Studies in Mass Spectrometry. XXVI.[1] Hydrogen Scrambling in Some $C_6H_5X\cdot^+$ and $C_6H_5^+$ Ions Generated upon Electron Impact. Comparison of the Spectra of Diphenyl Ether and Diphenyl Carbonate

Dudley H. Williams, S. W. Tam, and R. Graham Cooks

Contribution from the University Chemical Laboratory, Cambridge, England.
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Abstract: The kinetic approach to mass spectrometry has been utilized to illustrate that (i) only a minor portion of the molecular ion from diphenyl ether has the same structure and energy distribution as the $M - CO_2$ ion from diphenyl carbonate, *or* (ii) all (or part) of the $C_{12}H_{10}O\cdot^+$ ions from diphenyl ether have the same structure as the $M - CO_2$ ions from diphenyl carbonate but less internal energy. The species ($C_{12}H_{10}O\cdot^+$), which is common to the two spectra, undergoes randomization of the hydrogens within the phenyl rings prior to loss of a hydrogen atom, or prior to sequential loss of carbon monoxide and a hydrogen atom. Application of the kinetic approach suggests that two $C_6H_5^+$ species are generated from diphenyl carbonate at 70 eV, although the possibility that only the same $C_6H_5^+$ ion as from diphenyl ether is produced but with less internal energy cannot be excluded. Deuterium-labeling experiments establish that the $C_6H_5^+$ ions generated from chloro-, bromo-, and iodobenzenes, and from diphenyl ether undergo randomization of the hydrogen atoms prior to the elimination of acetylene. The hydrogens of fluorobenzene are also randomized prior to the elimination of acetylene or hydrogen fluoride from the molecular ion. The randomization processes may well not involve C–H bond breaking, but rather occur *via* benzvalene and prismane structures, in analogy to those generated by photochemical excitation.

One of the most interesting problems in mass spectrometry concerns the details of the reactions undergone by benzene and its mono- and disubstituted derivatives upon electron impact. It has recently been established[2] by deuterium labeling that the form (or forms) of the $C_6H_6\cdot^+$ ion from benzene which undergoes further fragmentation contains randomized hydrogens. Similarly, randomization of hydrogens on the fragmenting form(s) of $C_{12}H_{10}\cdot^+$ from biphenyl is observed,[3] and almost complete scrambling of hydrogens in the spectrum of toluene;[4] much of the isotopic labeling work performed with aromatic hydrocarbons and aromatic halides has been summarized by Grubb and Meyerson.[4b] More recently, McLafferty and coworkers[5] have established that the loss of ethylene from many *para*- and *meta*-substituted phenetoles proceeds at a rate which is independent of the *para* or *meta* position of the substituent and infer that a common intermediate is generated from *para*- and *meta*-substituted isomers which undergo this reaction after ionization. In contrast, randomization of substituent groups does not occur in reactions leading to $C_6H_5CO^+$ from substituted benzophenones,[6] or in the formation of M − NO ions from substituted nitrobenzenes.[7] Evidently, the distinction, or lack of distinction, between the behavior of isomeric *para*- and *meta*-disubstituted benzenes depends on both the reaction involved and the nature of the substituents. The statistical loss of DCN and HCN from 2,4,6-d_3-benzonitrile at 70 eV, but specific loss of DCN at low voltages, establishes that electron beam energy (not surprisingly) can also affect randomization reactions.[8]

In addition to the use of deuterium labeling and the kinetic method as briefly outlined above, the energetic approach can give valuable information as to the actual nature of aromatic ions generated from benzene and its derivatives. The kinetic energy released in the fragmentation $C_6H_6^{2+} \rightarrow C_3H_3^+ + CH_3^+$ indicates that the doubly charged molecular ion from benzene which undergoes this reaction is linear.[9] Appearance potential data and the spectra of C_6H_6 isomers suggest that $C_6H_5^+$ and $C_6H_4\cdot^+$ from benzene are not cyclic but linear,[10] while the increase in energy required to form M − 1 ions from aromatic hydrocarbons with increasing resonance energy indicates ring opening in the formation of these M − 1 ions.[11]

Despite the current interest in this field of research, investigation of hydrogen scrambling in $C_6H_5^+$ ions generated from compounds of the general formula C_6H_5X, where the substituent X is bound to a benzene ring *via* an atom other than carbon is confined to a single report; King and Kirby[12] have shown that the further loss of C_2H_2, C_2HD, and C_2D_2 from $C_6H_3D_2^+$ as generated by loss of NO from d_3-nitrosobenzene (**1**) occurs in a statistical manner, *i.e.*, is preceded by hydrogen–deuterium scrambling. We therefore thought it of interest to investigate other monosubstituted benzenes

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(1) Part XXV: J. H. Bowie, P. F. Donaghue, H. J. Rodda, R. G. Cooks, and D. H. Williams, *J. Org. Mass Spectry.*, in press.

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(8) R. G. Cooks, R. S. Ward, and D. H. Williams, *Chem. Commun.*, 850 (1967); metastable ion lifetime measurements establish two distinct processes for the loss of HCN from benzonitrile, the relative contributions of which are dependent upon electron beam energy (H. W. Brown and H. Benz, private communication).

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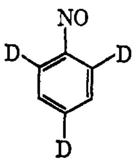
(12) I. R. King and G. W. Kirby, *J. Chem. Soc., C*, 1334 (1966).

by the deuterium-labeling technique and for the purposes of a preliminary investigation chose to label diphenyl ether (**2**) and diphenyl carbonate (**3**). These cases seemed particularly suitable for examination since energetic studies have already been carried out on **2** and **3** and indicated that, whereas $C_6H_5^+$ from **2** may well be an open-chain molecule, $C_6H_5^+$ from **3** is probably the phenyl ion.[13] Hence the possibility arose that deuterium–hydrogen scrambling might be associated with only one mode of formation of $C_6H_5^+$.



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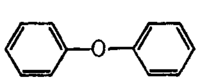

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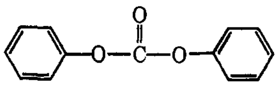

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Discussion

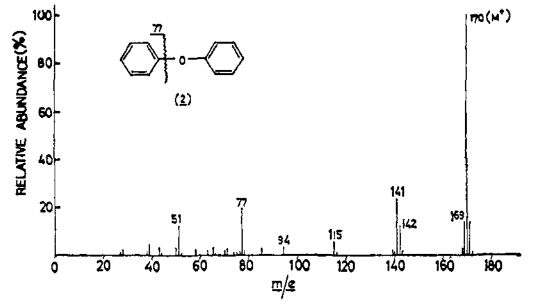

Figure 1. Mass spectrum (70 eV) of diphenyl ether (**2**).

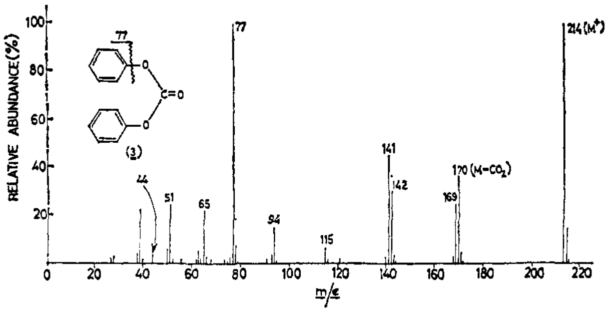

Figure 2. Mass spectrum (70 eV) of diphenyl carbonate (**3**).

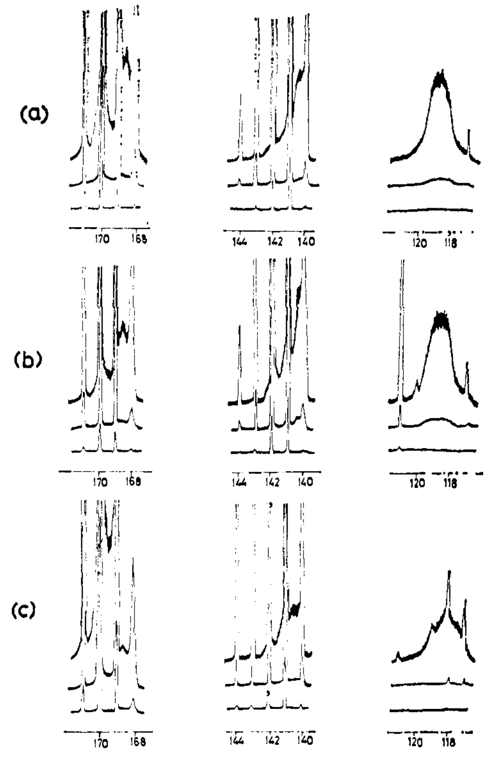

Figure 3. Comparison of the *m/e* 116–120, *m/e* 140–144, and M^+ regions of the mass spectra of diphenyl ether (**2**), diphenyl carbonate (**3**), and *o*-hydroxybiphenyl (**5**).

The mass spectra of diphenyl ether (**2**) and diphenyl carbonate (**3**) at 70 eV are reproduced in Figures 1 and 2, respectively. Application of the kinetic approach[6] to the analysis of these spectra at various electron beam energies amplifies previous observations[13–16] on the spectra. It has been suggested[16] that at least a portion of the M − CO_2 skeletal rearrangement ion from **3** may be identical with the molecular ion of diphenyl ether since both species undergo the loss of carbon monoxide followed by further loss of a hydrogen radical. Indeed, the intervention of a common intermediate[17] is assured by the presence in both spectra of a broad metastable peak of identical shape (Figures 3a and 3b) at *m/e* 118–119 for the step *m/e* 170 → 142 (calculated *m/e* 118.6 for the transition without release of kinetic energy). The abundances of these metastables [m*] relative to those of the daughter ions [*m/e* 142] are very similar at various voltages, but do not quite agree within the limits of experimental error (Table I). If the assumption is made that the small discrepancies in the [*m/e* 142]/[m*] ratios for the two compounds are not meaningful within the limits of accuracy of the kinetic approach,[6,17] then it must be concluded that a common $C_{12}H_{10}O\cdot^+$ ion having the same energy distribution is produced to some extent from **2** and **3**. Under these circumstances, the abundance of m* can be taken as a measure of the concentration of that common species. Therefore, if *m/e* 169, 142, and 141 in both spectra are produced only as further decomposition products of the common species (in *m/e* 170 − H, 170 − CO, and 170 − CO − H sequences), the ratios [*m/e* 169]/[m*], [*m/e* 142]/[m*], and [*m/e* 141]/[m*] should be the same at a given electron beam energy in both spectra. The results summarized in Table I for beam energies of 18, 20, and 25 eV (in which range the ratios change quite considerably) show that the ratios are very similar but do not quite agree within experimental error. Once more, the discrepancies are sufficiently small that the generation of a common intermediate with the same energy distribution is distinctly possible. If this possibility is accepted, then the observation that the ratio [*m/e* 170]/[m*] is *much* greater in the diphenyl ether (**2**) spectrum than in the diphenyl carbonate (**3**) spectrum

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(16) (a) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 2469 (1966); (b) P. Brown and C. Djerassi, *ibid.*, **89**, 2711 (1967).

(17) (a) T. W. Shannon and F. W. McLafferty, *ibid.*, **88**, 5021 (1966); (b) F. W. McLafferty, T. Wachs, and W. T. Pike, International Mass Spectrometry Conference, Berlin, Sept 1967.

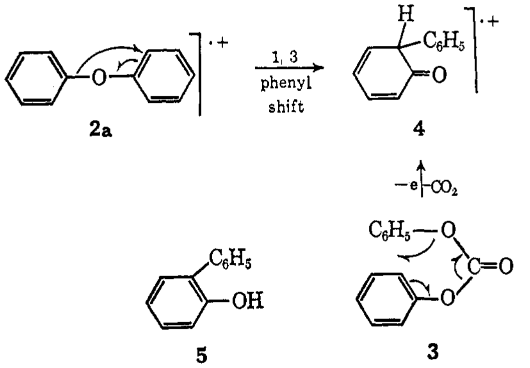
Table I. Abundances of *m/e* 170, 169, 142, and 141 Relative to the Metastable Peak *m/e* 118.6 (m*) in the Spectra of Diphenyl Ether (**2**) and Diphenyl Carbonate (**3**)[a]

Beam energy, eV	[*m/e* 170]/[m*]		[*m/e* 169]/[m*]		[*m/e* 142]/[m*]		[*m/e* 141]/[m*]	
	2	**3**	**2**	**3**	**2**	**3**	**2**	**3**
25	435	109	54	60	72	72	82	79
20	513	115	28	31	32	39	16	21
18	667	128	10	14	14	22	1	3

[a] The ratios represent in each case the average of six scans; the standard deviation from the averaged ratios was ±4%.

indicates that the major portion (~75% at 25 eV and ~81% at 18 eV) of $C_{12}H_{10}O\cdot^+$ from diphenyl ether does not have the same structure and/or energy distribution as the M − CO_2 ion from diphenyl carbonate. On the basis of the above interpretation, this second $C_{12}H_{10}O\cdot^+$ species does not undergo significant fragmentation by loss of a hydrogen atom or of carbon monoxide, and the relative amount of it increases at lower beam energies.

On the basis of the above plausible interpretation, it is tempting to speculate that the proposed relatively stable form of the molecular ion from diphenyl ether does indeed have the structure of ionized diphenyl ether (**2a**); it is clearly unlikely that **2a** should eliminate carbon monoxide in a one-step process since this would require breaking at least three bonds and forming another in a concerted reaction. Since, on the above interpretation, the "labile" form of $C_{12}H_{10}O\cdot^+$ from diphenyl ether and the M − CO_2 ion from diphenyl carbonate have the same structure and energy distribution, it is possible that the "labile" form corresponds to ionized 6-phenylcyclohexadienone (**4**), which can be generated from **2** and **3** *via* 1,3- and 1,5-phenyl shifts, respectively. As **4** is not a stable entity, and as phenol itself may possibly eliminate carbon monoxide *via* the dienone form,[14] the spectra of **2** and **3** have been compared with that of *o*-hydroxybiphenyl (**5**) in the relevant regions (Figure 3). The comparison leaves no doubt that the intermediate which is common from **2** and **3** does not occur to any significant extent in the spectrum of **5**. The ratios which correspond to those quoted for **2** and **3** in columns 4 through 9 of Table I are quite different for **5**,[18] and in addition the metastable profile in the *m/e* 118 region is markedly changed.



2a **4** **5** **3**

Alternatively, it is possible that the small but reproducible differences in the [*m/e* 169]/[m*], [*m/e* 142]/[m*], and [*m/e* 141]/[m*] ratios (Table I) are kinetically significant and a different interpretation of the results is then possible. This second interpretation is that all [or some fraction greater than 128/667 at 18 eV (Table I), for example] of the $C_{12}H_{10}O\cdot^+$ ions from diphenyl ether (**2**) are structurally identical with the M − CO_2 ions from diphenyl carbonate (**3**) but possess less internal energy. Under these circumstances, the [*m/e* 170]/[m*] ratios would be greater for **2** than for **3** (as observed, Table I) and, in addition, the summed intensities of the major daughter ions from *m/e* 170 relative to [m*] should be less for **2** than **3**.[19] The latter condition clearly holds for the 20 and 18 eV data (Table I, $28 + 32 + 16 < 31 + 39 + 21$, and $10 + 14 + 1 < 14 + 22 + 3$), although it is not claimed that the difference in the 25 eV data ($54 + 72 + 82 < 60 + 72 + 79$) is significant.

Of the two possible interpretations which have been offered, we have a definite preference for the second. For although Bursey and McLafferty[6] have usefully applied the kinetic approach on the basis that common ions with the same energy distribution may be produced from different compounds, in practice common ions produced from two species should in general possess finitely different internal energies. It is emphasized that the generation of the common $C_{12}H_{10}O\cdot^+$ ion from precursors having different numbers of degrees of freedom[17b] could in principle lead to a faster decomposition rate for $C_{12}H_{10}O\cdot^+$ derived from diphenyl ether. An exactly opposite effect seems to operate on the basis of our second interpretation. It is interesting that on the assumption that the $C_{12}H_{10}O\cdot^+$ ions from diphenyl ether and diphenyl carbonate have the same structure at their appearance potentials, it must be concluded that $C_{12}H_{10}O\cdot^+$ from the carbonate is formed with about 1 eV of excess energy.[13] Since the metastable peak for the loss of carbon dioxide from the diphenyl carbonate molecular ion is relatively narrow and is approximately gaussian in shape, this excess energy is not released as translational energy during the transition and therefore must be retained as internal energy. This observation is in accord with our most reasonable conclusion, namely that the $C_{12}H_{10}O\cdot^+$ ion from the carbonate possesses more internal energy.

If the possibility of hydrogen randomization in the further decomposition of $C_6H_5^+$ (*m/e* 77) by loss of acetylene to give *m/e* 51 (see Figures 1 and 2) is to be checked, it is most convenient to label alternate carbon atoms of the phenyl ring with deuterium; then in the absence of isomerization or rearrangements which can change the relative orientation of hydrogen or deuterium atoms, only the loss of C_2HD will be observed. Such labeling is conveniently carried out by base-catalyzed exchange of sodium phenate with deuterium oxide; repeated exchange affords sodium 2,4,6-d_3-phenate (**6**) which on reaction with 2,4,6-d_3-bromobenzene (prepared *via* a Sandmeyer reaction on 2,4,6-d_3-aniline) yields di(2,4,6-d_3-phenyl) ether (**7**). Alternatively, reaction with $COCl_2$ affords di(2,4,6-d_3-

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[18] Arguments against the operation of a six-center transfer (*e.g.*, **3** → **4**) have previously been presented for the reaction involving loss of carbon dioxide from the molecular ion of phenyl methyl carbonate.[16]

[19] For a discussion of the variation in relative intensities of parent, daughter, and metastable ions with rate constant (and hence with internal energy), see, for example, M. Krauss and V. H. Dibeler, ref 4b, p 140.

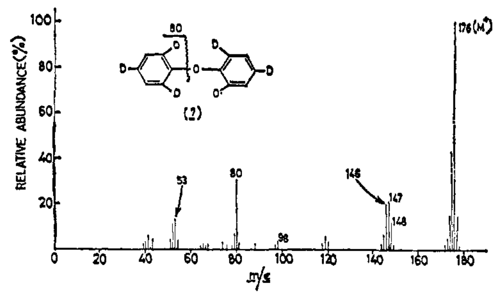


Figure 4. Mass spectrum (70 eV) of d_6-diphenyl ether (7).

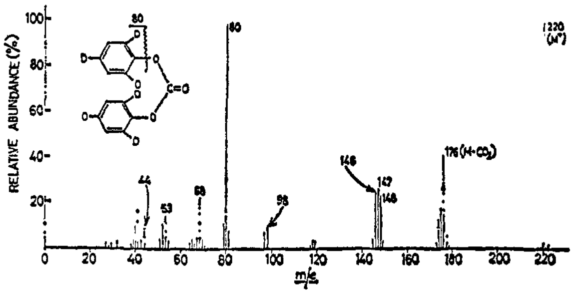
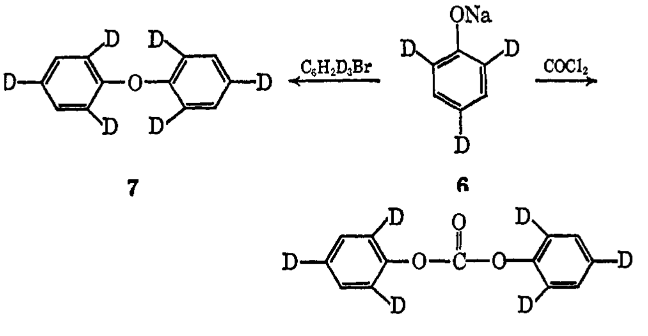


Figure 5. Mass spectrum (70 eV) of d_6-diphenyl carbonate (8).

phenyl) carbonate (8). The spectra of these compounds are reproduced in Figures 4 and 5. The isotopic purity of 7 was evaluated by running low-voltage spectra (to remove the M − 1 peak); 7 contained d_4, 4; d_5, 25; d_6, 71%, while 8 contained d_4, 2; d_5, 18; d_6, 80%. Inspection of Figures 4 and 5 suggests that the hydrogen and deuterium atoms are scrambled within a given phenyl ring in the form of the molecular ion from 7, and the M − CO_2 ion from 8, which undergo loss of H(D), or further loss of CO and H(D). The peak distribution in the molecular ion region (*m*/*e* 174–177) and M − CO region (*m*/*e* 146–149) of d_6-diphenyl ether (7) (Table II) has been calculated on the assumptions of (i) deuterium–hydrogen scrambling within a given phenyl ring, (ii) no isotope effect, and (iii) the d_5 contaminant exhibiting the same spectrum as the d_6 compound, but displaced one mass unit lower (the effect of the d_5 impurity is "added in" to the calculated spectra). It is clear that any errors introduced by the last assumption will be small at the concentration at which the d_5 contaminant is present.[20] Corresponding data for the labeled diphenyl carbonate (8) are given in Table III, and in both tables the observed peak distributions are presented for comparison. The agreement is good and it must be concluded that deuterium–hydrogen scrambling precedes the losses of H or D under discussion. In the light of earlier arguments, it was of course expected that the M − CO_2 ion from 8 and the "labile" form of $C_{12}H_4D_6O^{\cdot +}$ from 7 behave in the same manner, as indeed they do.



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8

By reference to the spectra of the unlabeled compounds 2 and 3, the kinetic approach[6,17] can be used to establish that the *m*/*e* 77 → 51 transition occurs from a common $C_6H_5^+$ species in both spectra since the abundance of *m*/*e* 51, relative to that of the appropriate metastable peak (m*, *m*/*e* 33.8) is the same within the experimental error in both spectra (Table IV). However, since the ratio [*m*/*e* 77]/[m*] is much larger for diphenyl carbonate (3) than for the diphenyl ether (2) (Table IV), either (i) the common $C_6H_5^+$ species have the same energy distribution and a second $C_6H_5^+$ ion (~60% of the total *m*/*e* 77 ions at 70 eV) must be produced from 3 or (ii) of the common $C_6H_5^+$ species, the one from diphenyl carbonate possesses less internal energy (decomposing at a slower rate) and can account for all of the *m*/*e* 77 ions from 3, or some fraction greater than 5.6/12.7 at 70 eV. The latter interpretation still allows, but does not necessitate, the intervention of a second $C_6H_5^+$ ion from diphenyl carbonate (3); it does demand[19] that the ratio [*m*/*e* 51]/[m*] be greater for 2 than 3 as indeed observed (Table IV) although, as already noted, the difference is not definitely significant, thus necessitating the additional possibility listed under (i) above. It is important to note that the heat of formation of $C_6H_5^+$ from diphenyl carbonate (3) is so low that Natalis and Franklin[13] have suggested that its

Table II. Calculated and Observed Peak Distribution in the M^+ and M − CO Regions of the Spectrum of d_6-Diphenyl Ether (7)[a]

	m/*e*							
	146	147	148	149	174	175	176	177
Calcd	38	30	28	4	10	23	60	7
Obsd	38	38	22	2	9	25	58	8

[a] The sum of the peak heights in a given region is normalized to 100 units.

Table III. Calculated and Observed Peak Distribution in the M − CO_2 and M − CO_2 − CO Regions of the Spectrum of d_6-Diphenyl Carbonate (8)[a]

	m/*e*							
	146	147	148	149	174	175	176	177
Calcd	35	29	33	3	20	24	50	6
Obsd	32	34	30	4	17	22	55	6

[a] The sum of the peak heights in a given region is normalized to 100 units.

Table IV. Abundance of *m*/*e* 77 and 51 Relative to the Metastable Peak *m*/*e* 33.8 (m*) in the Spectra of Diphenyl Ether (2) and Diphenyl Carbonate (3) at 70 eV[a]

[*m*/*e* 77]/[m*] × 10^{-2}		[*m*/*e* 51]/[m*] × 10^{-2}	
2	3	2	3
5.6 ± 1.0	12.7 ± 1.8	3.7 ± 0.6	3.1 ± 0.3

[a] The data represent the averages of five determinations.

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[20] In the "calculated" spectrum which is given in Table II, a contribution has been added to *m*/*e* 174 to allow for the 4% of d_4-diphenyl ether contaminant.

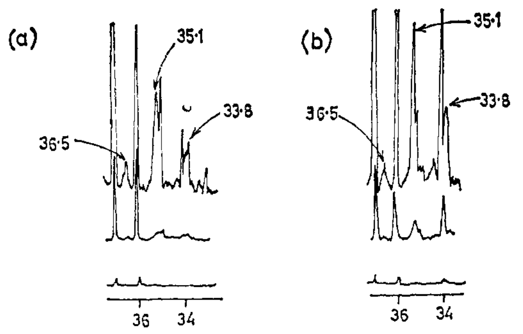


Figure 6. Metastable peaks at m/e 36.5, 35.1, and 33.8 for the statistical loss of C_2H_2, C_2HD, and C_2D_2 from $C_6D_3H_2^+$, generated from (a) 2,4,6-d_3-phenyl bromide and (b) 2,4,6-d_3-phenyl iodide.

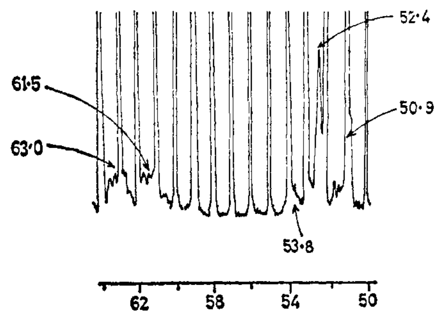
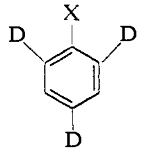


Figure 7. Metastable peaks in the mass spectrum of 2,4,6-d_3-fluorobenzene (**9**).

appearance potential $C_6H_5^+$ from **3** is the phenyl ion and probably of a different structure to $C_6H_5^+$ from diphenyl ether (**2**).[21]

The common $C_6H_2D_3^+$ ion which is produced from **7** and **8** decomposes by statistical loss of C_2H_2, C_2HD, and C_2D_2 (m/e 80 → 54, 53, and 52), *i.e.*, after randomization of the hydrogen and deuterium atoms. This is particularly clear from the ratios of the appropriate metastable peaks at m/e 36.5, 35.1, and 33.8 which correspond closely to the calculated ratios of 1:6:3.

Since all the reactions discussed above for diphenyl ether and diphenyl carbonate are preceded by hydrogen scrambling within a given monosubstituted phenyl ring, it was decided to synthesize 2,4,6-d_3-fluorobenzene (**9**), 2,4,6-d_3-chlorobenzene (**10**), 2,4,6-d_3-bromobenzene (**11**), and 2,4,6-d_3-iodobenzene (**12**), all available *via* appropriate Sandmeyer reactions on 2,4,6-d_3-aniline. The isotopic purity of all the compounds (**9–12**) was d_1 0%, d_2 6%, d_3 94% (calculated from spectra obtained at beam energies precluding the formation of M − 1 peaks from the unlabeled compounds).



9, X = F
10, X = Cl
11, X = Br
12, X = I

For the deuterium-free analogs of **10–12**, the major fragmentation pathway is $M^+ \rightarrow C_6H_5^+ \rightarrow C_4H_3^+$.[22] In all cases, the $C_6H_2D_3^+$ ions (m/e 80) generated by loss of chlorine, bromine, or iodine radicals from the molecular ions of **10–12** decompose by statistical loss of C_2H_2, C_2HD, and C_2D_2 to m/e 54, 53, and 52, respectively. In 70-eV spectra, this is most readily established by metastable peaks at m/e 36.5, 35.1, and 33.8 in the approximate ratio of 1:6:3; these peaks as they occur in the spectra of the labeled bromide **11** and iodide **12** are produced in Figure 6. Randomization still occurs at a nominal 20 eV, although at this voltage the metastable peaks are too weak to be measured directly. However, since the $C_4H_3^+$ ions (m/e 51) from the unlabeled compounds are in a region free from other ions at 20 eV, the direct observation of the m/e 52–54 ions from **10–12** suffices to establish randomization. For example, the relative intensities of m/e 52, 53, and 54 ions from the d_3-bromide **11** at 20 eV are 3.38:5.55:1.07 (after correction for ^{13}C satellite peaks and 6% of d_2 contaminant), in close agreement with the calculated ratio of 3.00:6.00:1.00.

The reactions undergone by fluorobenzene which are most amenable to analysis are somewhat different. Abundant metastable peaks are observed at m/e 60.2 for the transition $M^+ \rightarrow M - HF$ and at m/e 51.1 for the transition $M^+ \rightarrow M - C_2H_2$ (m/e 96 → 70). In the spectrum of 2,4,6-d_3-fluorobenzene (**9**), broad metastable peaks are observed at m/e 61.5 and 63.0 for the transitions m/e 99 → 78 ($M^+ \rightarrow M - DF$) and m/e 99 → 79 ($M^+ \rightarrow M - HF$); their relative intensities are not readily measured (Figure 7), but reasonably approximate the 3:2 ratio expected on the basis of randomization. Also in the spectrum of **9** the transitions $M^+ \rightarrow M - C_2H_2$, $M^+ \rightarrow M - C_2HD$, and $M^+ \rightarrow M - C_2D_2$ occur as evidenced by metastable peaks at m/e 53.8, 52.4, and 50.9 (Figure 7). The relative intensities of those metastables at m/e 53.8 and 52.4 is ~1:6, as expected on the basis of H/D scrambling; the relative abundance of that at m/e 50.9 cannot be measured, since it is partially obscured by the "normal" peak at m/e 51. However, in the 18-eV spectrum of 2,4,6-d_3-fluorobenzene (**9**), the m/e 51 peak has almost completely disappeared and all three metastable peaks (although weak) can clearly be seen in the ratio of approximately 1:6:3.

Thus the formation of $C_6H_5^+$ from nitrosobenzene,[12] chloro-, bromo-, and iodobenzenes is preceded by hydrogen scrambling in the phenyl ring, as are a number of other reactions in diphenyl ether, diphenyl carbonate, and fluorobenzene. A most attractive explanation for these observations is that the monosubstituted benzenes are reversibly equilibrated with benzene isomers such as prismanes or benzvalenes prior to the fragmentation reactions discussed. Such intermediates are generated from benzenes by photochemical excitation[23] and the reversible reactions result in 1,2 and 1,3 shifts in the benzene rings; the shifts have been demonstrated experimentally by means of isotope labeling.[24] The possibility that such intermediates might be produced by electron impact excitation was first noted by Jennings[2] and their possible role in deuterium–hydrogen

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(21) The possible occurrence of two $C_6H_5^+$ species from diphenyl carbonate (3) at 70 eV is in accord with the genesis of a form of the diphenyl ether molecular ion from 3 at this voltage.

(22) F. W. McLafferty, *Anal. Chem.*, **34**, 16 (1962).

(23) See, for example, D. Bryce-Smith, and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(24) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965)

scrambling in the mass spectra of labeled benzonitrile[8] and triphenylphosphines[25] has been emphasized. The intervention of this type of intermediate is conceivable following electron bombardment, but either prior to ionization[26] or after ionization. The postulate will also account for "substituent randomization"[5] without the necessity of ring expansion. It is noteworthy that if the isotope scrambling observed in benzene,[2] and the monosubstituted benzenes discussed in this paper, occurs only *via* benzene isomers such as prismanes and benzvalenes, it will do so without the breaking of C–H or C–D bonds. An attempt to synthesize benzenes simultaneously labeled with ^{13}C and deuterium is currently being undertaken to test this possibility.

Experimental Section

All the spectra were obtained on an AEI MS9 mass spectrometer operating at 70 eV unless otherwise stated. All samples were introduced through a heated inlet system at a temperature of approximately 180°.

2,4,6-d_3-Phenol. Sodium (500 mg) was added to a mixture of phenol (5 g) and deuterium oxide (20 ml) in a Carius tube under an atmosphere of nitrogen. The tube was sealed and heated at 100° for 24 hr. Solvent was then removed, a fresh sample of deuterium oxide (20 ml) added, and the heating process repeated after sealing. The exchange process was carried out for a third time, and the labeled phenol (3 g) then isolated by acidification of the solution with dilute hydrochloric acid and ether extraction. A low-voltage mass spectrum established the isotopic purity of the 2,4,6-d_3-phenol as d_2, 10; d_3, 90%.

Di(2,4,6-d_3-phenyl) ether (7) was synthesized by means of the published procedure[27] for diphenyl ether, but using 2,4,6-d_3-phenol and 2,4,6-d_3-bromobenzene (*vide infra*) as starting materials. The isotopic purity was d_4, 4; d_5, 25; d_6, 71%.

Di(2,4,6-d_3-phenyl) Carbonate (8). 2,4,6-d_3-Phenol (200 mg, prepared as above) was heated in a sealed tube with deuterium oxide (1.2 ml) containing dissolved sodium (30 mg) as described above. The resulting solution was cooled to 0° under a nitrogen atmosphere and phosgene (109 mg) in toluene (500 mg) added with stirring. After 1 hr, the solution was allowed to attain room temperature and then shaken for 3 hr. The resulting precipitate was collected and dissolved in ether and the ethereal solution washed with 10% aqueous sodium hydroxide solution and water and dried. Evaporation of the ether gave a pale yellow crystalline residue which was recrystallized from aqueous ethanol to give di(2,4,6-d_3-phenyl) carbonate (81 mg) as colorless needles, mp 77–78° (d_4, 2; d_5, 18; d_6, 80%).

2,4,6-d_3-Halobenzenes. All four d_3-halobenzenes (fluoro-, chloro-, bromo-, and iodobenzenes) were prepared by standard methods according to Vogel[28] from 2,4,6-d_3-aniline.[29] The isotopic purity of all four materials was d_2, 6; d_3, 94%.

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(28) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1957, pp 598, 601, 602, and 609.

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