formate all fail to give H_2 upon photolysis under the conditions used for BUP. Furthermore, as the data in Table II show, our results from this system agree well with the H-atom data obtained from our thiol systems and from studies of the high-energy radiolysis of aqueous solutions. Also, it might be pointed out that the photolysis of HCO_2O-*tert*-Bu to give H· and CH_3CO_2O-*tert*-Bu to give CH_3· seems quite analogous;[10a] unpublished data from our laboratories[10b] indicate that H atoms and methyl radicals show very similar selectivity in their reactions.[2a]

It is also possible that some as yet unknown type of photolytic interaction between a thiol and BUP could give H_2 or HD. This suggestion appears equally unlikely, since in a subsequent communication[11] we will describe a thiol-free perester system which gives relative k_H values very similar to those obtained when thiol is present.

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(10) (a) R. Sheldon and J. K. Kochi (*J. Amer. Chem. Soc.*, **92**, 5175 (1970)) have shown that peresters of the type RCO_3R', where R is an alkyl group, give R· when photolyzed in solution; (b) unpublished data of W. A. Pryor and D. Fuller.

(11) W. A. Pryor and R. W. Henderson, in preparation.

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Decomposition of Benzene under Electron Impact[1-3]

Sir:

Five primary decomposition reactions are readily discernible in the mass spectrum of benzene: the loss of H·, H_2, C_2H_2, C_3H_3·, and CH_3· to yield, respectively, $C_6H_5^+$, $C_6H_4\cdot^+$, $C_4H_4\cdot^+$, $C_3H_3^+$, and $C_5H_3^+$.[4] The spectra of variously deuterated benzenes show complete loss of position identity of the six hydrogens in the formation of the four of these products for which the available data permit confident conclusions.[5-7] This finding is, of course, implicit in the loss of H·, and it is not too surprising in the loss of CH_3·, which necessarily requires some drastic reorganization of the molecule. The loss of C_2H_2 and that of C_3H_3·, however, are so easily visualized as proceeding by rupture of appropriate pairs of carbon–carbon bonds in the original ring that the observed randomization has constituted a troublesome problem.

Similar loss of position identity of hydrogens and—although supporting data here are fewer—of carbons as well is widespread in formally benzylic ions, most notably $C_7H_7^+$, under electron impact.[8,9] However, much of this randomization seems to occur, probably *via* ring expansion, in the process of forming the benzylic ions. Perhaps more to the point, such randomization has been shown to occur in the molecular ions of many aromatic and heteroaromatic nuclei with no skeletal substitution.[5,10] In this context, benzene is of particular interest as the prototype aromatic compound and by virtue of its high symmetry.

The discovery in the past few years of the surprising skeletal isomerizations occurring in substituted benzenes[11,12] and thiophenes,[13] and in unsubstituted benzene[14] as well, under ultraviolet irradiation[15] offered an attractive rationale for randomizing processes in the same and related compounds under electron impact. In particular, interconversion and/or rearomatization of Dewar benzenes (**1**), prismanes (**2**), and benzvalenes (**3**) so formed, as is known to occur thermally and photochemically, could effect trans-

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(1) Taken in part from M.S. Thesis of W. O. Perry, Purdue University, 1970.

(2) Presented in part before the 21st Mid-America Symposium on Spectroscopy, Chicago, Ill., June 1970.

(3) Organic Ions in the Gas Phase. XXV. For paper XXIV in this series, see S. Meyerson, C. Fenselau, J. L. Young, W. R. Landis, E. Selke, and L. C. Leitch, *Org. Mass Spectrom.*, **3**, 689 (1970).

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Table I. Isotopic Composition of Labeled Benzene

No. of ^{13}C atoms	2	1	0	2	1	0
No. of D atoms	4	4	4	3	3	3
%	23.1	50.5	21.8	1.0	2.2	1.1

Table II. Isotopic Composition of $C_4H_4\cdot^+$ Ions

No. of ^{13}C atoms	0	1	0	2	1	0	2	1	2
No. of D atoms	2	2	3	2	3	4	3	4	4
Nominal mass	54	55	55	56	56	56	57	57	58
% obsd	18.5	19.2	23.1	4.8	22.6	3.9	5.4	2.6	ND[a]
Uncertainty	1.0	0.7	0.4	0.6	0.6	1.0	1.1	0.5	
% calcd, I	10.3	21.5	27.6	8.9	25.3	6.4			
II	17.5	16.3	22.2	4.5	27.4	2.9	5.6	2.7	0.9
III	17.5	19.2	22.3	3.7	25.3	2.9	4.8	3.3	0.9

[a] Not detected.

Table III. Isotopic Composition of $C_3H_3^+$ Ions

No. of ^{13}C atoms	0	1	0	2	1	0	2	1	2
No. of D atoms	1	1	2	1	2	3	2	3	3
Nominal mass	40	41	41	42	42	42	43	43	44
% obsd	10.4	8.3	30.3	2.7	25.0	15.0	2.9	5.5	ND
Uncertainty	1.5	0.5	1.4	0.3	0.4	1.9	0.3	0.6	
% calcd, I	4.8	11.5	30.5	4.6	29.1	19.5			
II	12.2	7.1	34.6	1.7	20.2	11.4	4.6	6.5	1.5
III	12.5	9.5	36.8	1.2	15.2	11.9	3.3	8.9	0.8

position of ring carbons without disturbing the carbon–hydrogen bonds.


1


2


3

To help define the mechanisms responsible for the observed loss of identity of the hydrogens in benzene, we postulated three cases: I, scrambling of the six carbon atoms without breaking the carbon–hydrogen bonds; II, scrambling of the hydrogens with no loss of position identity of carbon atoms; III, independent scrambling of carbons and hydrogens. To distinguish among these cases, we have prepared and examined the behavior under electron impact of benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4. Findings of two other closely related studies[16,17] appeared while our results were being prepared for publication. The isotopic distribution of $C_4H_4\cdot^+$ ions derived from benzene-*1,3,5*-$^{13}C_3$ *via* metastable transitions in the first field-free region of a double-focusing mass spectrometer agrees closely with that calculated for loss of random pairs of carbons as C_2H_2.[16] Similarly, the isotopic distributions of $C_6H_4S\cdot^+$, $C_7H_8\cdot^+$, $C_7H_5S^+$, and CHS^+ derived from benzo[*b*]thiophene-*2*-^{13}C, in which the sulfur atom serves as a second label, reveal extensive scrambling of the skeletal atoms.[17]

Benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4[18] was prepared by Diels–Alder condensation of maleic-*2,3*-$^{13}C_2$ anhydride with 1,3-butadiene-d_6, followed by simultaneous dehydrogenation and decarboxylation with lead tetraacetate in dimethyl sulfoxide in a sealed tube at 55°.[19] For safekeeping and for convenient introduction into the mass spectrometer, samples were sealed in indium tubes[20] containing an estimated 0.01–0.1 μl each. Mass spectral isotopic analysis of the product from an identical preparation using unlabeled maleic anhydride, estimated from a low-voltage spectrum[21] on a CEC Model 21-103 instrument, showed no more than a possible trace of benzene-d_5 and thus effectively ruled out hydrogen exchange in the synthesis. Nmr spectroscopy[22] confirmed the presence of a substantial amount of the desired species, benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4.

Mass spectra were measured on a Hitachi-Perkin-Elmer Model RMH-2 double-focusing instrument[23] at the following operating conditions: ionizing voltage, 70; total filament emission, 1 ma; ion-accelerating voltage, 7500; maximum resolution, 20,000 (5% valley definition). The comparatively low limiting resolution represents a compromise in the balance of resolution *vs.* sensitivity, necessitated by the small sample size, which gave nominal source pressures of $1\text{-}2 \times 10^{-7}$ Torr. A low-resolution spectrum revealed no appreciable impurity; subsequent high-resolution measurements were made at slow scan speeds only in mass regions of interest.

The isotopic composition of the benzene, derived from the intensity distribution of molecular ions, uncorrected for naturally occurring heavy-isotopic species, is shown in Table I. The values for the d_3 species are estimates at best because of incomplete resolution from corresponding isotopic $C_6H_5^+$ ions, in each case differing in mass from the ion of interest

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by about one part in 55,000. Summing the species having the same nominal mass leads to an isotopic distribution in fairly close agreement with that measured at low voltage[21] on a CEC Model 21-103 instrument, and the sum of the d_3 species agrees with that found by low-voltage low-resolution measurement on the benzene prepared from unlabeled maleic anhydride, 4.3%. Thus the analysis shown seems to be reasonably accurate.

Table II shows the observed isotopic distribution of $C_4H_4\cdot^+$ ions and the distribution calculated for cases I, II, and III from benzene with the isotopic composition listed in Table I. Table III shows the corresponding distributions of $C_3H_3^+$. The observed values are all averages of three measurements; the stated uncertainties are average deviations. Two conclusions can be drawn within the uncertainty limits of the experiment.

(1) The presence of $C_4H_4\cdot^+$ and $C_3H_3^+$ ions of nominal mass greater than 56 and 42, respectively, requires contributions from processes corresponding to case II, case III, or both. In view of the recently reported results on $C_4H_4\cdot^+$ ions from benzene-*1,3,5*-$^{13}C_3$[16] case III is preferred over case II.

(2) The yields of $^{12}C_4D_4\cdot^+$, $^{13}C_2{}^{12}CH_2D^+$, $^{13}C^{12}C_2HD_2^+$, and $^{12}C_3D_3^+$ are almost certainly greater and those of $^{12}C_3H_2D^+$, $^{12}C_3HD_2^+$, and $^{13}C^{12}C_2D_3^+$ less than can be accounted for by case II or III and therefore require contributions from processes corresponding to case I as well. The data permit a rough estimate of 30% for the fraction of $C_3H_3^+$ and—though with less confidence—$C_4H_4\cdot^+$ ions that arise by paths in which the carbon atoms are scrambled without breaking the carbon–hydrogen bonds. In the remaining 70%, the hydrogens are scrambled over and beyond whatever carbon scrambling may occur.[23a]

Further work on this system is in progress.

[23a] NOTE ADDED IN PROOF. A mass spectral study of scrambling in benzene-*1*-^{13}*C*-*1*-*d* was reported by D. H. Williams at the Fifth Triennial International Mass Spectrometry Conference, Brussels, Aug 31–Sept 4, 1970 (*J. Chem. Soc.*, in press). He reported that isotopic distributions derived from metastable-peak intensities indicate complete randomization of the carbons and hydrogens independently in the path $C_6H_6\cdot^+ \rightarrow C_4H_4\cdot^+ + C_2H_2$. The difference between our results and those on benzene-*1*-^{13}*C*-*1*-*d* and benzene-*1,3,5*-$^{13}C_3$[16] presumably reflects the difference in the lifetimes of the decomposing ions leading to normal and metastable peaks.

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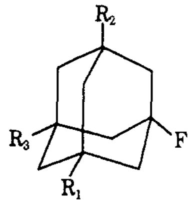
Alkyl Group Substituent Effects in the Adamantane System. Fluorine-19 Chemical Shifts

Sir:

There has been considerable controversy regarding the electronic effect of alkyl groups attached to sp^3-hybridized carbon atoms.[1] For example a methyl group at the 3 position retards the rate of solvolysis of 1-bromoadamantane,[2] thus apparently withdrawing electron density from the adamantane ring. However, Gleicher, *et al.*,[3] have presented data from radical abstraction reactions which indicate that the methyl group may also be electron donating in the adamantane system. In other systems there is additional confusion.[1]

We wish to present the results of our study of the ^{19}F nmr spectra of a variety of alkyl-substituted 1-fluoroadamantanes (I) which bear directly on this question. We chose ^{19}F nmr spectroscopy because the great range of chemical shifts usually encountered often makes possible the discrimination of subtle environmental differences. In this connection, several recent studies are pertinent.[4–6] All compounds[7] were prepared from the corresponding bromides by reaction with silver(I) fluoride in refluxing cyclohexane.[8] Our ^{19}F nmr results are collocated in Table I.



I

The most striking feature of the data is the large *shielding* effect exhibited by the methyl group. The value of +2.8 ppm should be compared with +3.6 and +5.0 ppm found for $-CO_2R$ and $-F$ as substituents in the same system.[9] This methyl effect is additive as

Table I. Fluorine-19 Nmr Chemical Shifts of Alkyl-Substituted 1-Fluoroadamantanes (I)

R_1	R_2	R_3	Chemical shift[a]	SCS[b]
H	H	H	130.0	0.0
CH_3	H	H	132.79	2.79 (2.79/CH_3)
CH_3	CH_3	H	135.29	5.29 (2.65/CH_3)
CH_3	CH_3	CH_3	137.78	7.78 (2.60/CH_3)
C_2H_5	H	H	132.29	2.29
i-C_3H_7	H	H	131.25	1.25
tert-C_4H_9	H	H	130.15	0.15

[a] Chemical shifts are in parts per million upfield from internal $CFCl_3$ in dilute CCl_4 solution measured at 56.4 or 94.3 MHz using the side-band modulation technique and reading shifts directly from an H–P 5212-A frequency counter. Precision was always better than ±0.05 ppm. Separate experiments showed that concentration variation had virtually no effect on the observed shift. [b] Substituent chemical shift = (chemical shift of compound) − (chemical shift of 1-fluoroadamantane).

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