Organic Ions in the Gas Phase. XIX. Hydrogen Randomization in Gaseous $C_7H_7^+$ Ions

Seymour Meyerson,[1a] Harold Hart,[1b] and L. C. Leitch[1c]

Contribution from the Research and Development Department, American Oil Company, Whiting, Indiana 46394; Department of Chemistry, Michigan State University, East Lansing, Michigan 48823; and Division of Pure Chemistry, National Research Council, Ottawa 7, Canada. *Received September 22, 1967*

Abstract: The proposal that the $C_7H_7^+$ ion in the mass spectra of benzyl compounds has the completely symmetrical, ring-expanded tropylium structure rather than that of benzyl has received wide acceptance, but mechanistic details remain unsettled. Isotopic distributions of $C_5H_5^+$ ions in the spectra of benzyl-α-d_2 chloride and alcohol and ethylbenzene-α-d_2 imply complete loss of positional identity of the two deuterium and five protium atoms in the $C_7H_7^+$ intermediate. The corresponding statistics for diphenylmethane-α-d_2 support tropylium-1,2-d_2 as the precursor of the $C_5H_5^+$ ion, but those for bibenzyl-α,β-d_4 indicate, again, complete scrambling. The data can be rationalized qualitatively in terms of energy distribution within the excited parent ion and between the primary decomposition products.

Some 10 years have passed since the $C_7H_7^+$ ion in the mass spectra of benzylic and related compounds was first postulated to have the fully symmetrical tropylium structure rather than that of the benzyl ion.[2-4] This formulation met with virtually no resistance even 10 years ago and seems to have been generally accepted as valid.[5] Although several investigators, in addition to our group at Whiting, have explored aspects of the underlying chemistry,[6,7] a central question, bearing on the mechanism of ring expansion and subsequent decomposition, has remained unsettled. The existence of a problem here was first recognized in the course of a study of the mass spectra of labeled benzyl chlorides and benzyl alcohols.[3,8] The isotopic distributions of $C_5H_5^+$ ions in the spectra of the α-d_2 species of these compounds and of ethylbenzene indicate complete scrambling of the two deuterium and five protium atoms in the $C_7H_7^+$ intermediates. These results rule out what would otherwise seem the simplest way to visualize the formation and further decomposition of a tropylium ion from the original benzyl group[9]—insertion of the α carbon between ring carbons 1 and 2, migration of an α hydrogen to carbon 1, and loss of random pairs of adjacent CH groups as acetylene. Such a sequence, proceeding through a tropylium-1,2-d_2 intermediate, would lead to isotopic distributions of $C_5H_5^+$ in poor agreement with observed values. A model based on labeling studies of methyl-, ethyl-, and dimethylethylbenzenes[6] calls for migration of an α hydrogen to carbon 1, as suggested here, but insertion of the α carbon between any two adjacent carbons in the original benzene ring.

In the hope of better defining the mechanisms involved, we have examined the spectra of diphenylmethane unlabeled, -α-d, and -α-d_2, and bibenzyl unlabeled and -α,β-d_4. In these compounds, the neutral products accompanying formation of $C_7H_7^+$ contain many more atoms than those in the compounds studied earlier, and the presumably changed distribution of excess vibrational excitation between the decomposition products might well alter the picture.

Experimental Section

Materials. To prepare diphenylmethane-α-d, 20.3 g (0.1 mol) of benzhydryl chloride in 75 ml of tetrahydrofuran was refluxed for 24 hr with 1.3 g (0.16 mol) of lithium deuteride and 0.4 g (0.01 mol) of lithium aluminum deuteride (both purchased from Metal Hydrides, Inc.). Hydrolysis and work-up yielded 4.0 g (20%) of *s*-tetraphenylethane, mp 208°, and 8.3 g (50%) of crude diphenylmethane-α-d. To prepare diphenylmethane-α-d_2, benzophenone was reduced with lithium aluminum deuteride in tetrahydrofuran. The resulting benzhydrol-α-d was converted *via* thionyl chloride to benzhydryl-α-d chloride, and the latter was reduced, as described above, to diphenylmethane-α-d_2. The unlabeled diphenylmethane was commercial material. Final purification of all three diphenylmethanes was by gas chromatography.

To prepare bibenzyl-α,β-d_4, 13.6 g (0.10 mol) of methyl benzoate in 50 ml of anhydrous ether was added dropwise to a stirred suspension of 3.0 g (0.11 mol) of lithium aluminum deuteride in 200 ml of anhydrous ether in a flask equipped with a reflux condenser. After 3–4 hr, ethyl acetate was carefully added dropwise through the funnel to decompose excess deuteride and then 100 ml of 10% hydrochloric acid was similarly added to decompose the complex. The ether solution was separated in a funnel, washed with water, and then dried over anhydrous potassium carbonate. Solvent was distilled off and the residue was purified by bulb-to-bulb distillation *in vacuo* to give 10.0 g of benzyl-α-d_2 alcohol, a nearly quantitative yield. The alcohol was converted to benzyl-α-d_2 bromide by heating it under reflux for 4 hr with 20 ml of 48% hydrobromic acid and 3.0 ml of 98.5% sulfuric acid. The reaction mixture was poured into water, and the oil was taken up in ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, and distilled. The residue was purified by bulb-to-bulb distillation under

---

(1) (a) American Oil Company; (b) Michigan State University; (c) National Research Council.

(2) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(3) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10, and references cited there.

(4) S. Meyerson, *Record Chem. Progr.*, **26**, 257 (1965), and references cited there.

(5) See, for example, K. Biemann, "Mass Spectrometry. Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 84; H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 162 ff; R. L. Platzman, *Sci. Am.*, 201, (3) 74 (1959); J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 1136; R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Inc., Boston, Mass., 1966, p 451; and C. R. Noller, "Chemistry of Organic Compounds," 3rd ed, W. B. Saunders Co., Philadelphia, Pa., 1965, p 722.

(6) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

(7) J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964); K. R. Jennings and J. H. Futrell, *ibid.*, **44**, 4315 (1966).

(8) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(9) No implication is intended here as to whether ring expansion precedes or follows loss of the substituent on the α carbon.

reduced pressure (0.03 torr) to give 15.0 g (87%) of nearly colorless bromide. The bromide (15.0 g, 0.09 mol) was dissolved in 100 ml of absolute ether and added to 1.1 g (0.045 g-atom) of magnesium turnings in 50 ml of absolute ether. The reaction mixture was refluxed for 5 hr and then poured into 100 ml of saturated aqueous ammonium chloride. The ether layer was separated, washed with water, dried over anhydrous magnesium sulfate, and freed of solvent. The residue, a mixture of toluene and bibenzyl, was separated by bulb-to-bulb distillation. The bibenzyl was then recrystallized from alcohol, mp 52°. Yield was 3.2 g (38%). Unlabeled bibenzyl, commercial material, was also purified by crystallization, mp 52°.

Mass Spectrometry. Mass spectra were measured on a modified[10] Consolidated Model 21-103 instrument with 70-V electrons, at an inlet temperature of 250°. Isotopic analyses were made in the usual way at reduced ionizing voltage,[11] with the repellers at an average potential of 3 V, the exact values being selected to give maximum sensitivity. The isotopic compositions of the labeled materials were as shown in Table I.

Table I

	Diphenylmethane		Bibenzyl
	α-d	α-d_2	α,β-d_4
d_0, %	2.5	1.0	...
d_1, %	96.9	6.8	0.1
d_2, %	0.6	92.2	2.2
d_3, %	...	...	8.8
d_4, %	...	...	88.9

Table II. Partial Spectra of Diphenylmethanes

Mass	Ion[a]	Unlabeled	α-d	α-d_2
170		...	...	100.0
169		...	100.0	79.9
168	$C_{13}H_{12}^+$	100.0	85.8	10.1
167	$C_{13}H_{11}^+$	92.7	10.0	16.9
166		4.9	24.1	11.7
165		32.0	8.2	2.4
155		...	...	7.5
154		...	9.8	12.0
153	$C_{12}H_9^+$	12.8	13.8	9.3
152		16.7	6.8	2.7
151		1.9	0.9	0.4
144		...	...	0.1
143		...	0.1	2.3
142		0.1	3.1	1.7
141	$C_{11}H_9^+$	4.0	1.2	1.6
140		0.3	2.7	2.1
139		4.7	1.9	0.8
93		...	...	19.7
92		...	21.5	7.3
91	$C_7H_7^+$	22.6	6.1	5.2
90		3.9	5.9	5.4
89		7.8	3.8	1.7
68		...	...	0.1
67		...	0.3	6.8
66		0.4	9.3	8.0
65	$C_5H_5^+$	14.2	6.4	4.8
64		2.1	4.8	5.4
63		10.4	7.3	5.6
62		3.3	2.4	1.9
61		0.7	0.5	0.4
43		0.5	0.6	1.2
42		0.1	1.7	1.4
41		2.6	1.6	3.4
40		1.0	6.1	7.3
39	$C_3H_3^+$	17.6	12.8	10.1
38	$C_3H_2^+$	2.7	2.3	1.9
37		0.6	0.6	0.6

[a] Formulas listed correspond to unlabeled ions of indicated masses.

Partial spectra, shown in Tables II and III, are corrected for contributions of species containing naturally occurring heavy isotopes. Those of the diphenylmethanes are corrected also for contributions of isotopic impurities. The intensity scale in each spectrum is defined by assigning a value of 100.0 to the parent peak; in bibenzyl-d_4, total parent-peak intensity of all the isotopic species present is set equal to 100.0.

Table III. Partial Spectra of Bibenzyls

Mass	Ion[a]	Unlabeled	α,β-d_4
186		...	88.9
185		...	10.5
184		...	5.5
183		...	1.2
182	$C_{14}H_{14}^+$	100.0	3.0
93		...	515
92		0.4	28.6
91	$C_7H_7^+$	554	8.4
90		4.0	5.4
89		8.6	0.8
69		...	0.2
68		...	0.4
67		...	28.1
66		...	30.4
65	$C_5H_5^+$	61.5	11.6
64		3.2	8.4
63		15.3	6.5

[a] See footnote *a* to Table II.

The spectra of both compounds show the expected metastable peaks corresponding to the process $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$.[3] The bibenzyl spectra also show metastable peaks for the process $C_{14}H_{14}^+ \rightarrow C_7H_7^+ + C_7H_7$. The diphenylmethane spectra show metastable peaks for primary loss of H and of CH_3, though not of C_6H_5.

Results

Diphenylmethane. Isotopic compositions of the $C_{13}H_{11}^+$, $C_{12}H_9^+$, and $C_{11}H_9^+$ ions, corresponding respectively to loss from the parent ion of H, CH_3, and C_2H_3 (most likely by successive loss of H and C_2H_2), indicate essentially complete scrambling of the 12 hydrogen atoms in the parent ion.[12] In sharp contrast, retention of the label in $C_7H_7^+$ from diphenylmethane-d and of both labels in $C_7H_7^+$ from the d_2 species—95.1%, and 87.2%, respectively—shows that most of these ions contain the elements of the methylene group. The three heavier fragment ions are thus ruled out as important precursors of $C_7H_7^+$, thereby strongly suggesting that the latter arises chiefly, if not solely, from a primary decomposition.[13]

---

(10) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

(11) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, 72, 5612 (1950); R. E. Honig, *Anal. Chem.*, 22, 1474 (1950).

(12) Calculated and observed retentions of one and two deuterium atoms, respectively, in the fragment ions derived from the singly and doubly labeled molecules are

Ion	Diphenyl-methane	Calcd for complete scrambling, %	Obsd, %
$C_{13}H_{11}^+$	α-d	92	93
	α-d_2	83	86
$C_{12}H_9^+$	α-d	75	77
	α-d_2	55	59
$C_{11}H_9^+$	α-d	75	77
	α-d_2	55	58

Isotope effects, ignored in these calculations, could account for the discrepancies between calculated and observed values.

(13) The same suggestion might be drawn from the substantially higher relative intensity of $C_7H_7^+$ in the spectrum of diphenylmethane than in those of the isomeric methylbiphenyls ["Catalog of Selected Mass Spectral Data," Serial No. 906 and 907, American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas (loose-leaf data sheets, extant, 1968)].

Retention values so close to 100% but yet differing significantly from it are somewhat disconcerting. They rule out the most readily visualized process—dissociation of the $C_6H_5CH_2$–C_6H_5 bond in the original structure—as the sole source of $C_7H_7^+$ ions, and they are not easy to rationalize.[14] The statistics can be approximated by assuming dissociation of this bond coupled with a 50:50 chance of exchanging one hydrogen atom taken at random from the benzyl group with one from the phenyl; the respective retention values so calculated for the d_1 and d_2 species are 92.9 and 85.7%. A similar situation was encountered in the decomposition under electron impact of labeled *p*-xylenes to $C_7H_7^+$ and CH_3.[15] Here, also, the deuterium labeling statistics can be accounted for by assuming a 50:50 chance of exchanging one hydrogen atom taken at random from the ring with one from the methyl group lost. In xylene, even this, however, is not the whole story, because an estimated 16% of the methyl radicals lost contain carbons originally in the ring. A further somewhat similar set of puzzling statistics occurs in the decomposition of labeled toluenes to $C_6H_5^+$ and CH_3.[16] Here, the ion seems to contain four hydrogens randomly selected from the five originally in the ring, plus one from the methyl group.

Regardless of the precise mechanistic path leading to $C_7H_7^+$, the ion is presumably best represented as tropylium. Table IV shows the values derived from the spectra for retention of one and two labels, respectively, in the $C_5H_5^+$ ions from the singly and doubly labeled compounds, and the corresponding values calculated for two postulated cases. In both, $C_5H_5^+$ is assumed to be derived solely from $C_7H_7^+$—in case I, by a process in which the seven hydrogens in the intermediate lose positional identity; in case II, by loss of random pairs of adjacent CH groups from an intermediate in which the originally α hydrogens are fixed on adjacent carbons. Unlike all previously studied benzyl-α-d_2 systems, the data on diphenylmethane-α-d_2 seem to favor a tropylium-1,2-d_2 intermediate rather than a species in which the seven hydrogens lose positional identity.

Table IV. Label Retention in $C_5H_5^+$ from Labeled Diphenylmethanes

Diphenyl-methane	Calcd, % Case I	Case II	Obsd, %
α-*d*	68.0	68.0	65.5
α-d_2	41.6	49.8	48.8

Bibenzyl. Spectra of the singly, doubly, and triply labeled bibenzyls, which would be needed to correct the bibenzyl-α,β-d_4 spectrum for isotopic impurities, are not available. However, the isotopic distribution corresponds to random pairs of benzyl groups from a population with the distribution: d_0, 1.0%; d_1, 4.7%; and d_2, 94.3%. Assuming that this is in fact the distribution of $C_7H_7^+$ ions formed and that the total $C_7H_7^+$ intensity in the spectrum of the labeled species equals 554 units, as in that of the unlabeled one, leads to calculated intensities of 522, 26.0, and 5.5 at masses 93, 92, and 91, respectively. The first two of these agree reasonably well with the observed intensities, and the third is compatible with the measured spectrum, in which the intensity at mass 91 doubtless includes contributions from labeled $C_7H_6^+$ and $C_7H_5^+$ ions.

Assuming now that the calculated distribution of $C_7H_7^+$ ions is correct, that $C_5H_5^+$ ions are derived solely from $C_7H_7^+$ precursors, and that the total $C_5H_5^+$ intensity in the spectrum of the labeled species equals 61.5 units, as in that of the unlabeled one, permits a similar calculation of the $C_5H_5^+$ intensities. Table V shows the values so calculated for the same two cases considered for diphenylmethane, as well as the observed values. Agreement is excellent for case I, poor for case II. The process leading to $C_5H_5^+$ from bibenzyl involves randomization of the seven hydrogen atoms in the $C_7H_7^+$ intermediate, as in benzyl chloride, benzyl alcohol, and ethylbenzene, but unlike diphenylmethane.

Table V. $C_5H_5^+$ Intensities in the Spectrum of Bibenzyl-α,β-d_4, Including Isotopic Impurities

No. of D atoms	Mass	Calcd, % Case I	Case II	Obsd, %
2	67	27.6	35.2	28.1
1	66	29.7	17.6	30.4
0	65	4.2	8.8	11.6[a]

[a] Includes contributions from labeled $C_5H_4^+$ and $C_5H_3^+$.

Discussion

The contrasting behavior of diphenylmethane and the smaller benzyl-containing molecules studied earlier can plausibly be accounted for in terms of differing distributions of vibrational excitation In each of the smaller molecules, the neutral product formed with $C_7H_7^+$ has no or few bonds, and excess vibrational excitation would seem of necessity to be heavily concentrated in the ionic product. But in diphenylmethane, the neutral product has almost as many bonds as the ion, and one might expect such excitation to be distributed about equally between the products. Although the available data can furnish no precise description of events at the molecular level, thus halving the excitation deposited in the $C_7H_7^+$ ion might yield a more "well-behaved" entity, less inclined to engage in the contortions of which hydrogen scrambling is the visible evidence.

Alternatively, a referee has suggested that the data might be accounted for by a quite different model. He points out that the greater $C_5H_5^+$:$C_7H_7^+$ intensity ratio in the spectrum of diphenylmethane (0.63) than in those of toluene (0.12),[3] benzyl chloride (0.11),[3] and bibenzyl (0.11) may mean that the $C_7H_7^+$ ions from diphenylmethane have greater internal excitation and consequently decompose so rapidly that there is not sufficient time for hydrogen randomization to occur. However, this intensity ratio in the spectra of benzyl alcohol (0.46)[3] and the benzyl free radical (0.71)[3] has values near that of diphenylmethane and in both of these cases the hydrogen atoms are fully scrambled in

---

(14) Similarly, in unpublished work on the mass spectra of triphenylmethane unlabeled and -α-*d*, we find that the label is neither retained quantitatively in the parent-minus-C_6H_5 ion nor lost quantitatively in the parent-minus-H ion, contrary to results reported by V. K. Potapov, D. N. Shigorin, A. D. Filyugina, and V. V. Sorokin, *Zh. Fiz. Khim.*, **40**, 2332 (1966).

(15) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

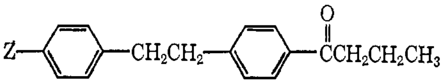
(16) P. N. Rylander and S. Meyerson, *J. Chem. Phys.*, **27**, 1116 (1957).

the process leading to $C_5H_5^+$. The relevance of this intensity ratio to the present problem is thus not clear. Moreover, label retentions in the $C_3H_3^+$ ions, estimated from the spectra of the labeled diphenylmethanes [$(C_6H_5)_2CHD$, 71%; $(C_6H_5)_2CD_2$, 47% including both singly and doubly labeled ions], agree closely with the corresponding values calculated for a process in which all the hydrogens in the parent ions are scrambled (75 and 45%). Label retentions so calculated for the $C_5H_5^+$ ions [$(C_6H_5)_2CHD$, 58%; $(C_6H_5)_2CD_2$, 15% for both deuterium atoms] do not agree well with the observed values, listed in Table IV. The $C_5H_5^+$ ion is known to break down further to $C_3H_3^+$ and C_2H_2 in toluene[17] and many other compounds, but the statistics rule out this process as the major contributor to $C_3H_3^+$ formation in diphenylmethane. Thus, although proportionately more of the $C_7H_7^+$ ions derived from diphenylmethane than from toluene decompose to $C_5H_5^+$, the extent of further decomposition to $C_3H_3^+$ seems to be less. Connecting links among these observations are not readily apparent. In the absence of any clear evidence to the contrary, we prefer the hypothesis introduced in the preceding paragraph, and it does seem to fit into a self-consistent framework with a number of independent results.

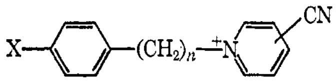
If this view is valid, bibenzyl might *a priori* be expected also to give rise to a "cool" $C_7H_7^+$ ion, but such an expectation is belied by the experimental data. A possible way of accommodating the bibenzyl results within the proposed framework is suggested by the electronic absorption spectra of compounds comprising two chromophoric groups separated by chains of zero to about 12 methylene groups.[18] If the chain contains two or more methylene groups, the absorption spectrum is essentially a summation of the absorption of the two chromophores. Thus, in bibenzyl, for example, the two-carbon chain insulates the phenyl groups from each other and the absorption of electronic excitation by either π-electron system is insensitive to the presence of a second such system in the molecule. Similarly, the charge and electronic excitation deposited in a bibenzyl molecule by electron impact may well be trapped in one or the other phenyl ring, which presumably acts as a potential well.[19] Any incipient transfer of vibrational energy through the connecting chain might be expected to have a high probability of rupturing the weak central bond. Thus, vibrational excitation also would in effect be trapped in the same half of the original molecule that contains the charge. The $C_7H_7^+$ ions arising from such a system would then retain essentially all the excess energy of the decomposing parent ion, as seems to occur in the smaller benzyl-containing compounds but not in diphenylmethane.

A similar suggestion has been offered by Svec and Junk,[20] who, from study of the ionization potentials of disubstituted alkanes and appearance potentials of derived fragment ions, found support for the occurrence of "isolated ionization" provided the substituents are separated by at least two carbon atoms. Similarly, the ionization potentials of 1,4-pentadiene and 1,5-hexadiene, in contrast with those of conjugated and allenic dienes, show no effect of the second double bond, but are essentially equal to those of 1-alkenes.[21]

In seeming sharp contrast to such postulated insulation of the two π-electron systems in bibenzyl are dramatic effects of substituents Z on the mass spectra of a series of substituted bibenzyls[22]



For Z = H, NO_2, or $COCH_2CH_2CH_3$, the spectra show intense peaks associated with reactions directed by the carbonyl group. But for Z = NH_2, these reactions are all but eliminated, and an ion consisting of the elements of the aminobenzyl group is the most abundant ion in the spectrum. These effects were interpreted[22] as signaling a high degree of localization of the charge and radical site in the aminobenzyl group, which implies rapid charge migration to the preferred site unless, as seems unlikely, the initial ionizing event itself is similarly localized. The apparent contradiction between this evidence and ours can be dispelled by assuming that substituting the two bibenzyl rings with groups having markedly different electron-withdrawing or -releasing properties can produce a steep enough potential gradient to effect transfer of charge, and possibly also excitation, from one π-electron system to the other through space. This suggestion also gains support from an apparent parallel in the electronic absorption spectra of a related series of compounds.[23] The spectra of substituted phenylalkylpyridinium chlorides



in which X = OCH_3, a strongly electron-releasing substituent, show absorption bands that appear to arise from intramolecular charge transfer between nonconjugated donor and acceptor groups. The wavelength of maximum absorption is independent of n, the length of the intervening chain, for values of n from 1 to 4, but the intensity of absorption goes through a pronounced maximum at $n = 2$. Inspection of models indicated[23] that at all values of n, the two rings can occupy positions that allow their π-electron systems to interact, and that increasing n from 1 to 2 facilitates such interaction. Further increase of the chain length apparently decreases the probability that the donor and acceptor groups will meet in a favorable conformation.

Finally, within the framework of the rationale offered here, the finding of even a single instance in which the $C_5H_5^+$ ions in the spectrum of a benzyl-α-d_2 compound are formed *via* a tropylium-1,2-d_2 intermediate furnishes strong support for ring expansion by the straightforward mechanistic path suggested in the introduction to this paper. The mechanism by which hydrogen randomization is effected in the other cases studied remains unsettled, although Meyer and Harrison's model[6] appears able to rationalize the data for

---

[17] S. Meyerson, *J. Am. Chem. Soc.*, **85**, 3340 (1963).

[18] P. Ramart-Lucas, *Bull. Soc. Chim. France*, **51**, 289, 965 (1932).

[19] Evidence has been reported for such localization of charge and excitation on the sulfur atom of γ-irradiated, amorphous *n*-alkyl disulfides: F. K. Truby, D. C. Wallace, and J. E. Hesse, *J. Chem. Phys.*, **42**, 3845 (1965).

[20] H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 790 (1967).

[21] J. Collin and F. P. Lossing, *ibid.*, **81**, 2064 (1959).

[22] T. Wachs and F. W. McLafferty, *ibid.*, **89**, 5044 (1967).

[23] J. W. Verhoeven, I. P. Dirk, and T. J. de Boer, *Tetrahedron Letters*, 4399 (1966).

at least some benzyl compounds. Further clarification may come from a study now in progress on a doubly ^{13}C-labeled toluene.[24]

Acknowledgments. We are indebted to A. W. Weitkamp, of the American Oil Company, for help in gas-chromatographic purification of the diphenylmethanes and to R. D. Hites, of the American Oil Company, and M. M. Green, of the University of Michigan, for directing our attention to relevant spectroscopic literature.

(24) K. L. Rinehart, University of Illinois, private communication; K. L. Rinehart and A. C. Buchholz, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, Paper S-85.

The Photochemistry of Acetylenic Compounds. The Photochemical Reduction of Some Conjugated Acetylenic Carbonyl Compounds

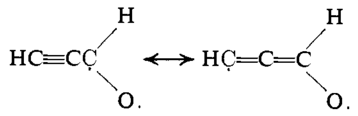
Joseph W. Wilson and Vernon S. Stubblefield

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. Received December 28, 1967

Abstract: The irradiation of 5,5-dimethyl-3-hexyn-2-one (**1**) in isopropyl alcohol produced: 2,3-dimethyl-2,3-butanediol (**3**), 2,3,6,6-tetramethyl-4-heptyn-2,3-diol (4), and 2,2,5,6,9,9-hexamethyl-3,7-decadiyn-5,6-diol (**5**). The irradiation of methyl 4,4-dimethyl-2-pentynoate (**2**) in methanol produced the reduction products, *cis*- and *trans*-methyl 4,4-dimethyl-2-pentenoates (**6**). These were transformed to methyl (2,2-dimethylcyclopropyl)acetate (**7**) on longer irradiation. A considerable amount (at least 60% of the total product) of higher molecular weight material was also formed. The contrasting nature of the products from the two similar starting materials is interpreted in terms of two different excited states.

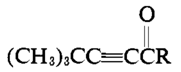
Although the solution photochemistry of the carbon–carbon double bond is becoming well understood, the corresponding excited-state reactivity of the carbon–carbon triple bond in solution has received much less attention. The most common photochemical reaction involving acetylenes is the intermolecular addition of a variety of functional groups,[1] *e.g.*, the carbonyl group,[1b] the carbon–carbon double[1c] or triple bond,[1d] a nitro group,[1e] or an aromatic ring,[1f] to an acetylenic bond. Some of these reactions probably involve the addition of an electronically excited molecule to a ground-state acetylene. There are few examples of reactions in which the excitation energy is known to reside in the acetylenic molecule. The photochemical dimerizations of phenylacetylene[1f] and tolan[1d] and the several intramolecular reactions of diacetylenes[2,3] necessarily belong to this category. There are three recent reports of this reaction type. Owen[4] has interpreted the photochemical oxidation of diphenylacetylene in solution as a reaction between oxygen and triplet tolan. Jorgenson[5] has studied the photochemical addition of acetylenic ketones to olefins and has found that only the carbonyl moiety is involved in the reaction. Recently Ben-Efraim[6] has discovered an interesting reduction of conjugated diacetylenes to vinylacetylenes.

Conjugated acetylenic carbonyl compounds offer several advantages for mechanistic studies of the effect of structural variations on reactivity that conjugated olefinic carbonyl compounds do not offer. The synthesis of a variety of conjugated acetylenic ketones and esters is relatively easy and their photochemistry is not complicated by two of the common reactions of acyclic olefinic ketones, *cis–trans* isomerization and dimerization to cyclobutanes. The possibility of observing some interesting photochemistry of acetylenic carbonyl compounds was suggested by a report[7] that the excited state resulting from the first singlet–singlet, n → π* transition in propynal is best represented as a planar delocalized species



$$HC\equiv\dot{C}\!<^{H}_{O\cdot} \longleftrightarrow H\dot{C}=C=C<^{H}_{O\cdot}$$

In this paper we report a study of the products obtained from the ultraviolet irradiation of compounds **1** and **2** in alcohol.



$$(CH_3)_3CC\equiv C\overset{\overset{O}{\|}}{C}R$$

1, R = CH_3
2, R = OCH_3

Results

5,5-Dimethyl-3-hexyn-2-one (**1**) was prepared by the oxidation of the propargyl alcohol derived from *t*-

---

(1) (a) A recent review contains many examples: R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966); (b) G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Am. Chem. Soc.*, **78**, 876, (1956); (c) R. Criegee, U. Zirngibl, H. Furrer, D. Seeback, and G. Freund, *Chem. Ber.*, **97**, 2942 (1964); (d) G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962); (e) M. L. Sheinbaum, *ibid.*, **29**, 2200 (1964); (f) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

(2) E. Müller, M. Sauerbier, and J. Heiss, *Tetrahedron Letters*, 2473 (1966).

(3) E. H. White and A. A. F. Sieber, *ibid.*, 2713, (1967).

(4) R. C. Henson, J. L. W. Jones, and E. D. Owen, *J. Chem. Soc.*, *A*, 116 (1967).

(5) M. J. Jorgenson, *Tetrahedron Letters*, 5811 (1966).

(6) D. A. Ben-Efraim, *ibid.*, 957 (1967).

(7) J. C. D. Brand, J. H. Callomon, and J. K. G. Watson, *Discussions Faraday Soc.*, **35**, 175 (1963).