line residue. The mixture was refluxed for 90 sec and cooled in a refrigerator to yield pseudothiohydantoin (0.78 g, 67%) as colorless needles, mp 233–235° dec. The filtrate was concentrated to dryness by rotary evaporation to give a crystalline residue, which was extracted with hot aqueous ethanol (90%, 40 ml). The extract upon cooling afforded glycylglycine hydrochloride monohydrate as colorless needles (1.13 g), mp 137–138°. The residue from the extraction was again extracted with the alcoholic filtrate to yield additional colorless needles (0.27 g), mp 136–138°. The total yield was 1.40 g. The product was substantially pure without further purification, and it was identical in melting point and ir spectrum with an authentic sample.[7]

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[7] E. Fischer and D. Fourneau, *Ber.*, **34**, 2870 (1904); H. F. Schott, J. B. Larkin, L. B. Rockland, and M. S. Dunn, *J. Org. Chem.*, **12**, 490 (1947).

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The Butatrienyl Radical

Sir:

In the course of studying the series of radicals having the general formula HC_nCH_2, we have prepared the hitherto unreported butatrienyl radical (n = 3) and observed its paramagnetic resonance spectrum in an argon matrix near 4°K. The radical was produced by photolyzing a mixture of diacetylene[1] with argon containing 1% hydrogen iodide during deposition on a sapphire surface in thermal contact with liquid helium. The dewar and spectrometer system have been described previously.[2] The essential reaction is the addition of hydrogen atoms, produced by photodissociation of HI, to diacetylene.[3] Addition appears to occur predominantly at the terminal positions.

Butatrienyl is the first vinylog of vinyl radical (n = 1), which has a bent, planar structure.[3–5] Unlike vinyl, any bending of HC_nCH_2 radicals with $n > 1$ would occur at the expense of optimum π bonding, so that the ground-state structures most likely have C_{2v} symmetry. There are then n π orbitals quantized in the molecular plane and $(n + 1)$ orbitals normal to this plane, so that one always has a linear polyyne which is even-alternant in one plane and odd-alternant in the other. In a neutral radical, the odd electron would be found in the essentially nonbonding orbital of the odd-alternant system, leading one to expect a $^2B_2$ ground state for radicals with n even and a $^2B_1$ ground state when n is odd. The unpaired electron in butatrienyl accordingly should be in the molecular plane and delocalized over three carbon atoms.

The electron-spin resonance spectrum, shown in Figure 1, confirms this prediction. It shows an anisotropic pattern corresponding to a rigid system containing three protons, two of which are structurally equivalent. Its preliminary analysis yields the hyperfine splittings listed in Table I. There are weak additional lines indicated by broken arrows in Figure 1 which could result from hyperfine splittings of ~45 and ~10 G by each of two protons in a second species, most likely the vinylacetylenyl radical produced by hydrogen atom addition to an internal carbon atom of diacetylene.

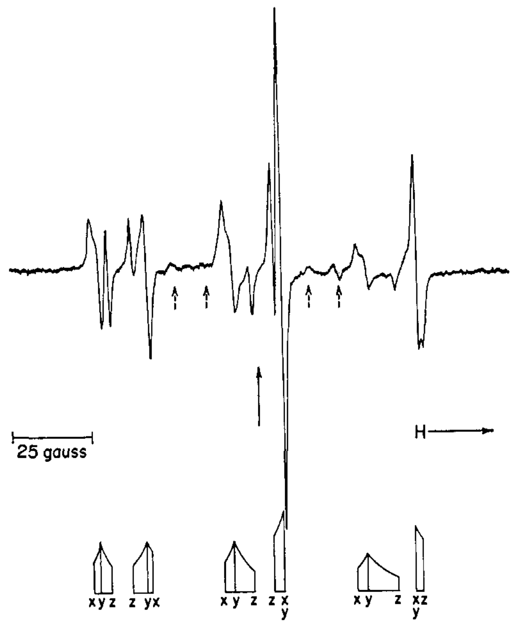
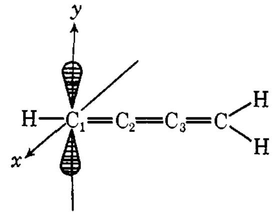


Figure 1. Esr spectrum (9436 GHz) of butatrienyl radical in argon near 4°K. A schematic analysis of the spectrum is indicated at the bottom. Weak signals indicated by broken arrows are believed due to vinylacetylenyl (see text). The solid arrow indicates the field corresponding to g = 2.0023.

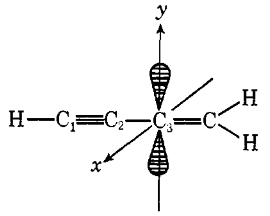
Table I. Hyperfine Splittings (in Gauss at 9.3 GHz) in the Epr Spectrum of Butatrienyl Radical

	Doublet		Triplet	
	Obsd splitting	Dipolar part	Obsd splitting	Dipolar part
A_x	19	±5.3	42.3	∓1.1
A_y	15	±1.3	42.3	∓1.1
A_z	7	∓6.7	45.7	±2.3
$A_{iso} = {}^1/_3(A_x + A_y + A_z)$	±13.7		±43.4	

In the main spectrum, the principal axes can be assigned by considering the dipolar couplings in the principal valence-bond structures I and II.[6] The



I



II

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[1] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 44 (1951).

[2] P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *J. Chem. Phys.*, **42**, 1120 (1965).

[3] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).

[4] P. H. Kasai and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 1033 (1967).

[5] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[6] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper & Row, Publishers, New York, N. Y., 1967, Chapter 7.

most unique direction of the dipole–dipole interaction between the unpaired electron and vinylidine protons in II should be parallel to the long axis of the molecule, and the sign should be positive. The implied sign of the isotropic coupling is accordingly positive, in agreement with the calculated couplings in the analogous vinyl radical.[7-9] The dipolar coupling to the acetylenic proton in I should also have positive sign in the direction of the molecular axis,[10] implying a negative sign for the scalar coupling to this proton. This is also consistent with theory[11] provided the C–H bond is not appreciably bent.

Both the isotropic and dipolar couplings to the acetylenic proton are very similar to those in the propargyl radical[12] and are mutually consistent with a spin density of $\rho_1 = 0.52$, provided a value of $Q = 25$ is employed in the McConnell relation.[11] A value of $\rho_3 = 0.85$ can be estimated from the hyperfine splitting of the vinylidene protons by using the vinyl radical as a model ($A_{\text{iso}} = 51.5$ G[4]). However, this value is probably high by about 20% due to the use of too small a value of the hyperfine splitting parameter from a model involving a hybrid orbital.[7-9] The true spin densities are, therefore, probably very close to those in the progargyl radical, including a negative spin density of about 0.4 on the second carbon atom.[12]

The most obvious difference between the butatrienyl and propargyl radicals is the hybridization at C$_3$, which would be manifest in the π orbitals through a shortening of lengths in the σ-band framework. Simple Hückel theory would predict, for example, that the spin density ratio on atoms 1 and 3 measures the ratio of their respective resonance integrals with atom C$_2$ directly. Our experimental results thus imply that the change from sp^2 to sp hybridization has little effect on the bond lengths.

Shostakovskii and coworkers[13] have studied the addition of thiyl radicals to diacetylene, and this appears to be the only such radical reaction reported in the literature. They observed only terminal addition, yielding stereoisomeric mixtures of 1,4-bis(phenylthio)-1,3-butadienes with thiophenol,[13a] and 1-butylthio-1-buten-3-yne together with 1,4-bis(butylthio)-1,3-butadiene in the case of *n*-butylmercaptan.[13b] Their method of analysis, however, probably could not have detected small amounts of products from nonterminal addition. Hence, as far as the site of addition is concerned, their results are in agreement with our observations. The apparent fact that the monoaddition product undergoes selective addition at the terminal acetylenic carbon is quite interesting and would not necessarily have been predicted.

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[7] F. J Adrian and M. Karplus, *J. Chem. Phys.*, **41**, 56 (1964).

[8] W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).

[9] G. A. Peterson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).

[10] H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

[11] H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

[12] P. H. Kasai and E. B. Whipple, to be submitted for publication.

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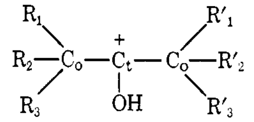
Bis-*t*-alkyl Ketone Rearrangements. Structural Environment Influences on the Migration of Ethyl and Methyl Groups

Sir:

Although it is to be expected that the migratory aptitudes of alkyl groups in carbonium ion rearrangements will depend on the detailed structure of the ion involved and upon the mode of its formation,[1] most studies have been restricted to the determination of a migration order related to the nature of the migrating group only. Little information has been presented concerning the effects of systematic structural modification upon the migration tendencies of alkyl groups.[2,3]

In order to obtain quantitative information on this point we have undertaken the study of the metathetical transpositions[5] of bis-*t*-alkyl ketones in sulfuric acid which involve rate-determining migration[6] of the primary alkyl group, ethyl or methyl, for the ketones studied here. In this communication we wish to show to what extent the migration of these groups depends on the structure of the hydroxycarbonium ion (IIa, IIb, IIc, or IId) in the neighborhood of the two carbon atoms, the termini of the migration. We have been able to estimate the acceleration due to the release of steric strain at the origin carbon, C$_o$, and to show that the migration is retarded by the fixed substituents at the terminal carbon, C$_t$. Since, during the migration,



C$_o$ and C$_t$ undergo inverse modifications of their orbitals (sp^3 → sp^2 for C$_o$ and sp^2 → sp^3 for C$_t$), the environments of C$_o$ and C$_t$ have contrasting effects upon the rates of migration.

The rearrangement of hexamethylacetone (Ia) (Scheme I) in sulfuric acid (96 wt %) consists of a 1,2-transfer of a methyl group (IIa → IIIa) followed by the intramolecular migration of the *t*-butyl group (IIIa → IVa), leading to 3,3,4,4-tetramethylpentan-2-one (Va) which breaks down to isobutylene and 3-methylbutan-2-one (VIa).[7]

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[1] C. J. Collins, *Quart. Rev.* (London), **14**, 357 (1960).

[2] R. L. Heidke and W. H. Saunders, *J. Amer. Chem. Soc.*, **88**, 5816 (1966).

[3] The migrating tendency of ethyl relative to methyl has been shown to be 17 for the pinacol rearrangement,[4] and a value of about unity has been obtained for the Wagner–Meerwein rearrangement.[2]

[4] M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, **81**, 1497 (1959).

[5] The transpositions of bis-*t*-alkyl ketones result from two successive crossed 1,2-transfers of a primary group and a tertiary group. At the end of this double rearrangement the two migrating groups have exchanged their positions. By analogy with the expression "metathesis," we propose to characterize this type of transposition as "metathetical."

[6] Stiles and Mayer[4] have observed that 2,3,4,4-tetramethylpentan-2,3-diol, with ^{14}C labeled on the carbon bearing the *t*-butyl group, rearranges, in 50 wt % H$_2$SO$_4$, to Va labeled on the carbonyl carbon (98.6%) and Ia (1.4%). We have repeated this experiment in 96 wt % H$_2$SO$_4$ and found very similar percentages, 97 and 3%, respectively. These results indicate that, in this medium, the only intermediate in the pinacolic transposition of this glycol is the 2,3,4,4-tetramethyl-3-hydroxy-2-pentyl carbonium ion (ion IIIa in Scheme I), which occurs also in the rearrangement of Ia. The lifetime of the glycol in concentrated H$_2$SO$_4$ is much shorter (about 2 min) than that of Ia (10 hr); this shows that the rate-determining step of the rearrangement of Ia to Va must precede the formation of the ion IIIa. It is in consequence the step IIa → IIIa in which the primary group migrates.

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