Carbonium Ions with Multiple Neighboring Groups.
II. Physical Studies[1a]

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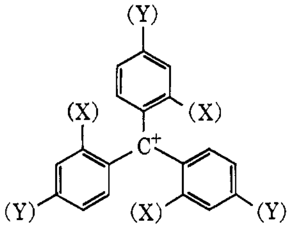
Abstract: Nmr and ultraviolet spectra, pK_{R^+} measurements, and studies of quenching rates of a series of triphenylmethyl cations with potentially coordinating side chains in the *ortho* positions show two classes of ions: those in which the side chains are completely uncoordinated with the central carbon and those in which cyclization with one side chain has occurred. With several groups, fluctuating structures are found in this latter class, but there is no evidence for partial or simultaneous multiple coordination of side chains. The ions with uncoordinated side chains show no special stabilization by intramolecular solvation, although the chains strongly shield the central carbon. A number of unusual conformational equilibria have been detected and studied. Evidence has been obtained that solvation effects on ketone ultraviolet spectra can be mirrored with two intramolecular solvating groups. An unusual zwitterion, in which a carbonium ion and the anion are part of the same molecule, has apparently been observed in solution.

In the previous paper[2] we reported the synthesis of a variety of carbonium ions of general type A, in which the side chains X may give neighboring-group interaction with the carbon cation while the groups Y can stabilize the cation by conjugation.



A

In general one could expect two classes of cations in this series, as was discussed in the accompanying paper.

1. Cases with good carbon bases in side chain X and/or relatively reactive carbon cations, in which the structure would involve complete covalent bonding between one side chain X and the central carbon. In compounds with more than one side chain X fluctuating structures are expected in which one after the other X chain is coordinated.

2. Cases in which the carbon basicity of the side chain X is low and/or the conjugative stabilization of the carbonium ion is high, in which the structure is an open carbonium ion with no interaction between the central carbon atom and the side chains X.

There might also be an intermediate class in which incomplete coordination occurs between the central carbon and a side chain. One of the major goals of this work is the detection of such intramolecular solvation, if it occurs. If two side chains X were simultaneously involved in such coordination the resulting pentacoordinate species would be a model for either the specifically solvated carbonium ion or the S_N2 intermediate, depending on the amount of charge transferred to the ligands.

The experimental distinction among these possible structures involved several techniques. Nuclear magnetic resonance spectra can be used to distinguish coordinated from uncoordinated side chains, since transfer of the positive charge to the side chain leads to significant differences in chemical shifts. The distinction between simultaneous coordination of two side chains (pentacoordinate carbon) and sequential coordination of two or more side chains (fluctuating structures) might be difficult because of the long time scale in nmr experiments, but this problem was solved in part with variable-temperature techniques.

The visible–ultraviolet spectra of triphenylmethyl cations were examined. This technique readily distinguishes completely cyclized from completely open cations. What the spectra should be of any intermediate structure, with partial coordination by side chain atoms, is less clear; however, such coordination should probably lead to detectable perturbation of the spectrum of the cation.

The stability of a cation reversibly convertible to a carbinol can be defined by its pK_{R^+},[3] which measures the activity of the medium required to dissociate the carbinol. Any sort of intramolecular solvation of a carbonium ion would presumably be stabilizing, and it should show up in a more positive pK_{R^+}. To correct for steric effects, we have used carbonium ions with saturated alkyl side chains as model compounds. Finally, intramolecular solvation should shield the central carbon so that rates of quenching with base to the carbinol would be diminished compared with isosteric model compounds.

Solvent effects on the ultraviolet absorption spectrum of ketones[4] generally go in two directions. The $n-\pi^*$ transition is shifted to higher energy in more polar solvents, while the $\pi-\pi^*$ is shifted to lower energy. Since molecular models show that in ketones of type B the side chains X can lie on the two faces of the carbonyl group, we have examined the solvent dependence of the ultraviolet spectra of such compounds. If two solvent

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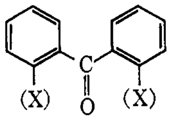
[1] (a) Partial support by the Hoffman-LaRoche Research Foundation is gratefully acknowledged; (b) NSF Postdoctoral Fellow, 1964–1965; (c) NIH Predoctoral Fellow, 1966–1967.

[2] R. Breslow, S. Garratt, L. Kaplan, and D. LaFollette, *J. Am. Chem. Soc.*, 90, 4051 (1968).

[3] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, 77, 3044 (1955).

[4] *Cf.* H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

molecules play the principle role in these solvation effects, then ketones of type B might have spectra which are independent of the polarity of the external medium, and which reflect the polar character of the side chains.



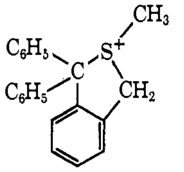
B

Experimental Section

New compounds were prepared as described in the accompanying paper. Nmr spectra were taken on a Varian A-60 or A-60A instrument at the normal probe temperature of 30–35° unless specified. Low- and high-temperature spectra were obtained with the standard Varian attachment, and all chemical shifts are relative to internal tetramethylsilane. Ultraviolet and visible spectra were obtained on a Cary 14 or Cary 15 recording spectrophotometer. pK_{R^+}'s were obtained by Deno's "method C" [5] using 10-cm quartz uv cells.

Results and Discussion

Our most thoroughly investigated series of trityl cations has CH_2-S-CH_3 as potential neighboring groups (A, X = CH_2SCH_3). The monosulfur cation (IIa) has been examined as both its perchlorate and its trifluoracetate salts, and it exists as a cyclic sulfonium ion (IIa'). In the nmr spectrum (SO_2 solution) the



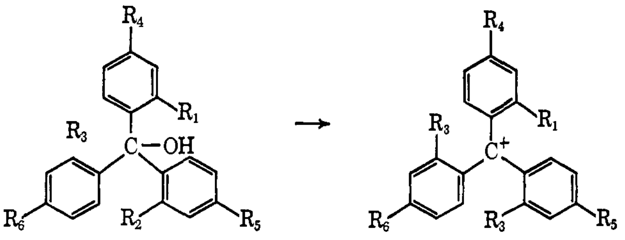
IIa'

methyl group is shifted downfield by 0.6 ppm relative to its position in the corresponding carbinol (Ia), while the methylene group suffers a 1.3-ppm downfield shift (in Chart I, all substituents are H unless otherwise specified). The methylene signal is an AB quartet, since the two protons are rendered magnetically nonequivalent by the asymmetric sulfur center. The nmr spectra of our compounds are summarized in Table I.

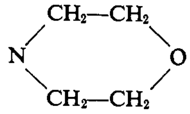
The aromatic protons in these compounds occur in the region from δ 6.3 to 7.6, and are shifted downfield in some of the cations. The temperature changes have been shown to be reversible. Values given without a specified temperature are at the normal probe temperature of 30–35°, and all peaks are singlets unless otherwise noted.

Further evidence that the monosulfur cation (IIa) has the cyclic structure IIa' is the absence of any absorption in the visible spectrum, and the finding that in base IIa quenches to the carbinol Ia, but at a very slow rate.

Chart I



I II

a, $R_1 = CH_2—S—CH_3$
b, $R_1 = R_2 = CH_2—S—CH_3$
c, $R_1 = R_2 = R_3 = CH_2—S—CH_3$
d, $R_1 = CH_2—S—CH_3$; $R_5 = OCH_3$
e, $R_1 = R_2 = CH_2—S—CH_3$; $R_6 = OCH_3$
f, $R_1 = R_2 = CH_2—S—CH_3$; $R_4 = R_5 = R_6 = OCH_3$
g, $R_4 = N(CH_3)_2$
h, $R_1 = CH_2—S—CH_3$; $R_5 = N(CH_3)_2$
i, $R_1 = R_2 = CH_2—S—CH_3$; $R_6 = N(CH_3)_2$
j, $R_1 = R_2 = CH_2—CH_2CH_3$; $R_6 = N(CH_3)_2$
k, $R_1 = R_2 = CH_2—S—CH_3$; $R_6 =$ 
$N\langle{}^{CH_2—CH_2}_{CH_2—CH_2}\rangle O$
l, $R_1 = CH_2—SO_2—CH_3$
m, $R_1 = R_2 = CH_2—SO_2—CH_3$
n, $R_1 = R_2 = R_3 = CH_2—SO_2—CH_3$
o, $R_1 = CH_2—O—CH_3$
p, $R_1 = R_2 = CH_2—O—CH_3$
q, $R_1 = R_2 = R_3 = CH_2—O—CH_3$
r, $R_1 = CH_2—CH_2—CH_3$
s, $R_1 = R_2 = CH_2—CH_2—CH_3$
t, $R_1 = R_2 = R_3 = CH_2—CH_2—CH_3$
u, $R_1 = CH_2—CH_2—CH_2—CH_3$
v, $R_1 = R_2 = CH_2—O—CH_3$; $R_6 = N(CH_3)_2$
w, $R_1 = SCH_3$
x, $R_1 = R_2 = SCH_3$
y, $R_4 = SCH_3$
z, $R_4 = R_5 = SCH_3$

The bissulfur cation IIb is also cyclic, since it also lacks typical trityl cation electronic absorption. The nmr spectrum at 10° shows that one side chain is coordinated, with its methyl and methylene groups shifted to the same regions as in IIa, while the other side chain is uncoordinated. The latter actually has its methylene signal at higher fields than in the carbinol Ib, due presumably to shielding by the phenyls. Both the shielded and the unshielded methylene groups in IIb are AB quartets, since in a molecule with an asymmetric center even "freely rotating" groups may in general have preferred conformations which render CH_2 protons magnetically nonequivalent. The coupling constants between such CH_2 protons, from Table I, are 13 cps for uncoordinated side chains and 16–18 cps for the cyclized chains.[6] On warming, the methyl signals in IIb coalesce at *ca.* 40°, and the methylene signals coalesce at *ca.* 55°. This difference is as expected, since the rate of equilibration required for coalescence of two signals in the nmr is proportional[7] to the difference in their chemical shifts. Thus both spectroscopic changes reflect a single process, the equilibration of the two side chains. Compound IIb has a fluctuating structure, but at any instant one of the side chains is fully coordinated and the other is free. As expected, the positions of nmr lines at higher temperatures are precisely the average of these from the lower temperature, and no new ultraviolet absorption is present.

The methylene groups of a number of the alcohols also show up as AB quartets, and two different phenomena appear to be involved. Thus in the bissulfur alcohol Ib the two methylene groups are equivalent, but in each one of them the two protons have different chemical shifts. This is as expected: the methylene

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[5] See ref 3, p 3046.

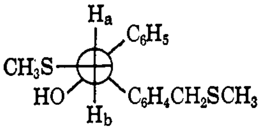
[6] A tabulation of geminal coupling constants has been presented by A. Bothner-By, *Advan. Magnetic Resonance*, 1, 195 (1965).

[7] J. Pople, W. Schneider, and H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

Table I. Nmr Data

Compound	Solvent	Chemical shift, δ (J, cps) CH$_2$	CH$_3$	R$_4$, R$_5$, R$_6$
Ia	SO_2	3.56	1.83	...
Ia	$CDCl_3$	3.55	1.82	...
IIa ClO_4^-	SO_2	5.19, 4.63 AB (16)	2.45	...
IIa $CF_3CO_2^-$	SO_2	5.09, 4.53 AB (16)	2.41	...
Ib	SO_2	3.80, 3.40 AB (13)	1.81	...
IIb $CF_3CO_2^-$	$CDCl_3$ (60°)	4.2 (very broad)	2.15	...
IIb $CF_3CO_2^-$	$CDCl_3$ (10°)	5.51, 4.87 AB (18)	2.39	...
		3.54, 2.88 AB (13)	1.90	
		Coalesces *ca.* 50°	Coalesces *ca.* 40°	
Ic	$CDCl_3$	3.36, 4.06 AB (13)	1.95	...
IIc $CF_3CO_2^-$	$CDCl_3$ (50°)	4.0 broad	2.04	
IIc $CF_3CO_2^-$	$CDCl_3$ (−10°)	4.5–5.3 broad 2.6–3.8 broad	2.32, 1.97, 1.68	...
		Coalesces *ca.* 15°	Coalesces *ca.* 5°	
Id	$CDCl_3$	3.53	1.89	3.73
IId ClO_4^-	SO_2	4.87	2.43	3.80
IId $CF_3CO_2^-$	$CDCl_3$	4.88	2.48	3.84
Ie	$CDCl_3$	3.94, 3.44 AB (13)	1.97	3.76
IIe $CF_3CO_2^-$	$CDCl_3$ (20°)	4.28 (broad)	2.21	3.79
IIe $CF_3CO_2^-$	$CDCl_3$ (−35°)	3.3 m, 5.2 m	2.0, 2.43	3.77
		Coalesces *ca.* −10°	Coalesces *ca.* −30°	
If	CCl_4	3.75, 3.45 AB (13)	1.90	3.70
IIf $CF_3CO_2^-$	SO_2–$CDCl_3$ (−10)°	3.98	2.13	3.88 (6 H), 3.84 (3 H)
	SO_2–$CDCl_3$ (−50°)	4.03 (broad)	2.18	3.90, 3.83
	SO_2–$CDCl_3$ (−90°)	3.85 (very broad)	1.9, 2.5 (broad)	3.85 (broad)
IIf ClO_4^-	$CDCl_3$ (80°)	4.03	2.15	3.8, 3.80
IIf ClO_4^-	$CDCl_3$ (20°)	4.18	2.23	3.88, 3.82
IIf ClO_4^-	$CDCl_3$ (−40°)	4.23 (broad)	2.23	3.88, 3.82
IIf ClO_4^-	$CDCl_3$ (−80°)	4.1 (broad)	2.24	3.86 (broad)
IIf ClO_4^-	*o*-Dichlorobenzene (20°)	4.26	2.10	3.73, 3.56
IIf ClO_4^-	*o*-Dichlorobenzene (80°)	4.12	2.10	3.74, 3.63
IIf ClO_4^-	*o*-Dichlorobenzene (120°)	4.03	2.07	3.75, 3.68
Ig	$CDCl_3$	...	...	2.90
IIg HCO_2^-	$CDCl_3$	...	...	3.65
Ih	$CDCl_3$	3.57	1.90	2.90
IIh ClO_4^-	$CDCl_3$	3.40, 3.04 AB (13)	1.82	3.58
IIh ClO_4^-	*o*-Dichlorobenzene (30°)	3.33, 3.00	1.80	3.6
IIh ClO_4^-	*o*-Dichlorobenzene (80°)	3.40, 3.04	1.8	3.6
IIh ClO_4^-	Coalesces *ca.* 70°			
IIh $CF_3CO_2^-$	$CDCl_3$	3.40, 3.04 AB (13)	1.82	3.58
Ii	$CDCl_3$	3.91, 3.51 AB (13)	2.00	2.95
IIi Cl^-	$CDCl_3$–SO_2 (40°)	3.25	1.80	3.70
IIi Cl^-	$CDCl_3$–SO_2 (−30°)	3.25, 2.85 AB (13)	1.72	3.70
Ij	$CDCl_3$	Propyl multiplets		2.85
IIj ClO_4^-	SO_2	As above, but slightly shifted upfield		3.64
Ik	$CDCl_3$	3.99, 3.43 AB (13)	1.97	3.2, 3.9 A_2B_2
IIu ClO_4^-	$CDCl_3$ (30°)	3.22	1.82	Broad multiplet centered at 4.0
IIu ClO_4^-	$CDCl_3$ (−60°)	3.38, 2.68 AB (13)	1.80	Broad multiplet centered at 4.0
Iv	$CDCl_3$	4.40	3.17	2.88
IIv ClO_4^-	$CDCl_3$	4.14 (40%) 3.90 (60%)	3.20 (40%) 3.08 (60%)	3.66
ClO_4^-	SO_2 (−60°)	Unchanged, but 3.90 → 3.75, 4.05 AB (13)		
Iw	$CDCl_3$	...	2.2	...
IIw $CF_3CO_2^-$	$CDCl_3$	...	2.38	...
Ix	$CDCl_3$	...	2.2	...
IIx $CF_3CO_2^-$	$CDCl_3$	...	2.42	...
Iy	$CDCl_3$	...	...	2.33
IIy	$CDCl_3$	...	...	2.78
Iz	$CDCl_3$	...	...	2.38
IIz $CF_3CO_2^-$	$CDCl_3$	...	...	2.69

group is in an asymmetric environment, as can be seen by considering the diagram C.[8] Here the CH_2 group



C

is lined up with the central carbon, to which it is joined by the benzene ring at the right. In the bissulfur alcohol Ib which is shown in C the substitution is unsymmetrical, whereas in the monosulfur alcohol Ia the central carbon would carry two phenyls and the diagram corresponding to C would have a plane of symmetry. The CH_2 group of Ia is in fact a singlet, as expected from these considerations. Of course, Ib is conformationally mobile, but it can never go to a mirror-image conformation in which H_a and H_b are interchanged. Experimentally, the CH_2 group remains a sharp AB quartet even at 190°, but the difference in the two chemical shifts goes from 0.4 ppm at 40° to 0.1 ppm at 190° (J = 13 cps throughout). A similar splitting is seen in all the alcohols with two thiomethoxymethyl side chains—Ie, If, Ii, and Ik. However, the dissymmetry in such compounds must be effective chiefly because the bulky *ortho* substituent makes the substituted phenyl in C very different conformationally from a simple phenyl group. Alcohols in which the two phenyls in a structure related to C are differentiated only by *para* substitution, Id and Ih, have singlet CH_2 groups even though they have formal dissymmetry.[9]

The other effect which operates is that some highly hindered molecules which lack the asymmetry symbolized in C show methylene groups as AB quartets because they do not interconvert rapidly between mirror image conformations on an nmr time scale. In particular, this has been found for the three *ortho*-trisubstituted alcohols Ic, In, and Iq. Thus for the tris(methoxymethyl) alcohol Iq the CH_2 groups are equivalent at 40°, but as an AB quartet with 0.70-ppm difference in the two chemical shifts. However, in this case heating to 190° leads to standard coalescence behavior as expected, since the molecule is not intrinsically dissymmetric.

In the case of the trissulfur cation IIc, an interesting situation is observed. At low temperature there are three kinds of side chains: one is coordinated, with its methyl nmr signal at δ 2.32 as in IIa and IIb, one is uncoordinated, with its methyl nmr signal at δ 1.97 as in IIb or in the carbinol Ic, and a third one is at δ 1.68. This last is, of course, also uncoordinated but it is held in a magnetically shielded environment relative to the second side chain, and the molecule is rigid enough that these two do not interchange positions. This can be more or less rationalized with molecular models, which show a "pocket" in a structure like IIa′ into which a second, but not a third, side chain can fit; the distinction between the two uncoordinated chains is presumably a result of the chirality of the system. When the temperature is raised all three signals coalesce smoothly to a single peak (Figure 1) at a temperature somewhat lower than that required for the bissulfur cation IIb. The widely distributed methylene signals also coalesce to a singlet, showing not only that all three chains are equilibrating but also that each coordinated chain equilibrates between coordination in the two mirror-image senses; thus, the asymmetry at sulfur is averaged out and the quartets collapse to a singlet. Apparently all three chains equilibrate at once, consistent with a mechanism which involves opening to the carbonium ion by an S_N1 process. Further evidence that this is the mechanism is presented below.

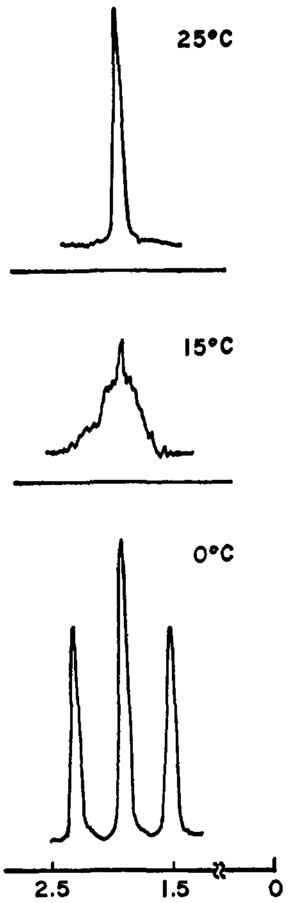


Figure 1. Coalescence of the methyl nmr signals in IIc.

Since these side chains are strong enough ligands to give complete coordination with trityl cation, albeit with fluctuating structure, we modified the molecules so as to decrease the tendency toward coordination. The original proposition is, of course, that somewhere between completely coordinated structures and completely open cations may lie a region in which partial coordination is observable, possibly pentacoordination. Accordingly, we examined molecules in which conjugative stabilization of the cation is increased over that in IIa, b, and c. Trityl cations are stabilized by *p*-methoxy and *p*-dimethylamino groups, as is shown by the pK_{R^+}'s presented in Table II. Naturally, these values are only a vague guide to what we may expect from substitution in our series, since our side chains lead to considerable twisting of the phenyl rings.

The monosulfur cation with one *p*-methoxy group in another ring (IId) exists with the side chain completely cyclized, with the methyl and methylene nmr signals

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(8) *Cf.* the similar situation in diethylacetal, in which two protons in a CH_2 group are magnetically nonequivalent.

(9) The bisether Ip also has a singlet CH_2 signal; thus formal dissymmetry is by no means a sufficient condition to guarantee observable splitting.

Table II

Triphenylcarbinol	pK_{R^+}
Unsubstituted	−6.6^a
p-CH$_3$O	−3.4^a
(p-CH$_3$O)$_2$	−1.2^a
(p-CH$_3$O)$_3$	+0.8^a
p-N(CH$_3$)$_2$	+3.7^b

^{a} N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc*, **77**, 3044 (1955). ^{b} This work.

at the same places as in IIa and IIa′. This is also clear from the nmr shift of the methoxy group, almost unchanged from the alcohol since the positive charge is not delocalized into it, and from the absence of appreciable electronic absorption for a trityl cation. Apparently equilibrium with an open cation is more rapid in the methoxy-substituted case, however, since at ambient temperature the methylene signal is a singlet, not a quartet as in IIa. The sulfur asymmetry can be averaged out by ionization, rotation of the rings, and reattachment of the side chain; either rotation of the rings through the plane and reattachment on the opposite face of the central carbon, or rotation perpendicular to the plane and reattachment on the same face of the central carbon, causes mirror inversion (*cf.* discussion below, and Figure 2).

With one p-methoxy group and two sulfur side chains, the cation II is again cyclic but fluctuating. Coalescence of the signals occur at considerably lower temperatures than in IIb, without the methoxyl, again suggesting an S$_N$1 mechanism with the carbonium ion intermediate. As expected, the p-methoxy signal is unaffected by the temperature variation which equilibrates the side chains.

With three p-methoxy groups a new phenomenon is observed. The bissulfurtrismethoxy cation IIf at low temperatures is chiefly a fluctuating cyclized cation, and at −90° the two kinds of S-methyl groups are resolved in the nmr spectrum. Above this temperature only averaged nmr spectra are observed, but additionally the ion has some color. In ethanol, λ_{max} of IIf chloride is at 504 mμ and the extinction coefficient varies reversibly from 28 at −45° to 2700 at 59°. This is the expected situation if the cyclic ion is in equilibrium with an uncyclized trityl cation, and the usual ln K *vs.* $1/T$ plot gives a good straight line whose slope corresponds to $\Delta H° = +6.7$ kcal/mol.

At a given temperature the intensity of the spectrum is greater in less polar media, and IIf trifluoroacetate in o-dichlorobenzene has λ_{max} at 507 mμ and ϵ at 25° of 2.4×10^4. This solvent effect is reasonable since the cyclized ion has a localized charge, requiring good solvation, while the delocalized charge in the open cation is more compatible with a nonpolar medium. Although the ϵ of the open cation may also be solvent dependent, the large increase in intensity undoubtedly reflects mainly an increase in the amount of open cation which is present. On heating the dichlorobenzene solution rapidly to 130° the ϵ rises to 3.2×10^4 before decomposition sets in, but this small temperature effect suggests that in dichlorobenzene, even at 25°, a large fraction of the cation is not cyclic. For comparison,[8] p,p',p''-trismethoxytriphenylmethyl cation has λ_{max} at 483 mμ (ϵ 29.0 × 10^4) while the p,p'-bismethoxytriphenylmethyl cation has λ_{max} at 500 mμ (ϵ 5.6 × 10^4). It is not clear which, if either, is a good model for our cation IIf with its twisted phenyls, but an ϵ for our open cation of the order of 5×10^4 seems reasonable.

The nmr spectrum adds little information about the equilibrium between cyclic and open-chain ions. As is seen in Table I, there is some change in the chemical shifts of CH$_2$, SCH$_3$, and OCH$_3$ groups on changing from SO$_2$–CDCl$_3$ at low temperatures (completely cyclic) to o-dichlorobenzene solution at high temperature (largely open chain). The small magnitudes of these changes are as expected from the other examples in Table I, but they do not furnish independent information on the position of the equilibrium.

As Table II shows, a single p-dimethylamino group should strongly favor the open cation, especially if it is placed on an unhindered phenyl ring. A considerable amount of the positive charge will be delocalized onto the nitrogen, as the nmr shift between Ig and IIg indicates. The cations with such a dimethylamino group and one (IIh) or two (IIi) sulfur side chains are completely uncyclized, as revealed by their nmr spectra with strongly shifted dimethylamino groups and methylene and S-methyl groups which see no appreciable positive charge and are actually shifted upfield. Their behavior is mirrored almost exactly by the molecule with two n-propyl side chains (IIj) in which neighboring group participation is impossible.

Although IIh and IIIi are not cyclized, their nmr spectra show the methylene groups as AB quartets, at ambient temperature in IIh and at lower temperature in IIi. The coupling constant, 13 cps, is typical of noncyclized chains on a molecule with another asymmetric center, and it undoubtedly reflects the asymmetry in a twisted trityl cation. Such a molecule in general will have a propeller conformation, and the propeller may have either a right-handed or left-handed screw sense. In order that the two methylene protons on IIh, for instance, be magnetically equivalent it is not sufficient that the side chain simply rotate more or less freely; only inversion of the trityl cation propeller to its mirror image interconverts the environments of the two protons. Thus we are looking at flipping of the trityl propeller, a process which we have also detected[10] in a free radical derived from our present series and which is also involved in the nmr effects described by Kurland.[11]

There are two pathways by which the left-handed and right-handed propeller conformations can be interconverted (Figure 2). Either the phenyls may rotate, more or less concertedly, so that they become perpendicular to the plane defined by the bonds to the central carbon atom (path A), or they may pass through that plane (path B).

We can make a choice of path A, since the cation IIi with two side chains undergoes coalescence at a lower temperature than does the one (IIh) with a single side chain. These bulky groups should strongly destabilize the coplanar arrangement in path B, but they facilitate interconversion by path A. A similar choice is available for the process by which the AB quartets in the side chains of cyclized cations such as IIb coalesce. We have described the process as ionization and reco-

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(10) J. Hyde, R. Breslow, and C. de Boer, *J. Am. Chem. Soc.*, **88**, 4763 (1966).

(11) A. K. Colter, I. I. Schuster, and R. J. Kurland, *ibid.*, **87**, 2278 (1965).

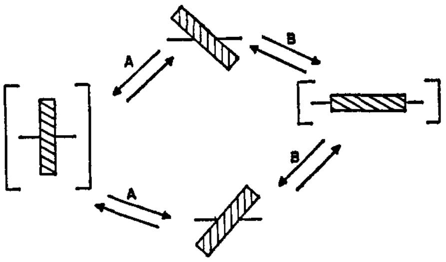


Figure 2. Interconversion of trityl cation conformations through perpendicular (A) or planar (B) intermediates.

ordination in the mirror image sense, but two modes of rotation are possible, related to paths A and **B**. The pathway (Figure 3) related to process A is probably the preferred path to the mirror image cyclic cation, as path A is for the trityl cations.

The visible spectrum of IIi is included in Table III along with those for other compounds of interest in this work. It can be seen that it is very similar in λ_{max} and ϵ to the spectrum of the analogous cation with *n*-propyl side chains (IIj), in which neighboring group participation of any sort is excluded, and they both are almost the same as the spectrum of IIg, in which there are no other groups.

Table III

Compound	λ_{max}, mμ[a]	ϵ ($\times$ 10^{-4})[a]	pK_{R^+}
Triphenylmethyl	430	3.83	−6.6 ± 0.1
IIe	475	0.029[b]	...
IIf	507	3.2[c]	. .
IIg	460	3.6	+3.6[d]
IIg·H$^+$ (80% H_2SO_4)	445	3.5	...
IIIh	450	3.0	...
IIi	458	2.8[e]	. .
IIj	458	3.5[e]	.
IIk	480	2.8[f]	
IIl	440	3.45	−6.6 ± 0.2
IIm	445	2.96	−7.4 ± 0.2
IIn	464	2.73	−9.2 ± 0.2
IIo	440	4.13	−6.6 ± 0.3
IIp	445	3.57	−6.6 ± 0.3
IIq	450	3.18	−6.5 ± 0.3
IIr	432	3.16	−5.5 ± 0.5
IIs	435	2.36	−5.5 ± 0.5
IIt	465	1.93	−5.2 ± 0.5
IIv	453	3.2[c]	
IIw	440	2.4	−6.8 ± 0.3
	680	0.21	
IIx	440	2.1	−7.4 ± 0.5
	650	0.38	
IIy	400	1.31	−5.1 ± 0.1
	543	4.32	
IIz	465	3.93	−4.6 ± 0.1
	594	8.40	

[a] The spectra are reported for solutions of the corresponding carbinols in aqueous sulfuric acid sufficiently strong for complete conversion to the cation, unless otherwise noted. [b] This ϵ temperature dependent; the value reported is for a solution of the trifluroacetate salt in *o*-dichlorobenzene at 25°. [c] As in footnote *b*, but at 130°. [d] The difference from the literature value is discussed in the text. [e] For the perchlorate salt in $CHCl_3$ solution. [f] For the trifluoroacetate in *o*-dichlorobenzene.

When these cations are put in very strong acid then they can protonate on nitrogen as well. In the case of the simple *p*-dimethylaminotrityl cation (IIg) this leads to a new chromophore (Table III) but in the case

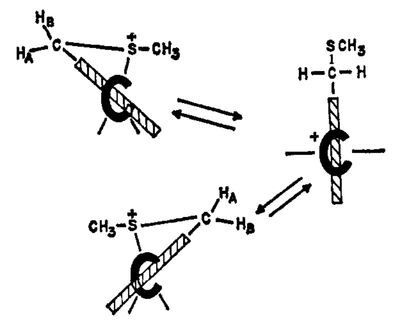
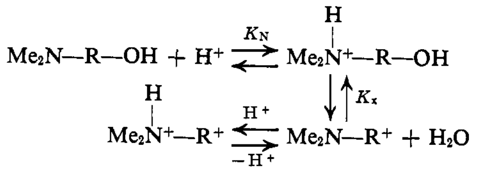


Figure 3. A mechanism for collapse of the CH_2 AB quartets in the nmr spectrum of cations such as IIb.

of IIh and IIi protonation of the stabilizing dimethylamino group leads to coordination of the sulfur side chains; the visible spectrum disappears and the nmr spectra are as expected for cyclic sulfonium ions.

Because a carbinol such as Ig can undergo three difference processes in acid—protonation on nitrogen, formation of the carbonium ion, or formation of the N-protonated carbonum ion—the pK_{R^+} determination is not completely straightforward. The pK_{R^+} for Ig



$$\begin{tikzcd}
Me_2N{-}R{-}OH + H^+ \arrow[r, shift left, "K_N"] & \overset{H}{Me_2N^+}{-}R{-}OH \arrow[l, shift left] \arrow[d, shift right] \\
\overset{H}{Me_2N^+}{-}R^+ \arrow[r, shift right, "-H^+"'] & Me_2N{-}R^+ + H_2O \arrow[l, shift right, "H^+"'] \arrow[u, shift right, "K_x"']
\end{tikzcd}$$

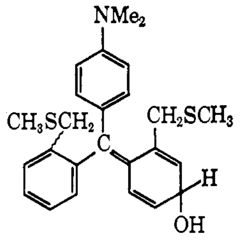
has been reported[12] to be 4.75, but this is simply the pK_a of the amine, since N-protonation is the most facile process. Solutions of Ig at this pH have only a weak absorption, and not until the acid strength is increased to H_R −2.95 does 50% of the final absorption develop. However, this is not the pK_{R^+} for Ig either, since the equilibrium being observed is the one with constant K_x, and the one of interest has constant K_NK_x. The K_x equilibrium has no formal acid dependence at all, and is shifted in strong acid only because the activity coefficient of H_2O is changed. Experimentally, the intensity of the visible absorption of solutions of Ig is constant from pH 0.6 to 2.2 with an ϵ of 10% of the strong-acid ϵ. Accordingly, K_x has a value of 0.1 in this region and the true pK_{R^+} of Ig is 3.7, not 4.7. In very strong acid, the second protonation occurs.

Unfortunately this pK_{R^+} could not be compared with the pK_{R^+}'s of related carbonium ions with side chains in the *ortho* position because of a remarkable new phenomenon. For such carbinols as Ii, both the conversion to carbonium ion and the quenching of the carbonium ion are very slow processes. Thus, when Ii was treated with formic acid in $CDCl_3$, the first protonation was on the nitrogen, with a shift of the amino methyls in the nmr from δ 2.95 to 3.3. Only over 1.5 hr did this then change to the δ 3.7 of the carbonium ion, with corresponding changes in the nmr of the side chains and in the visible spectrum. More unusual is the quenching behavior of this cation. At pH 11.0, in aqueous dioxane, the cation disappears with a halftime of 30 min, but it is converted not into the starting carbinol Ii, but into a new intermediate with λ_{max}

(12) R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949).

380 mμ, which only very slowly ($t_{1/2}$ = 45 hr) goes to Ii. The ionization is more rapid in strong acid, while the quenching is faster in strong base, but at any intermediate pH the rate of equilibration is so slow that a pK_{R^+} could not be determined.

Nothing of the kind is observed in the cation IIg without *ortho* side chains. Thus when IIg is placed in aqueous dioxane even at pH 2.0, it quenches to the (N-protonated) carbinol with $t_{1/2}$ = 90 sec, while at pH 10 reaction is essentially instantaneous. The cation with *one* thioether side chain (IIh) quenches relatively slowly ($t_{1/2}$ = 16 min at pH 10.5) but directly to the carbinol Ih rather than to an intermediate. The intermediate in the case of IIi is probably a carbinol which has quenched at some carbon other than the central one, *e.g.*, Ii′. Thus the pattern is that the simple cation IIg quenches at the central carbon readily, with one thioether side chain this is slower in IIh, while IIi has such a hindered central carbon that quenching occurs elsewhere, with very slow rearrangement to Ii. Since the ionization rates are also slow these data do not necessarily imply higher pK_{R^+} for Ih and Ii.



Ii′

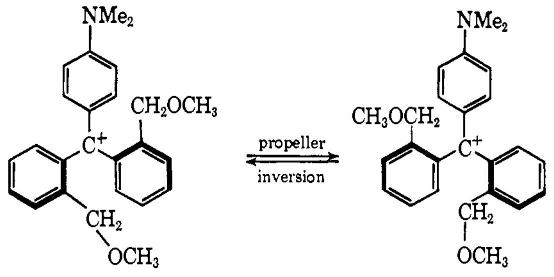
The shielding of the central carbon in IIi shows that the two side chains do indeed cover the two faces of the carbonium ion. However, no other than a steric interaction need be involved since an identical phenomenon, two-step quenching, is found in the case with two ether side chains (IIv) or with two *n*-propyl side chains (IIj). This last is the slowest of the trio at all pH's examined, so no special solvation interaction can be involved for the other side chains.

Since morpholine has a pK_a of 8.7, compared with 10.9 for dimethylamine, a carbinol was synthesized with a *p*-morpholinyl group to provide a case intermediate in stability between the tris-*p*-methoxy and the *p*-dimethylamino cations. The nmr and visible spectra show that the ion has an open-chain structure. As in the dimethylamino analog IIi, the methylene group becomes an AB quartet at low temperature because the propeller inversion becomes slow on the nmr time scale.

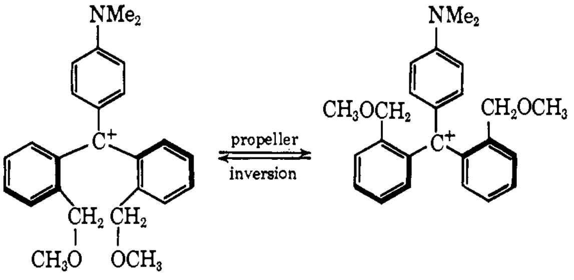
For a thioether to interact with a carbonium ion, at least partially covalent bonding would be involved. Accordingly, three carbonium ions were prepared (IIl, IIm, and IIn) with one, two, or three sulfone side chains, which might furnish intramolecular solvation by ion–dipole interaction. As Table III shows, all three have normal trityl cation spectra; the pK_{R^+}'s, compared with -6.6 for simple trityl cation, show no net stabilization although in IIl intramolecular solvation may be compensating for unfavorable steric and inductive effects.

Similarly, the cations IIo, IIp, and IIq with one, two, or three ether side chains are open cations with no remarkable difference in pK_{R^+} or spectrum compared with the isosteric cations IIr, IIs, and IIt with one, two, and three *n*-propyl groups. However, as described in the accompanying paper, IIo undergoes a cyclization with loss of methyl to produce a cyclic ether.

The cation IIv with two ether side chains and a *p*-dimethylamino group is of course completely an open carbonium ion, but as Table I shows there are *two* ions present in a 60:40 ratio.[13] The solution quenches to the carbinol Iv in good yield, and both ions have the dimethylamino nmr signal in the same place, although the side-chain protons have different chemical shifts. We suggest that these two ions are the two possible conformer sets IIv′ and IIv″. Propeller inversion through the perpendicular mechanism we have discussed above interconverts conformers within each set, although not between sets. On cooling, one of these isomers develops structure in the methylene group nmr signal.



IIv′



IIv″

When thiomethoxy groups are directly attached to the *ortho* position of a trityl cation, in IIw and IIx, cyclic sulfonium ion formation would require a strained four-membered ring. These cations are in fact noncyclic, as the spectra in Tables I and III show. Furthermore, the *ortho* groups do not furnish any special stabilization since the pK_{R^+}'s for the *ortho* compounds are lower than those for trityl or for the *p*-thiomethoxy cations IIy and IIz. The pK_{R^+}'s of IIy and IIz show that *p*-thiomethoxy groups are stabilizing, as expected, but our values correspond to a σ^+ of only 0.41 for the first group, and a very small value for the second, compared with the accepted $\sigma^+_{p\text{-CH}_3\text{S}}$ of 0.604.[14] It is also noteworthy that these thioether substituents are less stabilizing than corresponding methoxy groups, but that they exert a much stronger bathochromic effect on the electronic spectrum. Sulfur differs from oxygen in both its electronegativity and its π-bonding ability, and these two factors come to a different extent into the

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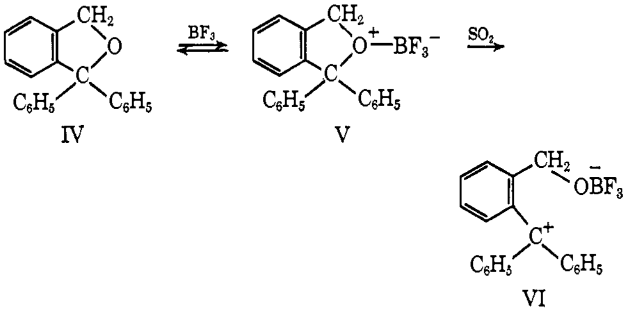
[13] *Cf.* the similar situation described in ref 11.

[14] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

substituent interaction with the ground and the excited states of the carbonium ion. The long-wavelength bands in the *o*-thioethers IIw and IIx may involve some direct charge–transfer interaction.

The neighboring groups considered so far are nonpolar except for the sulfone group. The availability of the cyclic ether IV from demethylation of IIo suggested a synthesis of an internally connected ion pair, by treatment of IV with neutral Lewis acids. When IV was treated with $AlCl_3$ or SbF_5 in various solvents, 9-phenylanthracene was formed. Treatment of IV with BF_3 in $CDCl_3$ affords the coordinated species V, whose aromatic protons are unshifted at δ 7.5 while the CH_2 signal of IV has moved from δ 5.12 to 5.52 and the electronic spectrum shows λ_{max} 437 mμ with ε only 5.2 × 10^1. However, with BF_3 in SO_2 the ion pair VI is apparently formed, since the aromatic protons are spread from δ 7.1 to 8.3, the CH_2 is at δ 4.72, and the solution shows λ_{max} 442 mμ (ε 3.5 × 10^4).



IV

V

VI

Complete conversion to VI requires an excess of BF_3, and attempted isolation of VI yields recovered IV (quenching the solution of VI in methanol forms IV in 100% recovery). The structure seems very likely in view of the reconversion to IV, the electronic spectrum, and the upfield shift of the CH_2 nmr compared with IV and V (which excludes[15] a neutral CH_2OBF_2 side chain). However, further work would be required to establish the structure and properties of VI and related compounds in detail.

The final study of potential intramolecular solvation concerns the benzophenones (III). In general, the n → π* transition in a ketone moves to shorter wavelengths with increasing solvent polarity, while the π → π* transition goes in the opposite direction.[4] This trend can be seen for benzophenone in Table IV, although solvent "polarity" includes factors, such as hydrogen bonding, which are not completely reflected in the simple bulk dielectric constant. It was of interest to see whether two neighboring groups in III can furnish such effective shielding of the ketone that external solvent effects disappear, and further, whether the ketone spectrum reflects the polarity of the particular side chain. The results in Table IV show that two *o*-propyl groups in IIIs diminish the solvent effects somewhat, but that the solvent effects are completely removed by two methanesulfonylmethyl groups in IIIm. Furthermore, IIIm has in all media the spectrum found for the others in strongly polar solvents. Thus, the anticipated intramolecular solvation is apparently seen in IIIm, but further work will be needed to establish the generality of these findings.

Table IV. Ultraviolet Absorption Maxima of a Series of *ortho*-Substituted Benzophenones[a]

Solvent	Dielectric constant	Benzophenone	Mono-SO_2 (IIIl)	Bis-SO_2 (IIIm)	Bis-*n*-propyl (IIIs)
n-Hexane	1.89				
n–π*		345	333	. . .	338
π–π*		247	251	252	246
Benzene	2.28				
n–π*		342	332	329	336
p-Dioxane	2.21				
n–π*		341	333	328	336
π–π*		250	252	254	250
1,2-Dichloroethane	10.65				
n–π*		338	332	330	335
π–π*		252	253	255	250
Sulfolane	. .				
n–π*		338	. . .	328	334
Dimethyl sulfoxide	45.0				
n–π*		338	330	328	333
Acetonitrile	37.5				
n–π*		338	330	328	333
π–π*		250	251	252	250
Ethanol	25.1				
n–π*		332	328	328	330
π–π*		252	253	253	251

[a] The maxima are expressed in millimicrons and are good to 2 mμ (because of flat maxima in some cases).

Conclusions

1. *o*-Thiomethoxymethyl groups in trityl cations may be coordinated or not with the central carbon, depending on the nature of the other substituents.
2. When two or three such groups are present in a structure in which coordination occurs, fluctuating structures are found. The rate of equilibration, as a function of other substituents, suggests an internal "SN1" rather than "SN2" mechanism.
3. The nmr spectra of the methylene groups in these side chains are sensitive probes for conformational dissymmetry. This tool has detected intrinsic structural dissymmetry (Ib, Ie, If, Ii, and Ik), but also slow conformational equilibration which is temperature dependent. This can be used by simple crowding (Ic, In, and Iq), by a barrier requiring decoordination of the side chain and propeller inversion of the trityl cation (IIa, IIb, IIc, and IIe), or by the barrier to inversion of chirality of the trityl cation propeller in cations whose side chains are not coordinated (IIh, IIi, IIk, and IIv). This latter process occurs by rotation of the phenyl rings through planes perpendicular to the normal plane of the molecule.
4. No evidence was found requiring the postulation of partial or multiple coordination of side chains, although a closely graduated series of carbonium ion stabilities was examined and in one case (IIf) both closed and open forms could be produced by varying solvent and temperature.
5. With methoxymethyl (IIo, p, q, v), methanesulfonylmethyl (III, m, n), and thiomethoxy (IIw, x) groups in the *ortho* positions all the carbonium ions examined were uncyclized. The properties of these ions, es-

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[15] For the strong downfield shift which would be expected in the CH_2 signal in this case, *cf.* A. L. Allred and E. G. Rochow, *J. Am. Chem. Soc.*, 79, 5361 (1957).

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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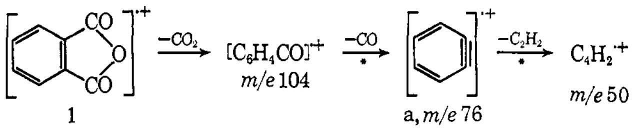
Received February 14, 1968

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 $C_6H_4\cdot^+$



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

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[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).