Figure 2; the G molecule, which is sandwiched between the two G′ molecules, would make impossibly short contacts with the neighboring G′ molecules were it to react.

The crystallographic result has provided us with the means of differentiating between possible reaction pathways. Moreover, the stereochemical correlation of the absolute configuration of the product PFDCA with the relative orientation of G′ to the reactive center C5–H5 of the steroid indicates a net rotation of 180° of the photoexcited acetyl group prior to bond formation. This is the same behavior found previously in DCA–acetophenone, supporting once again the previously suggested mechanism of hydrogen abstraction by the Py orbital solely and not by the π^* orbital.[2]

This work suggests that in order to obtain the lacking diastereomer it is necessary to design a looser packing arrangement where G′ is still further separated from G. Such an arrangement appears to be fulfilled by propiophenone, on which work is in progress.

Acknowledgment. We thank the U.S./Israel Binational Science Foundation, Jerusalem, for financial support. We are indebted to Dr. Felix Frolow for assistance in structure determination.

Experimental Analysis of γ-Hydrogen Hyperfine Splittings in Acyclic Aliphatic Radicals. Confirmation of Theoretical Predictions[1]

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Received July 13, 1981

Ellinger et al.[4,5] have reported the results of an ab initio investigation of the methyl (i.e., γ-H) proton hyperfine splittings (hfs's) for the *n*-propyl radical (**1**). It was predicted[4,5] that the γ-H hfs's would be dependent on θ_{Me}, the dihedral angle between the $C_\beta(H_\gamma)_3$ group[6] and the semioccupied $\dot{C}$ $2p_z$ orbital (see **1a**), *and* θ_γ, the dihedral angle between the $C_\beta H_\gamma$ bond and the $\dot{C}C_\alpha C_\beta$ plane[6] (see **1b**). Values of a^{H_γ} (together with other H and ^{13}C hfs's) were computed for various *n*-propyl conformations. In agreement with experiment,[7-12] the minimum energy geometry for a "freely rotating"[13] CH_3 group was found to have $\theta_{Me} = 90°$ [14] and $a^{H_\gamma}(3H) = -0.21$ G[15] which was compared with a measured $|a^{H_\gamma}(3H)| = 0.27$ G at 163 K.[9] There was no experimental data to support their conclusion that a^{H_γ} depended on θ_{Me}. While there was evidence to support a dependence of a^{H_γ} on θ_γ, it was not explicitly employed in support of the calculations. The evidence in question consisted of the EPR observation[7] that the three H_γ of *n*-propyl are equivalent[13] at 128 K, $|a^{H_\gamma}(3H)| = 0.38$ G, but at 93 K the spectrum represents a single orientation of the CH_3 in which coupling to only two of the three protons can be seen, $|a^{H_\gamma}(2H)|$ 0.69 G, the hfs due to the third H_γ bein$\leq$0.1 G. It was pointed out[7] that the H_γ hfs's must be strongly orientation dependent.

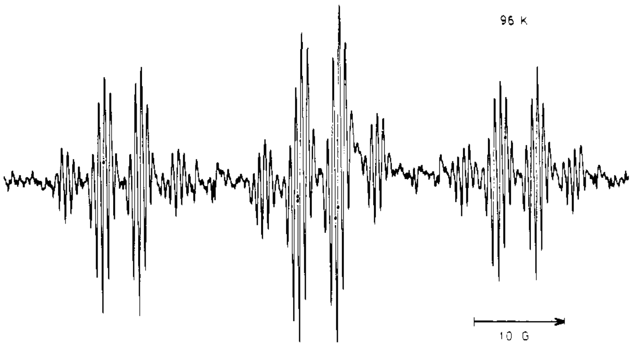


Figure 1. EPR spectrum of neopentyl radical at 96 K in *n*-propane. Several lines from the isopropyl radical can also be observed.

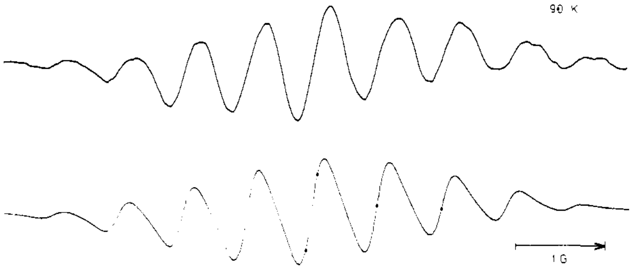
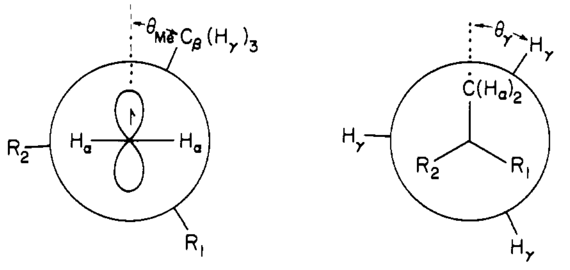


Figure 2. Fine structure of the central line in the low field triplet of isobutyl radical. Top: experiment at 90 K; bottom: simulation with $a(2H) = 1.45$ G, $a(4H) = 0.72$ G.



1a	$R_1 = R_2 = H$	1b	$R_1 = R_2 = H$
2a	$R_1 = H$, $R_2 = CH_3$	2b	$R_1 = H$, $R_2 = CH_3$
3a	$R_1 = R_2 = CH_3$	3b	$R_1 = R_2 = CH_3$

It occurred to us that Ellinger et al.'s[4,5] ab initio calculations should be subject to qualitative and even quantitative experimental verification since at low temperatures the propyl[7] (**1**), isobutyl (**2**), and neopentyl (**3**) radicals should provide probes of the $a^{H}{}_{\gamma}$ dependence on θ_{Me} and, incidentally, on θ_γ. That is, the conformational preferences of these radicals are $\theta_{Me} = 90°$ for *n*-propyl,[7-12] $\theta_{Me} = 60°$ for isobutyl,[7-12,16] and $\theta_{Me} = 45°$ for neopentyl.[17] For the latter two radicals the barrier to CH_3 rotation

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[1] Issued as N.R.C.C. No. 19923.

[2] N.R.C.C.

[3] St. Andrews.

[4] Ellinger, Y.; Rassat, A.; Subra, R.; Berthier, G. *J. Am. Chem. Soc.* **1973**, *95*, 2372–2373.

[5] Ellinger, Y.; Subra, R.; Levy, B.; Millie, P.; Berthier, G. *J. Chem. Phys.* **1975**, *62*, 10–29.

[6] Following Ellinger et al.'s nomenclature[5] the atoms in all radicals considered herein are identified as follows: $H_\alpha\dot{C}C_\alpha H_\beta C_\beta H_\gamma$.

[7] Fessenden, R. W.; Schuler, *J. Chem. Phys.* **1963**, *39*, 2147–2195.

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[9] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846–860.

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[13] That is, rapid jumping between the three orientations allowed by the threefold barrier to rotation about the C_α–C_β bond.[7]

[14] The possibility that this is a double minimum potential well, i.e., $\theta_{Me} = (90 + \delta)°$ and $(90 - \delta)°$, rather than a single minimum is discussed.[5]

[15] Following Ellinger et al.[5] only the results obtained with quasi-localized MO's will be discussed. The canonical MO's led to similar conclusions.[5]

[16] That is, the tertiary H is eclipsed by the $\dot{C}$ $2p_z$ orbital, probably for steric reasons: Ingold, K. U.; Kemball, M.; Walton, J. C., manuscript in preparation.

[17] Rotation about the $\dot{C}$–C_α bond is expected to be rapid[13] because two groups of C_{2v} and C_{3v} symmetries attached to the same single bond lead to a very small ($\leq$0.5 kcal/mol[7-10,18,19]) sixfold rotation barrier; θ_{Me} therefore has an average value of 45°.

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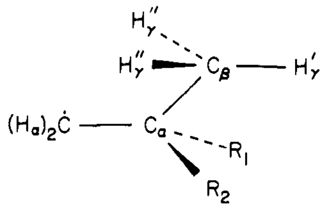
Table I. Comparison of Measured γ-Hydrogen Hyperfine Splittings with Values Calculated for *n*-Propyl in the Appropriate Conformation (hfs in G)

radical	θ_{Me}, deg	H′γ (θ_γ = 180°) measd	H′γ (θ_γ = 180°) calcd[a]	H″γ (θ_γ = 60°) measd	H″γ (θ_γ = 60°) calcd[a]
1	90	+0.10[b]	−0.26	−0.59	−0.27
2	60	+1.45	+0.89	−0.72	−0.49[b]
3	45	+4.04	+2.06[c]	−0.62	−0.48[c]
	0		4.37		−0.69

[a] From Table XIV of ref 5. [b] For θ_γ = −60° the calculated value is −0.23. [c] Estimated from data in Table XIV.

is expected to be somewhat larger than that found for CH_3 rotation in *n*-propyl, viz.,[7] 3.7 kcal/mol.[20] The CH_3 groups in **2** and **3** are therefore expected to be frozen (on the EPR time scale) into the conformation (**4**) having minimum steric interaction at temperatures above that at which the methyl of *n*-propyl freezes out, i.e. at ca. 110 K.[7] For all three radicals the preferred conformation of each methyl should have one hydrogen (H'_γ) with θ_γ = 180° and two hydrogens (H''_γ) with θ_γ = 60°, see **4**.



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As we expected, the neopentyl radical (generated photochemically from di-*tert*-butyl peroxide, triethylsilane, and neopentyl bromide in *n*-propane) at 96 K gave an EPR spectrum (Figure 1) in which the nine γ hydrogens were not all equivalent: $a^{H_\alpha}(2H)$ = 21.4 G; $|a^{H'_\gamma}(3H)|$ = 4.04 G; $|a^{H''_\gamma}(6H)|$ = 0.62 G. As the temperature is raised the lines broaden until at 175 K only a broad triplet remains. At higher temperatures, a new γ structure appears and sharpens until at ca. 225 K hfs's from nine equivalent γ–H can, as previously reported,[21,22] be observed: $|a^{H_\gamma}(9H)|$ = 0.96 G. Similarly, isobutyl (generated by the same technique) at 90 K gave an EPR spectrum having the following hfs's:[23] $a^{H_\alpha}(2H)$ = 21.3 G; $a^{H_\beta}(1H)$ = 35.3 G; $|a^{H'_\gamma}(2H)|$ = 1.45 G; $|a^{H''_\gamma}(4H)|$ = 0.72 G (see Figure 2). At temperatures above 125 K the γ structure broadens and coalesces into a single line. The septet splitting from six equivalent γ-H cannot be resolved.[23]

For neopentyl the spectral width due to the γ hydrogens is 15.84 G at low and 9.64 G at high temperatures. *The signs of the H′ and H″ hfs's must therefore be different*, which confirms the fact that a^{H_γ} is strongly dependent on θ_γ. Following Ellinger et al.[4,5] we assign H′ a positive and H″ a negative sign, i.e., a^{H_γ} (high temperature, 9H) = $(3a^{H'_\gamma} + 6a^{H''_\gamma})/9 = (12.12 - 3.72)/9 = +0.93$ G, which is in satisfactory agreement with the experimental value of 0.96 G. Similarly, for isobutyl we assign $a^{H'}$ = +1.45 G and $a^{H''}$ = −0.72 G; this yields a^{H_γ} (high temperature, 6H) = +0.003 G; which serves to explain why the γ hydrogens of this radical cannot be resolved at high temperatures! Finally, from our own data for *n*-propyl we assign $a^{H''_\gamma}$ = −0.59 and from our $|a^{H_\gamma}$ (high temperature, 3H)$|$ = 0.36 G we conclude that $a^{H'_\gamma}$ = +0.10 G.

The foregoing results are summarized in Table I, where they are compared with the results computed by Ellinger et al.[5] for *n*-propyl in the appropriate conformation. Four facts are clear: (i) a^{H_γ} is strongly dependent on θ_γ for all three radicals; (ii) $a^{H'_\gamma}$ (θ_γ = 180°) is strongly dependent on θ_{Me}, rising from near zero for *n*-propyl (θ_{Me} = 90°) to a predicted maximum of ca. 8 G in the ideal W-plan[25] (θ_{Me} = 0°) arrangement; (iii) $a^{H''_\gamma}(\theta_\gamma = 60°)$ is virtually independent of θ_{Me}; (iv) ab initio calculations give an excellent qualitative and a satisfactory quantitative description of our experimental results.

Registry No. **1**, 2143-61-5; **2**, 4630-45-9; **3**, 3744-21-6.

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[20] Calculation gave 4.79 kcal/mol.[5]

[21] Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3940–3942.

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Electron Transfer Initiated Photoaddition of Allylsilanes to 1-Methyl-2-phenylpyrrolinium Perchlorate. A Novel Allylation Methodology

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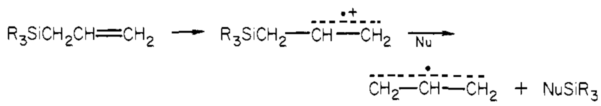
Received September 8, 1981

In previous reports[1-3] we have described our initial exploratory and mechanistic studies of olefin iminium salt photochemistry. In these we described irradiations of 2-phenyl-1-pyrrolinium perchlorate (**1**) in the presence of electron-rich olefins and methanol which lead to formation of interesting adducts. The stuctural, regiochemical, and stereochemical characteristics of these processes are best rationalized by mechanisms involving one electron transfer from the olefins to the singlet excited state of **1** followed by nucleophilic capture of the derived cation radical **3** and coupling, as outlined for isobutylene addition in Scheme I. In some cases the intermediate cation radicals undergo another characteristic reaction involving deprotonation. This is demonstrated in the photochemistry of **1** with cyclohexene which produces the allylic addition product **6** via deprotonation of **4** as outlined in Scheme I. Analogous electron–proton-transfer pathways operate in additions of alcohols and ethers to iminium salts[2] as well as in amine–ketone reductions[4] and amine–aromatic hydrocarbon additions.[5] Another route open to the oxygen-based cation radical generated by electron transfer from 1,1,2-trimethylcyclopropanol is cleavage of the weak, alkyl-substituted cyclopropane bond leading to the 4-butan-2-onyl radical.[2]

Thus, the results of these preliminary studies suggest that cation radicals, generated by one electron transfer from n- and π-electron donors to iminium salts excited states, undergo predictable transformations leading to radical precursors of addition products. We felt that this postulate might be useful in designing new systems to test the validity of the mechanistic rationale and to probe further the synthetic potential of this class of excited-state reactions. In particular, we felt that cation radicals generated by electron transfer from allylsilanes would undergo ready desilylation in the presence of even weak nucleophiles to produce allyl radicals (reaction 1).[6] This pathway should compete ef-



$$R_3SiCH_2CH{=}CH_2 \longrightarrow R_3SiCH_2{-}\overset{\bullet +}{CH{-}CH_2} \xrightarrow[Nu]{} \overset{\bullet}{CH_2{-}CH{-}CH_2} + NuSiR_3 \quad (1)$$

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