calculated spectra precludes a rate of more than 2×10^6 and therefore any process exchanging the CH₂ protons requires a free energy of activation of more than 17 kcal/mol (Eyring equation⁵).

High-temperature esr spectra of the 1,1-dimethylallyl radical were also sought on the assumption that the steric rigidity of the allylic framework in this radical should decrease, since methyl substitution could stabilize the orthogonal form II (R = CH₃) by the same effects which confer greater stability to tertiary alkyl radicals than to primary radicals and destabilize the



coplanar form I (R = CH₃) by steric crowding on the syn side of the molecule. Such steric crowding is no doubt responsible for our observation of only the *anti-tert*-butylallyl radical by hydrogen abstraction from 4,4-dimethyl-1-pentene up to 85°.

The spectrum of the 1,1-dimethylallyl radical was examined up to 180° by photolysis of a solution composed of hexadecane, 3-methyl-1-butene, and di-*tert*-butyl peroxide. Density matrix calculations show that neither the terminal protons nor the terminal CH₃ groups can exchange at this temperature at rates of 2×10^6 sec⁻¹. Hence, the activation energies for non-concerted rotations about either allylic bond cannot be lower than 14 kcal/mol.

The spectra for the 1,1-dimethoxy- and 1,1-difluoroallyl radicals were also scrutinized for possible dynamic effects. The former was generated from acrolein dimethylacetal while the latter was produced from 3-

(3) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(4) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); (b) P. J. Krusic, W. Mahler, and J. K. Kochi, *ibid.*, **94**, 6033 (1972).

(5) W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935); *cf.* also P. J. Krusic and P. Meakin, *Chem. Phys. Lett.*, **18**, 347 (1973).

bromo-3,3-difluoropropene by bromine abstraction with photochemically generated diethylphosphonyl radicals.⁶ The esr spectra were interpreted in terms of nonequivalent substituents in the 1 and 3 positions (Table I).

While the coupling constants of the terminal protons in the allyl radical are essentially constant over a broad temperature range, the magnitude of the coupling to the 2 proton has a notable *positive* temperature coefficient. Similar temperature coefficients are observed for all the allylic radicals of Table I. They are attributed to out-of-plane vibronic motions of the hydrogens in the 2 position. The signs of these coefficients are opposite to that of the protons in the methyl radical indicating a *positive* sign for $a(H_2)^7$ and therefore a negative π spin density on C_2 in agreement with theory.⁸ The greater temperature dependence of all couplings in the substituted radicals compared to the allyl radical imply greater amplitudes for torsional motion about the allylic bonds and therefore a reduced rigidity of the planar structures.

It is noteworthy that 1,1-difluoro and 1,1-dimethoxy substitution *increases* the π spin density on C_3 judging by the increase in the average magnitude of the H_3 couplings for these radicals relative to the allyl radical. The fluorine hyperfine couplings⁹ can be compared with those for α,α -difluorobenzyl¹⁰ (51.4 G) since in the parent hydrocarbon radicals the unpaired π spin densities on the benzylic and the terminal allylic carbon atoms are comparable.^{11,12} The larger α -fluorine coupling in the former indicates either some degree of nonplanarity at the benzylic carbon atom or out-of-plane vibronic and torsional motions of greater amplitudes than in the difluoroallyl radical. Thus, a coplanar vinyl group is more effective than a coplanar phenyl group in counteracting the strong inherent propensity of the $-\dot{C}F_2$ radical fragment toward a pyramidal structure.^{6a,13}

(6) (a) P. Meakin and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 8185 (1973); (b) A. G. Davies, D. Griller, and B. P. Roberts, *ibid.*, **94**, 1782 (1972).

(7) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 1516 (1973).

(8) H. M. McConnell, *J. Chem. Phys.*, **28**, 1188 (1958); C. Heller and T. Cole, *ibid.*, **37**, 243 (1962); A. Hinchliffe and N. M. Atherton, *Mol. Phys.*, **13**, 89 (1967); J. R. Bolton, "Radical Ions," Wiley-Interscience, New York, N. Y., 1968, Chapter 1.

(9) Cf. L. D. Kispert, C. U. Pittman, Jr., D. L. Allison, T. B. Patterson, Jr., C. W. Gilbert, Jr., C. F. Hains, and V. Prather, *J. Amer. Chem. Soc.*, **94**, 5979 (1972).

(10) L. D. Kispert, H. Liu, and C. U. Pittman, Jr., *ibid.*, **95**, 1657 (1973).

(11) Cf. (a) R. V. Lloyd and D. E. Wood, *J. Amer. Chem. Soc.*, **96**, 659 (1974); (b) M. Raimondi, M. Simonetta, and G. F. Tantaridini, *J. Chem. Phys.*, **56**, 5091 (1972).

(12) The unpaired π spin densities on the fluorinated carbon atoms of $CH_2=CH\dot{C}F_2$ and $\phi\dot{C}F_2$ have been calculated by the INDO method.^{9,10} For the former radical $\rho_C = 0.59^9$ and for the latter $\rho_C = 0.65^{10}$. A portion of the difference in fluorine splittings for these radicals may, therefore, be due to a small difference in unpaired spin density at carbon. The same authors, however, calculated a much flatter potential well for a torsional motion of the CF_2 group in $\phi\dot{C}F_2$ than in $CH_2=CH\dot{C}F_2$ in agreement with our conclusion. We thank a referee for these observations.

(13) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968); (c) L. Pauling, *ibid.*, **51**, 2767 (1969); (d) R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7180, 7182 (1973).

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Addition Reactions of Allenes. V.¹ 2,4-Dinitrobenzenesulfonyl Chloride²

Sir:

Addition of organic sulfonyl chlorides to olefins is well known, but the corresponding reaction of allenes has not been thoroughly explored.³ The recent paper on addition of 2,4-dinitrobenzenesulfonyl chloride to phenylallene⁴ leads us to give a preliminary report of our work on addition of this reagent to ten aliphatic allenes. Results are summarized in Table I.

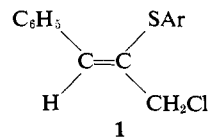
Table I. 2,4-Dinitrobenzenesulfonyl Chloride Adducts from $RCH=C=CHR'^a$

R	Allene	R'	% yield crystals	Oil	Mp, °C (crude)
CH ₃		H ^b	75	11.5	45-48.5
C ₂ H ₅		H ^b	73	17	72.5-75
<i>n</i> -C ₃ H ₇		H ^c	23	42	62-65
CH ₃		CH ₃ ^d	60	32	89-91
CH ₃		C ₂ H ₅ ^b	32	55	68-72
C ₂ H ₅		C ₂ H ₅ ^{b,e}		79	
	-(CH ₂) ₆ - ^f		75	17	142-144
	-(CH ₂) ₁₀ - ^g		35	35	109-113
Adm		Adm ^{b,h}	35	42	215-219

^a All of the allenes are known compounds and were synthesized by conventional methods. For 1,3-di(1-adamantyl)allene see T. L. Jacobs and R. C. Kammerer, *J. Amer. Chem. Soc.*, **94**, 7190 (1972). Additions were carried out in CHCl₃ at room temperature unless otherwise indicated. All crystalline adducts gave correct C and H values; Cl and either N or S values were obtained for most of them and all were correct. Expected nmr spectra were obtained on all adducts; chemical shifts for olefinic and allylic protons are given in Table II. Results for tetramethylallene are not included in the table. ^b At 0°. ^c Reaction time 48 hr, unreacted allene present. ^d In CH₂Cl₂. ^e All attempts to obtain crystals failed. Analysis of the oil gave C, 45.96; H, 5.05. Calcd for C₁₃H₁₅ClN₂O₄S: C, 47.20; H, 4.57. ^f In HOAc, 3 hr. ^g About 15% of the crude product lost. ^h Adm, 1-adamantyl.

Equimolar amounts of the allene and sulfonyl chloride were allowed to react for 1-8 weeks at 0° or room temperature. Mixtures were obtained in every instance as shown by isolation of both crystals and oils or by the nature of the nmr spectra.

The major adduct from each monosubstituted allene had the type B structure,¹ $RCHClC(SAr)=CH_2$, rather than type A, $RCH(SAr)CCl=CH_2$. Neither this type A adduct nor any adduct in which attack occurred on the terminal double bond was detected by nmr of crude reaction mixtures or of the oils although presumably some of these were present in minor amounts. These results contrast with those for phenylallene⁴ which gives



as the only product. The general pattern in electrophilic additions to allenes is attack on the more elec-

(1) Paper IV: T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).

(2) From the Ph.D. Thesis of R. C. Kammerer, University of California, Los Angeles, 1972.

(3) For a brief review see M. C. Caserio, *Selec. Org. Transform.*, **1**, 259 (1970).

(4) K. Izawa, T. Okuyama, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 4090 (1973).