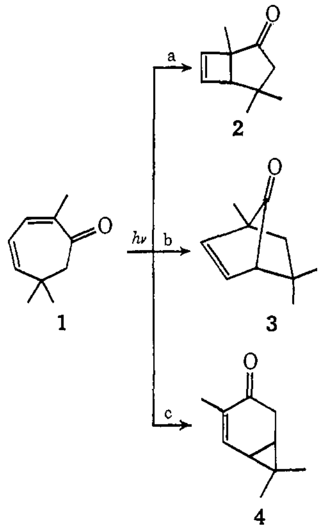
Direct Evidence for an Ionic Intermediate in the Photoisomerization of Eucarvone in Acidic Media[1,2]

Sir:

The photoisomerization of eucarvone (**1**) initially reported by Büchi[3a] is remarkably complex for an ostensibly simple molecule. It has been shown that **1** rearranges by three presumably independent pathways to yield **2**, **3**, and **4** as primary products.[3] Although paths a and c have received some mechanistic consideration,[4] very little has been done to investigate path b. As **3** only becomes an important photoproduct of **1** in acidic media, it would appear that a protonation step is required for the operation of path b. However, interpretation of these results is not straightforward as the distribution of photoproducts from eucarvone is exceedingly sensitive to changes in solvent polarity. We have examined the photochemistry of **1** in buffered solutions of constant polarity, but differing acidity, and find that **2** and **3** may both be derived from the same excitation pathway. An ionic intermediate leading to **3** can be trapped in nucleophilic, acidic solvents.



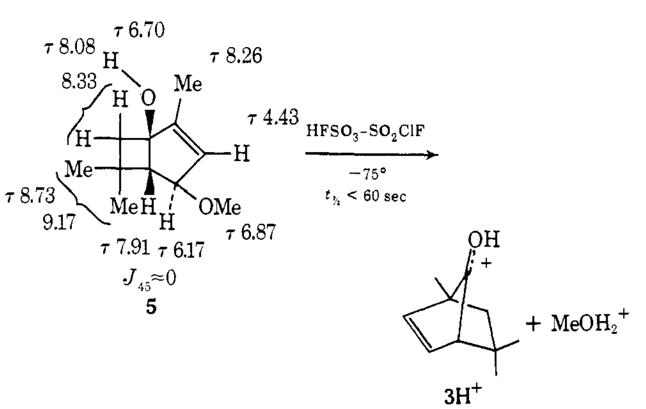
Nitrogen purged 1% solutions of **1**, in standard phosphate buffer solutions[5] (30%) diluted with methanol (70%), were irradiated at 350 nm in a merry-go-round apparatus. The unreacted starting material and products were recovered in high yield by standard procedures and analyzed by glpc. Essentially all material was accounted for and there were no detectable nonvolatile products. The product distribution as a function of the apparent pH is given in Table I. It should be noted that as the acidity of the medium is increased, the amount of **1** reacted and **4** formed both remain constant. This indicates that these solutions have a constant polarity.[3c]

Table I. Product Distribution as a Function of Solvent Acidity

"pH"[a]	% recovery[b]	% conversion[b]	Product ratios, %[b,c]			
			2[d]	3	4[d]	5
6.16	98	9.5	73	nd[e]	27	nd[e]
3.34	98	8.5	70	≤0.5	29	≤0.5
1.62	100	8.5	53	2	27	18
0.7	97	8.5	45	4	28	23

[a] Apparent pH, measured with glass calomel electrodes, 23°. [b] Analysis by glpc using chlorobenzene as internal standard, ∓2%. [c] Expressed as per cent of products. [d] Total per cent includes photoproducts of **2** and **4**, ref 3. [e] Nondetectable <0.5%.

While it is quite clear from the results in Table I that **3** is produced exclusively in the more acidic solvents, only modest amounts of this product were formed. This contrasts with photolyses in other comparable acidic solvents where up to 23% of **3** has been detected.[3b,6] However, in the aqueous methanol solvents an additional, previously unobserved photoproduct was obtained in addition to **3**. This was isolated by preparative glpc and identified as the methoxy alcohol **5** by its spectral properties and analytical data.[8]



Strong supportive evidence for the structure of **5** and its relationship to **3** is the observation that when **5** was dissolved in HSO_3F-SO_2ClF at −110° and observed by nmr after 4 min at −75°, only **3H**$^+$ and protonated methanol could be detected.[3d,9] That **5** was a primary photoproduct of **1** was shown by control experiments in which **2**, **3**, and **4** were each irradiated under conditions where **5** was produced.[10]

The results in Table I strongly indicate that a protonation step occurs at some stage in the route to **3**. The concomitant formation of **5** suggests that the cation **6** must be an intermediate in the reaction sequence, undergoing competitive capture by a nucleophile to give **5** or a 1,2-alkyl shift and deprotonation to give

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[1] Research supported by the National Research Council of Canada.

[2] The Chemistry of Cycloheptadienones. VII. Part VI: K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, **95**, 3289 (1973).

[3] (a) G. Büchi and E. M. Burgess, *ibid.*, 82, 4333 (1960); (b) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 710 (1963); (c) D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Lett.*, 1375 (1964); T. Takino and H. Hart, *J. Amer. Chem. Soc.*, **93**, 720 (1971); (d) K. E. Hine and R. F. Childs, *ibid.*, **93**, 2323 (1971); (e) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1657 (1970).

[4] (a) D. I. Schuster and M. A. Tainsky, *Mol. Photochem.*, **4**, 437 (1972); H. Hart and A. F. Naples, *J. Amer. Chem. Soc.*, **94**, 3256 (1972); (b) K. E. Hine and R. F. Childs, *J. Chem. Soc., Chem. Commun.*, 145 (1972).

[5] R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," 2nd ed, Academic Press, New York, N. Y., 1959; H. T. S. Britton, "Hydrogen Ions," Vol. 1, Van Nostrand, New York, N. Y., 1956.

[6] In dioxane (96%)-1.8 *N* H_2SO_4 (4%) solution the product composition after 2% reaction was **2**, 71%; **3**, 23%, and **4**, 6%. Preferential nucleophilic capture of an intermediate carbonium ion by dioxane would be expected in this medium to give an oxonium ion. Repeated reionization of this ion could allow the 1,2-alkyl shift to compete effectively with the formation of stable covalent products.[7]

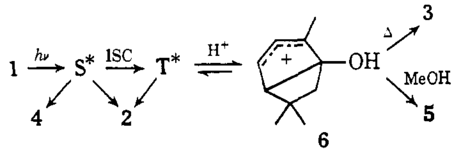
[7] *Cf.* H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 87, 287, 292 (1965).

[8] The 100-MHz pmr spectrum was assigned on the basis of double and triple irradiation experiments: ir (CCl_4) 3550–3150, 3040, 2950, 2930, 2868, 2818, 1690, 1641, 1440, 1455, 1348, 1358, 1290, 1240, 1202, 1164, and 940 cm^{-1}; mass spectral *m/e* 182; uv (MeOH) featureless above 220 nm; satisfactory elemental analysis.

[9] *Cf.* R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **94**, 2347 (1972), and references therein.

[10] Small amounts of other products (<1%) with very similar retention times to **5** were produced after prolonged photolysis. These remain, as yet, unidentified.

3.[9,11] Moreover, these results show that the formation of **3** and **5** with increasing acid concentration occurs solely at the expense of **2**. It would appear that the protonation of a precursor of **2** is giving rise eventually to **6** and thence **3** and **5**. A very close parallel exists between the relative geometry changes and bonding required to form **2** and **6**. Formation of **2** must arise from a disrotatory motion resulting in bonding between C_5 and C_2 in an excited state of **1**, while bonding between C_5 and C_1 is required for the formation of **6**. Unless a proton is available, it would seem that this latter bonding is either of prohibitively high energy to effectively compete, or very rapidly reverts to C_5–C_2 bonding. A possible reaction sequence is shown.



On the basis of quenching studies, Schuster[3e] has suggested that the formation of **2** in benzene occurs from both singlet (n,π*), 60%, and triplet (π,π*), 40%, states of **1**. Analogous results have been obtained by us in 96% dioxane-4% H_2O, although no quenching of **2** and **3** could be detected in acidic solutions.[12] Since under no conditions where unprotonated eucarvone is absorbing energy can all of **2** be diverted to **3** and **5**, it is attractive to consider that in acidic solvents these products derive from protonation of the triplet state of **1**.[14] While the exact timing of this protonation is not known,[15] it is interesting to note that the corresponding hydroxy dienylic cations undergo an exactly comparable C_5–C_1 bonding upon π,π* excitation.[3d,4b]

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(11) It is quite possible that **6** is a ground state, ionic intermediate. *Cf.* H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 84, 4527 (1962), and subsequent papers.

(12) The rate of protonation of a triplet state of **1** is expected to be sufficiently fast to effectively compete with the rate of quenching by piperylene or 1,3-cyclohexadiene.[3d,13]

(13) *Cf.* A. Weller, *Progr. React. Kinet.*, 1, 187 (1961); E. Vander Donckt, *ibid.*, 5, 273 (1970); M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 3, 1 (1964).

(14) Hart[3c] has provided strong evidence that **4** comes from a π,π* singlet state of **1**.

(15) Alternatively protonation may occur after formation of the ground-state zwitterion corresponding to **6**.[16] This seems less likely as the results in Table I would then demand that in the absence of a proton this zwitterion rearranges exclusively to give **2**.

(16) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, 88, 4895 (1966).

K. E. Hine, R. F. Childs*
Department of Chemistry, McMaster University
Hamilton, Ontario, Canada
Received June 13, 1973

On Segmental Motion in Short Aliphatic Chains

Sir:

Segmental motions along short (*e.g.*, four-carbon) aliphatic chains, as observed from ^{13}C spin-lattice relaxation (T_1) measurements, are generally not as marked as are analogous motions along linear aliphatic chains containing $\gtrsim$eight carbons.[1-5] With four-carbon chains rapid overall molecular reorientation masks the internal motions. However, in cases where an *n*-butyl group is effectively anchored at one end, segmental motion can result in observed ^{13}C T_1 ratios of 3–4 between the CH_3 carbon farthest from the anchored end (the δ-CH_3 group, or in general the ω carbon) and the CH_2 carbon α to the site of restriction. Two such instances are the *n*-butylammonium ion in nonpolar solvents[3] and the butyl groups in *N*,*N*-di-*n*-butylformamide.[4]

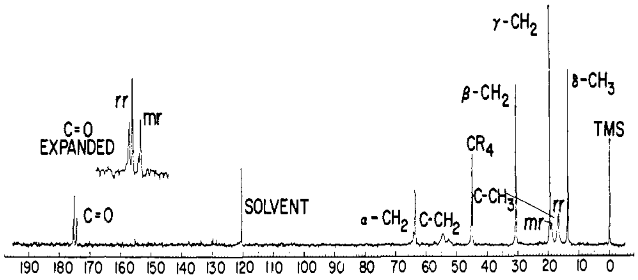

Figure 1. ^{13}C FT nmr spectrum of PBMA. Assignments noted; C–CH_3 and C–CH_2 represent main chain groups. Tacticity assignments are based on analogies with PMMA (tacticity assignments from poly(methyl methacrylate): I. R. Peat and W. F. Reynolds, *Tetrahedron Lett.*, 1359 (1972); J. Schaefer, *Macromolecules*, **4**, 99 (1971); L. F. Johnson, F. Heatley, and F. A. Bovey, *ibid.*, **3**, 175 (1970)); mr and rr refer to meso–racemic and racemic–racemic triads, respectively.

In order to further examine segmental motion along *n*-butyl chains, particularly at the limits of maximum observable internal motion, we have examined the ^{13}C relaxation behavior of a synthetic high polymer, poly(*n*-butyl methacrylate) (PBMA). The ^{13}C Fourier transform (FT) nmr spectrum of PBMA is given in Figure 1. ^{13}C relaxation data for a 25% (w/w) solution of PBMA [mol wt 143,000 by intrinsic viscosity (≡0.583) in $CCl_2{=}CCl_2$] are given in Table I. The T_1 values for the protonated main chain carbons in PBMA are very short, indicative of highly restricted overall and main-chain segmental motions. The overall molecular correlation time for this polymer, $\tau_c \simeq 3 \times 10^{-10}$ sec, is similar to τ_c for synthetic polymer systems previously studied.[6,7] The longer T_1 values for the *n*-butyl chain carbons indicate that each carbon is able to introduce substantial "rotational" contributions to butyl chain segmental motions.

In spite of the large macroscopic viscosity of this solution (~150 cP) the free ends of the short side chains in PBMA have (effective) correlation times more typical of low molecular weight (mol wt 200–400) molecules in mobile solutions ($\lesssim$1 cP).

The ω/α ratio (defined as the T_1 for the terminal CH_3 carbon divided by T_1 for the α-CH_2 carbon in the chain) for this four-carbon chain is >11 with adjacent CH_2 carbons having *ca. threefold* T_1 differentials!

In the much longer 10-carbon chain of 1-decanol[1] an ω/α ^{13}C T_1 ratio of ~5 was observed while in the 15-carbon chains of sonicated dipalmitoyllecithin the ω/α ratio was *ca.* 30.[2] In these as well as other previous cases the T_1 differentials for adjacent CH_2 carbons were always $\lesssim$1.5, considerably smaller than observed in PBMA.

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(1) D. Doddrell and A. Allerhand, *J. Amer. Chem. Soc.*, **93**, 1558 (1971).

(2) Y. K. Levine, N. J. M. Birdsall, A. G. Lee, and J. C. Metcalfe, *Biochemistry*, **11**, 1416 (1972).

(3) G. C. Levy, *J. Chem. Soc., Chem. Commun.*, 768 (1972).

(4) G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972).

(5) G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973).

(6) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).

(7) Note that τ_c is outside of the so-called region of extreme spectral narrowing.[6]