pecially pK_{R^+}'s and rates of quenching to carbinols, do not suggest any special intramolecular solvation by the side chains. However, the rates of quenching (of IIi, j, and v) show that the side chains do cover the two faces of the central carbon atom.

6. In the case of ketone solvation, evidence has been obtained that two *o*-methanesulfonylmethyl groups can effectively solvate benzophenone so that the normal solvent dependence of the ultraviolet spectrum disappears.

Studies in Mass Spectrometry. XXIX.[1] Hydrogen Scrambling in Some Bicyclic Aromatic Systems. Randomization over Two Rings

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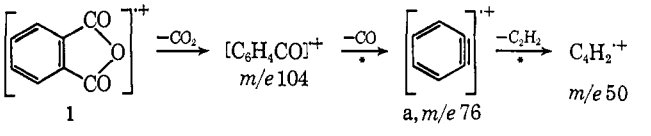
Abstract: Deuterium labeling of some bicyclic aromatic systems has established that complete or partial randomization of the aromatic hydrogens can occur upon electron impact in (i) phthalic anhydride prior to loss of acetylene from the M $-$ C_2O_3 ion, (ii) biphenyl prior to loss of CH_3, C_2H_2, or C_3H_3 from the molecular ion, (iii) 1- and 2-cyanonaphthalenes before HCN expulsion, (iv) benzothiophene before C_2H_2 expulsion. Surprisingly, although the electron impact induced loss of HCN from thiazole specifically involves loss of the C-2 hydrogen, the corresponding HCN expulsion from benzothiazole does not involve specific loss of hydrogen from C-2.

The scrambling of aromatic hydrogens with those attached to α-carbon atoms in the mass spectra of alkylbenzenes can be elegantly accommodated in terms of ring expansion reactions to cycloheptatriene structures, and also in many cases in terms of tropylium ion structures.[2,3] During the course of such reversible ring expansions, the hydrogens of the aromatic nucleus also become equivalent to one another. However, the observations that the hydrogens of benzene[4] and pyridine[5] are randomized prior to the major fragmentation pathways establish that the hydrogens of a six-membered aromatic ring can become equivalent without ring expansion. The mechanism might involve scrambling of the hydrogens *via* rupture and re-formation of C–H bonds, or scrambling of the carbons (and hence of their attached hydrogens) *via* benzvalene and/or prismane intermediates,[6] or a combination of both the above mechanisms may operate. In the light of the above findings, it was obviously important to determine if (i) a bicyclic structure could inhibit or preclude randomization of aromatic hydrogens and if (ii) the randomization process could occur over two aromatic nuclei whether (a) directly bonded but not having common carbon atoms or (b) possessing common carbon atoms. In all cases we chose to investigate compounds in which ring expansion to cycloheptatriene or tropylium structures was either impossible or very unlikely. Previous investigations in this field have been limited to an examination of partially deuterated naphthalenes, phenanthrene, and carbazole;[4a] complete or partial H–D scrambling was found to precede the major fragmentation pathways.

Discussion

To investigate the first problem enumerated above we decided to utilize phthalic anhydride (**1**), which decomposes quite specifically upon electron impact at 70 eV by successive losses of CO_2 and CO to *m/e* 76 ($C_6H_4\cdot^+$);[7] heat of formation data[8] have been interpreted to suggest that $C_6H_4\cdot^+$ has the structure of ionized benzyne (a) at its appearance potential, but other than this we have no information on the structure of $C_6H_4\cdot^+$

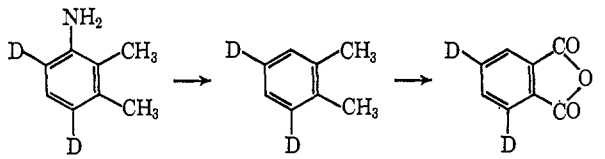


1 a, *m/e* 76

The phthalic anhydride spectrum was suitable for our purposes since hydrogen scrambling in the aromatic nucleus could be investigated by partial deuteration of the benzene ring, followed by analysis of those transitions analogous to *m/e* 76 → *m/e* 50 in the undeuterated material. 3-Amino-*o*-xylene was exchanged as its hydrochloride with deuterium oxide in a sealed tube[9] to give 3-amino-*o*-xylene-4,6-d_2 (**2**), which was deaminated. The resulting *o*-xylene-3,5-d_2 (**3**) was oxidized with permanganate and the labeled

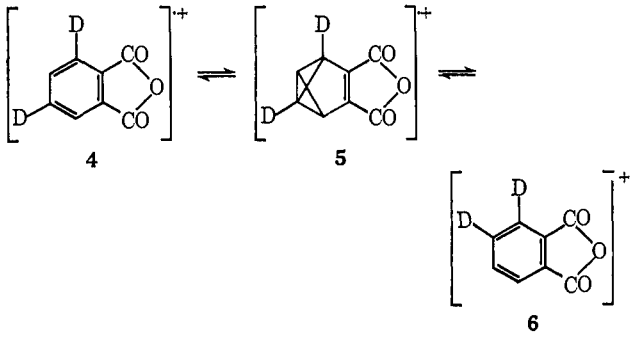
(1) Part XXVIII: D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Chem. Soc., B*, 522 (1968).
(2) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.
(3) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).
(4) (a) C. G. Mcdonald and J. S. Shannon, *Australian J. Chem.*, **15**, 771 (1962); (b) K. Jennings, *Z. Naturforsch.*, **22a**, 454 (1967).
(5) D. H. Williams and J. Ronayne, *Chem. Commun.*, 1129 (1967).
(6) See, for example, D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966), and references cited therein.
(7) "Catalog of Mass Spectral Data," Manufacturing Chemists Association Research Project, Carnegie Institute of Technology, Pittsburgh, Pa., Spectrum No. 85.
(8) H.-F. Grutzmacher and J. Lohmann, *Ann.*, **705**, 81 (1967).
(9) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 241 (1946).

phathalic acid so obtained converted to the anhydride-d_2 (**4**, d_1, 5%; d_2, 94%; d_3, 1%).



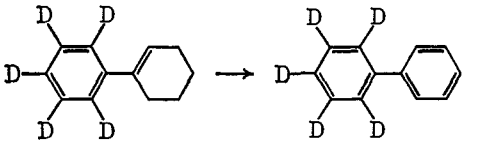
2 **3** **4**

In the mass spectrum of **4**, peaks due to $C_4H_2\cdot^+$, $C_4HD\cdot^+$, and $C_4D_2\cdot^+$ occur in the ratios 0.8:4.0:0.8. These results are in close agreement with the ratios 1.0:4.0:1.0 calculated for H–D randomization prior to the expulsion of C_2H_2, C_2HD, and C_2D_2; only the expulsion of C_2HD could occur if the alternating arrangement of H and D present in the original anhydride were maintained. In addition, metastable transitions for the steps $C_6H_2D_2\cdot^+ \rightarrow C_4D_2\cdot^+ + C_2H_2$ and $C_6H_2D_2\cdot^+ \rightarrow C_4HD\cdot^+ + C_2HD$ are observed at *m/e* 34.7 and 33.3 in the intensity ratio 1.00:3.94 (relative peak areas determined from an average of ten scans; standard error in 3.94 was ±0.17).[10] Although these results establish that hydrogens can randomize in the spectrum of an *ortho*-disubstituted benzene in which the substituents are initially constrained in a five-membered ring, it is of course impossible to say at which stage(s) in the breakdown randomization occurs. If it occurs in the molecular ion, then prismane or benzvalene isomers (*e.g.*, **4** ⇌ **5** ⇌ **6**) can still accommodate the results.



4 **5** **6**

A detailed analysis of the mass spectra of a number of symmetrically deuterated biphenyls has previously been carried out,[11] and the spectra can reasonably well be predicted by assuming that "'each carbon or group of carbons becomes associated with a quite random collection of H and D atoms." However, such symmetrically labeled biphenyls are not ideal for a study of inter-ring scrambling, as the discrepancies between calculated and observed spectra are frequently of similar magnitude to the differences between spectra calculated on the basis of scrambling within one ring and spectra calculated on the basis of scrambling over both rings. We have therefore synthesized biphenyl-2,3,4,5,6,-d_5 (**7**) by dehydrogenation of 1-phenyl-d_5-cyclohexene (**8**), which was in turn available from a Grignard reaction utilizing bromobenzene-d_5 and cyclohexanone; the isotopic purity of **7**, calculated from low-voltage spectra, was d_0, 2%; d_4, 2%; d_5, 92%; d_{10}, 4%.[12]



8 **7**

The fragmentation reactions of biphenyl which are most amenable to analysis are those involving loss of CH_3, C_2H_2, and C_3H_3 from the molecular ion. Metastable peaks were not observed for any of these processes, but at low electron voltage, the M − CH_3, M − C_2H_2, and M − C_3H_3 daughter ions occur in regions virtually free of other ions (Table I). Table II gives the observed and calculated peak distributions for the M − C_2 region of biphenyl-d_5 (**7**) at 16 eV. The calculated values have been corrected for the small amounts of isotopic impurities, and ^{13}C isotopic contributions are included. Table III gives the corresponding data for the M − C_1 and M − C_3 regions of **7** at 20 eV.

Table I. The M − CH_3, M − C_2H_2, and M − C_3H_3 Regions in the Mass Spectrum of Biphenyl at Low Voltage[a]

C_3H_3		C_2H_2		CH_3	
m/e	Rel abund	*m/e*	Rel abund	*m/e*	Rel abund
114	4	127	2.5	138	2
115	87	128	85.5	139	87
116	9	129	9	140	11
117	0	130	3	141	0

[a] The M − CH_3 and M − C_3H_3 regions refer to the 20-eV spectrum and the M − C_2H_2 region refers to the 16-eV spectrum; at these voltages the respective regions were most amenable to analysis in the deuterated analog. In each region the total fragment ion intensity is normalized to 100 units.

Table II. Observed and Calculated Peak Distributions for the Loss of Acetylene and Deuterioacetylenes from Biphenyl-d_5 (**7**) at 16 eV[a]

Ion	*m/e*	Obsd	Calcd for various degrees of randomization 0% random	100% random	70% random
M − C_2D_2	131	26	46	22	29
M − C_2HD	132	40	7	53	40
M − C_2H_2	133	34	47	25	31

[a] The observed values represent the averages of five scans; for each set of values the total fragment ion intensity is normalized to 100 units.

The data presented in Table II show that the expulsion of acetylene-d_1 is more probable than expulsion of acetylene-d_0 or acetylene-d_2. Likewise, the probability of methyl-d_1 or methyl-d_2 radical elimination is greater than that of methyl-d_0 or methyl-d_3 radical elimination, and C_3H_2D and C_3HD_2 are expelled with greater frequency than C_3H_3 or C_3D_3 (Table III). These results immediately suggest that the hydrogens of

(10) The analysis does not include the metastable peak for the transition $C_6H_2D_2\cdot^+ \rightarrow C_4H_2\cdot^+$ (calcd *m/e* 32.05) since this is not resolved from the "normal" peak at *m/e* 32.

(11) J. G. Burr, J. M. Scarborough, and R. H. Shudde, *J. Phys. Chem.*, 64, 1359 (1960).

(12) The 4% of d_{10} contaminant can arise *via* reaction between phenyl-d_5-magnesium bromide and bromobenzene-d_5 whereas the 2% of d_0 contaminant will be generated from reductive dimerization of cyclohexanone and subsequent dehydrogenation.

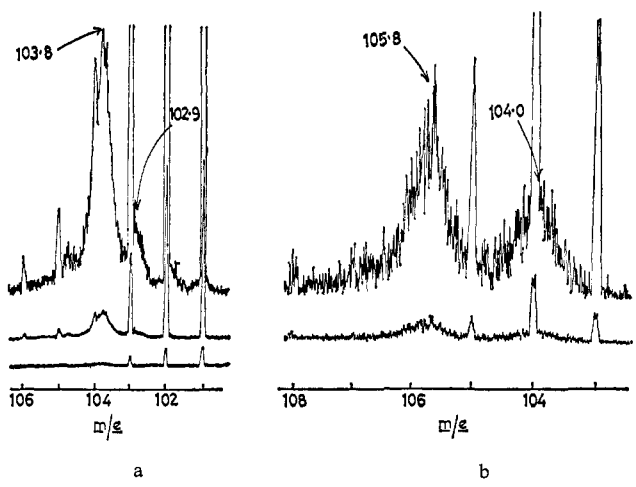


Figure 1. (a) Metastable peaks for the transitions $M^+ \rightarrow M - HCN$ (*m/e* 103.8) and $M - H \rightarrow M - H_2CN$ (*m/e* 102.9) in the 70-eV spectrum of α-cyanonaphthalene. (b) Metastable peaks for the transitions $M^+ \rightarrow M - HCN$ (*m/e* 105.8) and $M^+ \rightarrow M - DCN$ (*m/e* 104.0) in the 15-eV spectrum of 1-cyanonaphthalene-2,4-d_2 (**9**).

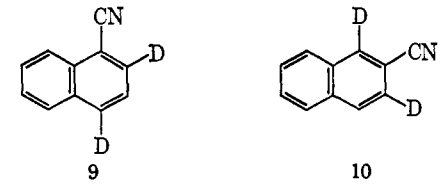
Table III. Observed and Calculated Peak Distributions in the $M - C_1$ and $M - C_3$ Regions in the Spectrum of Biphenyl-d_5 (**7**) at 20 eV[a]

Ion	*m/e*	Obsd	Calcd for various degrees of randomization 0% random	100% random	75% random
$M - C_3D_3$	117	17	47	10	19
$M - C_3HD_2$	118	37	5	39	31
$M - C_3H_2D$	119	26	2	40	30
$M - C_3H_3$	120	20	46	11	20
$M - CD_3$	141	16	46.5	8	17
$M - CHD_2$	142	30	5	39	30
$M - CH_2D$	143	29	2	41	32
$M - CH_3$	144	25	46.5	12	21

[a] See corresponding footnote in Table II.

biphenyl are to a large degree randomized over both rings prior to CH_3, C_2H_2, or C_3H_3 expulsion, since in a statistical process the calculated ratios are 1.0:2.5:1.0 (for loss of C_2H_2, C_2HD, C_2D_2) and 1.0:5.0:5.0:1.0 (for loss of CH_3, CH_2D, CHD_2, CD_3 or of C_3H_3, C_3H_2D, C_3HD_2, C_3D_3) in biphenyl-d_5 (**7**). However, it can be seen (Tables II and III) that in all cases, the loss of species containing both H and D is slightly less than that calculated on the basis of 100% randomization. In all three regions, the best fit of the data is obtained if it is assumed that 70–75% of the fragment ions are formed from a molecular ion in which all H and D have become equivalent, and that 25–30% of the fragment ions arise from one or the other phenyl ring in a form of the molecular ion which has not undergone H–D exchange between rings.

To study the possibility that all the hydrogens of a naphthalene nucleus might become randomized prior to certain fragmentation reactions upon electron impact, we chose to synthesize the partially deuterated nitriles 1-cyanonaphthalene-2,4-d_2 (**9**) and 2-cyanonaphthalene-1,3-d_2 (**10**). These compounds were available *via* Sandmeyer reactions on the corresponding α- and β-naphthyl-d_2-amines; the isotopic purities of **9** and **10**, calculated from low-voltage spectra, were d_0, 14.3%; d_1, 5.0%; d_2, 78.0%; d_3, 2.7% and d_0, 7.8; d_1, 5.6; d_2, 85.0; d_3, 1.6%, respectively.



9 **10**

Both unlabeled α- and β-cyanonaphthalenes give abundant metastable peaks in their 70-eV spectra at *m/e* 103.8 due to the loss of HCN from the molecular ion, and, in addition, a much less abundant metastable peak at *m/e* 102.9 due to the transition $M - H \rightarrow M - H_2CN$ (Figure 1a); the intensity of the metastable peak due to the latter transition was negligible at a nominal 15 eV. In 15-eV spectra of **9**, the metastable transitions for loss of HCN and DCN from the molecular ion are observed in the ratio 2.5:1.0 at *m/e* 105.8 and 104.0 (Figure 1b). This ratio corresponds to scrambling of all hydrogens in 1-cyanonaphthalene prior to HCN expulsion in the metastable transition. At a nominal 15 eV, the M – HCN peak (*m/e* 126) of the 1-cyanonaphthalene spectrum lies in a region in which other peaks are of almost negligible abundance. It was therefore possible to calculate the peak distribution in the "M – HCN" region of the spectrum of 1-cyanonaphthalene-2,4-d_2 (**9**) on the basis of assumed complete randomization of H and D prior to the loss of HCN and DCN. The spectrum so calculated is compared with the observed spectrum in Table IV, and it can be seen

Table IV. Observed and Calculated Peak Distributions for the Loss of HCN and DCN from 1-Cyanonaphthalene-2,4-d_2 (**9**) and Its Associated Isotopic Contaminants at 15 eV.

Ion	*m/e*	Obsd	Calcd
DCN-d_1, HCN-d_0	126	11.4	13.4
DCN-d_2, HCN-d_1	127	21.5	25.4
DCN-d_3, HCN-d_2	128	50.6	53.9
HCN-d_3	129	14.3	7.1
	130	2.2	0.2

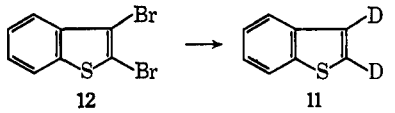
that the agreement is good. Even in the absence of this quantitative treatment, it is quite obvious that HCN loss from **9** is much more pronounced than DCN loss.

Since M – HCN and M – DCN peaks from **9** are observed in approximately the same ratio as the metastable transitions for HCN and DCN loss, it seems probable that the daughter ions are produced only by the same reaction as that affording the metastable peaks. It must be concluded that a hydrogen scrambling reaction occurs in 1-cyanonaphthalene upon electron impact and that the rate of scrambling is fast relative to HCN expulsion. The spectra of 1- and 2-cyanonaphthalenes were identical and the conclusions from the spectrum of 2-cyanonaphthalene-1,3-d_2 (**10**) identical with those drawn from the spectrum of **9**; for example, the metastable transitions for loss of HCN and DCN from **10** are observed in the ratio 2.5:1.0 at 15 eV (*cf.* Figure 1b).

Since we have recently been able to show that the hydrogens of thiophene are all involved with equal probability in acetylene loss from the molecular ion,[13] it was next of interest to investigate whether C_2H_2, C_2HD, and C_2D_2 would be expelled statistically from

(13) D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Letters*, 1777 (1968).

benzothiophene-2,3-d_2 (**11**) upon electron impact. It was anticipated that metastable transitions would be useful in the study of this and related reactions, since benzothiophene itself gives metastable peaks for the following decomposition pathways involving loss of hydrogen atoms: $M^+ \rightarrow M - C_2H_2$, $M^+ \rightarrow M - CH_3$, $M^+ \rightarrow M - H$, and $M - CS \rightarrow M - HCS$. Benzothiophene-2,3-$d_2$ (**11**) was prepared by successive



12 11

treatment of 2,3-dibromothiophene (**12**) with phenyllithium and deuterium oxide; the isotopic purity as established from its low-voltage spectrum was d_1, 2%; d_2, 98%. If C_2H_2, C_2HD, and C_2D_2 are expelled statistically from the molecular ion of **11** in metastable transitions, the ratios of intensities of the respective metastable peaks would be 6:8:1. While it is not possible to determine the relative abundances of the metastable peaks with great accuracy, the observed intensities closely correspond to the calculated 6:8:1 ratio at both 70 (Figure 2) and 30 eV. There is no doubt whatsoever that in the metastable transitions the loss of C_2HD is slightly more pronounced than the loss of C_2H_2, which in turn is much more pronounced than the loss of C_2D_2, and once more an interesting rearrangement reaction is demanded prior to the fragmentation reaction.

The loss of a hydrogen atom from the molecular ion of benzothiophene, and of a hydrogen atom from the M − CS ion, was replaced by the loss of both hydrogen and deuterium atoms in the spectrum of the d_2 derivative **11**. The relative daughter ion intensities given in Table V for various beam energies are again compatible

Table V. Relative Abundances of M − H, M − D, M − CHS, M − CDS, CDS^+, and CHS^+ Ions from Benzothiophene-2,3-d_2 (**11**) at Various Electron Beam Energies[a]

Ion	m/e	70 eV	40 eV	30 eV	25 eV	17 eV	15 eV
M − H	135	2.2	2.7	2.3	1.3	...	...
M − D	134	1.2	1.4	1.1	0.6	...	...
M − CHS	91	7.1	...	...	2.7	...	...
M − CDS	90	3.2	...	...	1.3	...	...
CDS^+	46	1.00	1.00	...	1.00	1.00	1.00
CHS^+	45	0.57	0.57	...	0.59	0.70	0.86

[a] Values are corrected for the 2% of d_2 contaminant, but ^{13}C isotope contributions are included. The abundances are relative to the base peak molecular ion as 100 units, with the exception of data for CDS^+ and CHS^+, for which intensities relative to each other are recorded (since CDS^+/M^+ and CHS^+/M^+ ratios became very small at 15–17 eV).

with scrambling of all the hydrogens of benzothiophene prior to fragmentation. However, in these cases the rate-determining steps probably involve the cleavage of C–H bonds, and in such circumstances primary isotope effects can be large.[14] Such primary isotope effects can be even more marked ($k_H \gg k_D$) in determining the relative abundances of metastable peaks,[14] and

(14) See, for example, C. Ottinger, *Z. Naturforsch.*, 20a, 1232 (1965), and C. Ottinger, *J. Chem. Phys.*, 47, 1453 (1967). Secondary isotope effects are very much less marked and hence processes such as acetylene elimination are not subjected to discrimination (due to isotope effects) which would be significant in the present context.

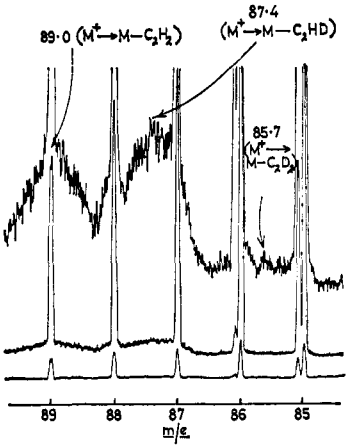


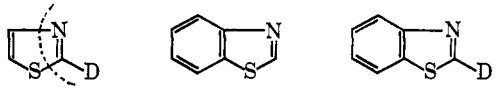
Figure 2. Metastable peaks for the transitions $M^+ \rightarrow M - C_2H_2$ (*m/e* 89.0), $M^+ \rightarrow M - C_2HD$ (*m/e* 87.4) and $M^+ \rightarrow M - C_2D_2$ (*m/e* 85.7) in the 70-eV spectrum of benzothiophene-2,3-d_2 (**11**).

therefore in these cases an analysis of the metastable transitions has not been attempted.

Two additional fragmentation reactions of benzothiophene are noteworthy. The first is that leading to the CHS^+ ion (*m/e* 45), and data for this reaction in the d_2 analog **11** have also been summarized in Table V. The formation of CDS^+ and CHS^+ occurs in the ratio 1.00:0.57 at 70 eV, but the proportion of CHS^+ increases at low voltage (15–17 eV). Exactly analogous behavior was observed in the formation of CDS^+ and CHS^+ from thiophene-2,5-d_2.[13] The results are consistent with competition between "random" and "specific" processes leading to CHS^+ from benzothiophene itself, with the proportion of CHS^+ formation from a molecular ion containing randomized hydrogens increasing at lower voltage. Alternatively, CHS^+ formation may occur from only one reactant with the rate of a reversible hydrogen scrambling reaction being comparable to the rate of fragmentation.

The second reaction of interest concerns the loss of a methyl radical from benzothiophene. The d_2 derivative **11** loses CHD_2 with approximately 90% specificity at 70 eV, but we can see no obvious reason for this specific loss to be favored.

As a final example, we decided to compare the behavior of thiazole and benzothiazole upon electron impact. Thiazole-2-d_1 (**13**) was available *via* addition of deuterium oxide to the Grignard reagent derived from 2-bromothiazole; the isotopic purity of **13** was d_0, 2%; d_1, 98%. In **13** the M − HCN peak of thiazole was replaced virtually completely by an M − DCN peak at either 20 or 70 eV (98% specific loss of deuterium from C-2 as indicated by the dotted lines in **13**); the only metastable peak which could be detected was that at *m/e* 39.1 corresponding to the transition 86 → 58 (loss of DCN).



13 14 15

In the light of the above result, it was confidently felt that benzothiazole-2-d_1 (**15**) would specifically lose DCN, but its preparation was nevertheless undertaken *via* deuteration of benzothiazole (**14**) itself; the isotopic

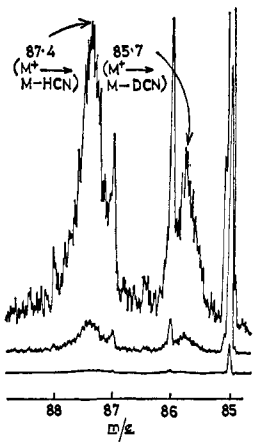


Figure 3. Metastable peaks for the transitions $M^+ \rightarrow M - HCN$ (*m/e* 87.4) and $M^+ \rightarrow M - DCN$ (*m/e* 85.7) in the 70-eV spectrum of benzothiazole-2-d_1 (**15**).

purity of **15** was d_0, 4%; d_1, 96%. For benzothiazole (**14**), the relative intensities at 70 eV of the base peak molecular ion, *m/e* 108 (M − HCN), and its attendant weak satellite peaks are given in Table VI; it can be seen that the loss of HCN is quite a specific process, the peak at *m/e* 109 (2.4 units) being largely (1.9 units) associated with the ^{33}S- and ^{13}C-satellite peaks of *m/e* 108, and that at *m/e* 110 (1.3 units) being completely associated with the ^{34}S satellite of *m/e* 108. The corresponding intensities in the spectrum of the 2-d_1 derivative **15** are also given in Table VI; these

Table VI. Relative Abundances of Peaks in the M^+ and "M − HCN" Regions of the Spectra of Benzothiazole (**14**) and Benzothiazole-2-d_1 (**15**)

Compd	*m/e* 136	135	134	110	109	108	107
14		100 (M^+)	1.3	1.3	2.4	25.0 (M − HCN)	1.1
15	100 (M^+)	1.1	0.0	1.7	4.7	25.0 (M − DCN)	1.1

figures are corrected for the 4% of d_0 contaminant. The results summarized in the table establish that benzothiazole-2-d_1 (**15**) very predominantly (~92%) loses DCN, but that there is a significant loss of HCN (~8%). The latter process is unequivocally established from an analysis of metastable peak intensities; the metastable peaks for loss of HCN and DCN from the molecular ion of **15** are observed in the ratio 2.5:1.0 at 70 eV (Figure 3). Since the ratio of metastable peak intensities is markedly different from the ratio of the daughter ion intensities, there must be at least two processes with different rate constants for loss of HCN from benzothiazole (**14**).[15] The most plausible interpretation of the results would appear to be that direct elimination of DCN occurs from the 2-d_1 derivative **15** in a relatively fast reaction (giving rise to an abundant daughter ion and a weak metastable peak), and that HCN and DCN are eliminated in the ratio 4:1 (following a H–D scrambling reaction) in a relatively slow reaction which gives rise to low-abundance daughter ions but abundant metastable peaks. On the basis of this interpretation, the observed ratio of metastable peaks would be less than 4:1, as is found experimentally.

The experiments described in this paper illustrate that our knowledge of rearrangement reactions undergone by aromatic nuclei upon electron impact is far from complete. Certainly, the mechanisms (such as reversible ring expansions, and possible intervention of benzvalene and/or prismane intermediates) mentioned in the introductory section are inadequate to rationalize the data, and further experimental work will be necessary in the field.

Experimental Section

The mass spectra were determined with an AEI MS-9 mass spectrometer, using beam energies as indicated in the discussion; the source temperature was approximately 200°, and the accelerating voltage was 8 kV.

Phthalic-3,5-d_2 Anhydride. 3-Amino-*o*-xylene hydrochloride (11 g) was heated in a sealed tube with deuterium oxide at 100° for 24 hr. The hydrochloride was extracted and dried and the exchange repeated with further deuterium oxide (20 ml). The free amine was liberated with sodium hydroxide solution (10%), extracted with ether, and dried with anhydrous sodium sulfate. After filtration, and evaporation of the ether, distillation gave the 3-amino-*o*-xylene-4,6-d_2 (10 g, d_2, 94%).

3-Amino-*o*-xylene-4,6-d_2 (2.46 g) was diazotized in the usual manner at 0°. Sodium hydroxide (4 g) in water (45 ml) was cooled to 0°, a 37% aqueous solution (6 ml) of formaldehyde added, and the mixture cooled. The cold diazonium chloride solution was poured slowly into the rapidly stirred alkaline formaldehyde solution. A steady evolution of nitrogen occurred. After complete addition, stirring was continued for another hour while the temperature was allowed to reach 20°. The solution was acidified with dilute hydrochloric acid and nonbasic material extracted with ether. The dark oil obtained after evaporation of the ether was distilled to give *o*-xylene-3,5-d_2 (1.10 g; d_2, 94%).

o-Xylene-3,5-d_2 (800 mg) was refluxed for 3 hr with potassium permanganate (9.0 g), in aqueous alkaline solution (1 g of potassium hydroxide in 30 ml of water). The solution was cooled and acidified (pH ~4) with concentrated hydrochloric acid. Manganese dioxide was filtered off and the filtrate evaporated to dryness. The remaining white solid was partially dissolved in dry methanol (5 ml) and filtered. After evaporation of the methanol, the residual solid was sublimed. The white needles of phthalic-3,5-d_2 anhydride so obtained (150 mg) melted at 127° (slow heating). The isotopic purity was d_1, 5%; d_2, 94%; d_3, 1%.

Biphenyl-2,3,4,5,6-d_5. The Grignard reagent from bromobenzene-d_5 (265 mg) and magnesium (40 mg) was allowed to react with cyclohexanone (162 mg) according to the procedure of Haworth.[16] The resulting phenyl-d_5-cyclohexene (203 mg) had bp 250–255°, and 150 mg of this material was dehydrogenated by heating with chloranil (457 mg) in xylene (1.4 ml) under reflux for 4 hr.[17] Repeated chromatography of the resulting product through a column of alumina gave biphenyl-2,3,4,5,6-d_5 (61 mg), mp 63–66°; d_0, 2%; d_4, 2%; d_5, 92%; d_{10}, 4%.

1-Cyanonaphthalene-2,4-d_2. 1-Naphthylamine hydrochloride (5 g) was heated in a sealed tube with deuterium oxide (20 ml) at 100° for 24 hr. The hydrochloride was extracted and dried and the exchange repeated with further deuterium oxide. The 1-aminonaphthalene-2,4-d_2 hydrochloride which crystallized on cooling was filtered and dried.

1-Aminonaphthalene-2,4-d_2 hydrochloride (3.3 g) was diazotized in the usual manner at 0°. The cold diazonium chloride solution was poured into a solution of cuprous cyanide (3.0 g) and potassium cyanide (4.5 g) in water (15 ml), which had previously been heated

(15) For analogous arguments regarding the elimination of a hydroxyl radical from the benzoic acid molecular ion, see J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch.*, **20a**, 883 (1965); for a discussion of the variation in relative abundance of metastable ions and normal daughter ions for superficially similar reactions, see F. W. McLafferty and T. A. Bryce, *Chem. Commun.*, 1215 (1967).

(16) W. N. Haworth, *J. Chem. Soc.*, 1242 (1913).

(17) R. T. Arnold and C. J. Collins, *J. Am. Chem. Soc.*, **61**, 1407 (1939).

to 60°. The mixture was refluxed for 30 min, cooled, and made basic with aqueous sodium bicarbonate. The nonacidic fraction was extracted with ether and the ether solution washed successively with dilute hydrochloric acid and water. After drying with anhydrous sodium sulfate and filtration, the ether was evaporated to yield the crude product (2.0 g). A small sample was injected into a 6-ft silicone rubber column at 150° and a pure sample of 1-cyanonaphthalene-2,4-d_2 was obtained; crystals (mp 36–37°) formed on standing. The percentages of isotopic incorporation were: d_0, 14.3%; d_1, 5.0%; d_2, 78.0%; d_3, 2.7%.

2-Cyanonaphthalene-1,3-d_2 was prepared from 2-naphthylamine hydrochloride in a manner exactly analogous to the above. The percentages of isotopic incorporation were: d_0, 7.8%; d_1, 5.6%; d_2, 85.0%; d_3, 1.6%.

Benzothiophene-2,3-d_2. 2,3-Dibromobenzothiophene (1.46 g) in benzene (5 ml) was added dropwise with stirring into a solution of phenyllithium in ether (prepared from 430 mg of lithium and 3.2 g of phenyl bromide in 20 ml of ether at room temperature) under an atmosphere of nitrogen. The mixture was heated at 45° for 6 hr and then was kept stirring at room temperature for another 12 hr. Organic material was isolated from the reaction in the usual manner and then dissolved in petroleum ether (bp 40–60°). The solution was filtered through a column of alumina and the light yellow liquid obtained from the first two fractions was rechromatographed in the same manner. Benzothiophene-2,3-d_2 (304 mg, d_1, 2%; d_2, 98%) was obtained as a low-melting colorless crystalline solid (mp 30–32°) from the first two fractions off the column.

Thiazole-2-d_1. Methylmagnesium bromide in ether (14 ml) was prepared from magnesium (365 mg) and methyl bromide (1.2 g). 2-Bromothiazole (820 mg) in ether (4 ml) was added dropwise with stirring. After 1 hr, deuterium oxide (1 ml) was added and the ethereal solution separated. Evaporation of the ether and distillation of the residue gave thiazole-2-d_1 (40 mg, d_0, 2%; d_1, 98%) as a colorless liquid, bp 110–114°.

Benzothiazole-2-d_1. Benzothiazole (250 mg) was added to a solution of sodium deuterioxide (80 mg) in deuterium oxide (1.0 ml), and the mixture was heated on a water bath at 60° with stirring for 12 hr. The solvent was removed and the heating repeated with a fresh sample of deuterium oxide. The organic material was isolated in the usual manner to give benzothiazole-2-d_1 (168 mg, d_0, 4%; d_1, 96%), bp 108–112° (18 mm).

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The Relative Nucleophilicity of Some Common Nucleophiles toward Sulfenyl Sulfur. The Nucleophile- and Acid-Catalyzed Racemization of Optically Active Phenyl Benzenethiolsulfinate[1]

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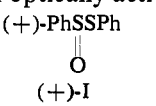
Abstract: In acidic aqueous dioxane in the absence of added nucleophiles optically active phenyl benzenethiolsulfinate, (+)-I, racemizes only very slowly, but the addition of small amounts of alkyl sulfides, halide ions, or thiocyanate ion leads to quite rapid racemization of (+)-I. The racemization reaction is first order in both nucleophile and hydrogen ion; its solvent isotope effect indicates that it is specific H^+ catalyzed. Although only the acid- and nucleophile-catalyzed racemization of (+)-I occurs in their absence, addition of sulfinic acid or mercaptan to such aqueous dioxane solutions leads to the disappearance of I *via* acid- and nucleophile-catalyzed reactions with the sulfinic acid or mercaptan. The formal kinetics and the rate constants of these latter reactions are exactly the same under a given set of conditions as those for racemization, indicating that all the processes have the same rate-determining step. The only satisfactory mechanism which can accommodate these observations is the one shown in Chart I. This involves a rate-determining attack of the nucleophilic catalyst on the sulfenyl sulfur of sulfinyl-protonated I. This means that data on the relative reactivity of various nucleophiles as catalysts for the racemization (Table V) provide a quantitative measure of the relative reactivity of these species in a substitution at sulfenyl sulfur. Comparison of such data with data (Table VI) for the relative reactivity of the same nucleophiles in substitutions at sulfinyl sulfur and peroxide oxygen shows not only that sulfenyl sulfur is, as expected, a "softer" electrophilic center than sulfinyl sulfur but also that it is about as "soft" as peroxide oxygen. The latter was not expected on the basis of previous predictions.

Optically active phenyl benzenethiolsulfinate (I) can be prepared by asymmetric oxidation of phenyl disufide with an optically active peracid.[2a,b]



(+)-I

In aqueous dioxane this thiolsulfinate undergoes a facile nucleophile- and acid-catalyzed racemization which forms the subject of the present paper.[2c] This racemization is of interest for two reasons. First, it represents another example of cooperative electrophilic and nucleophilic catalysis of the scission of a sulfur–sulfur bond.[3] Second, and more important, the data obtained for various nucleophiles as catalysts provide a quantitative measure of the relative reactivity of these

(1) This research was supported by the National Institutes of Health under Research Grant GM-12104.

(2) (a) J. L. Kice and G. B. Large, *Tetrahedron Letters*, 3537 (1965); (b) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (c) A. Fava and P. Koch (private communication) have studied the purely thermal racemization of (+)-I and also the racemization as catalyzed by nucleophiles alone in aprotic solvents. Under the reaction conditions used in the present work both of these reactions are much slower than the acid- and nucleophile-catalyzed racemization of (+)-I.

(3) (a) J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **86**, 2270 (1964); (b) J. L. Kice and G. Guaraldi, *ibid.*, **88**, 5236 (1966); **89**, 4113 (1967); (c) J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967). (d) For a general review see J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).