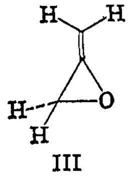
values of 2.93 and 2.34 in acetone[12] and formaldehyde,[18] respectively.

The moments of inertia are easily determined from the rotational constants in Table I, giving $I_a = 25.1$ amu Å^2, $I_b = 67.70$ amu Å^2, and $I_c = 86.10$ amu Å^2. These moments indicate that most of the mass is contained in a plane. The combination of moments, $(I_a + I_b - I_c)$, leads to the value of $2\Sigma_i m_i c_i^2 = 6.70$ where m_i is the mass of the ith nucleus and c_i is the distance of the ith particle along the c axis (axis of largest moment of inertia). The values of $(I_a + I_b - I_c)$ are listed in Table II for several molecules with known out-of-plane protons. There seems to be no doubt that the present molecule has four out-of-plane protons. Note the similarity in Table II for the values of $(I_a + I_b - I_c)$ in ethylene oxide and the present molecule. If we assume $\Sigma_i m_i c_i^2$ is caused by four hydrogen atoms we get $c_H = 0.91$ Å. If we further assume that the molecule has two identical HCH structural subunits as in ethylene oxide with a H–C distance of 1.085 Å, we obtain a HCH angle of 115 ± 3°, which is again close to the result in ethylene oxide or the cyclopropanes. Thus, this simple analysis points strongly toward a simple ring-closed structure of cyclopropanone with three carbon atoms and one oxygen atom in a plane and four protons out of the plane (I). Another possible structure, allene oxide (III), is ruled out: only two protons are out of the plane, and two dipole components would have been observed as in methylcyclopropene.[19]

Table II. $(I_a + I_b - I_c)$ for Several Molecules[a]

Molecule	$(I_a + I_b - I_c)$	No. of out-of-plane protons	Ref
trans-Acrolein	0.0212	0	16
1,2,5-Oxadiazole	0.0707	0	*b*
Furan	−0.0481	0	*c*
Cyclopropene	3.31	2	*d*
Cyclopentadiene	3.11	2	*e*
Ethylene oxide	6.83	4	*f*
β-Propiolactone	6.50	4	*g*
Cyclopropanone	6.70	4	*h*

[a] In atomic mass units ångströms squared. [b] E. Sagebarth and A. P. Cox, *J. Chem. Phys.*, **43**, 166 (1965). [c] M. H. Sirvetz, *ibid.*, **19**, 1609 (1951). [d] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *ibid.*, **30**, 512 (1959). [e] V. W. Laurie, *ibid.*, **24**, 635 (1956). [f] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, and W. D. Gwinn, *ibid.*, **19**, 676 (1951). [g] N. Kwak, J. H. Goldstein, and J. W. Simmons, *ibid.*, **25**, 1203 (1956). [h] This work.



III

Further manipulation with the moments of inertia shows that the C_2–C_3 distance is larger than the C_1–C_2 and C_1–C_3 distances.[20] A structure which fits the observed moments is listed in Table III. Further work on this molecule, including a complete isotopic structure analysis, is in progress.

Table III. Structural Parameters for Cyclopropanone[a]

Bond	Length, Å	Angle
C_1–O	1.18	$C_3C_1C_2$, 64°
C_1–$C_{2,3}$	1.49	HCH, 117° 35′
C_2–C_3	1.58	
$C_{2,3}$–H_{1-4}	1.085	

[a] The HCH plane bisects the CCC angle. The molecule has C_{2v} symmetry. Calculated moments of inertia (amu Å^2): $I_a = 25.060$, $I_b = 68.040$, $I_c = 86.155$. Experimental moments of inertia (amu Å^2): $I_a = 25.1$, $I_b = 67.70$, $I_c = 86.10$.

There appears to be little doubt that cyclopropanone (I) has been isolated and identified. There is also no doubt that the molecule identified herein is in a singlet ground state. The observed spectrum shows no magnetic hyperfine structure as is characteristic of radicals. In addition, we have observed the $2_{21} \rightarrow 3_{22}$ transitions (Table I) in a high magnetic field (11,000 gauss).[21] The zero-field line was 300 kHz at half-height. No additional splitting or broadening was observed at the high magnetic field.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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(19) M. K. Kemp and W. H. Flygare, *J. Am. Chem. Soc.*, **89**, 3925 (1967).

(20) R. Desiderato and R. L. Sass, *Acta Cryst.*, **23**, 430 (1967), have uncovered a long C–C bond in *cis*-2-butene episulfone. We thank R. Hoffmann for bringing this work to our attention.

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(22) (a) Standard Oil of California Fellow; (b) Alfred P. Sloan Fellow.

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Received December 11, 1967

Mass Spectral Fragmentation of Aniline-1-^{13}C[1]

Sir:

The major electron impact fragmentation pathway of aniline is that shown in eq 1,[2] as demonstrated by studies with aniline-^{15}N.[3] In view of the well-documented rearrangement of toluene in its mass spectral fragmentation (eq 2), most readily explained by a tropylium ion intermediate (I),[1,4,5] we have examined the possible intermediacy of an analogous azepinium ion (IIa) in the fragmentation of aniline[6] by studying

$$\underset{m/e\ 93}{C_6H_7N\cdot^+} \xrightarrow[m^*]{-HCN} \underset{m/e\ 66}{C_5H_6\cdot^+} \qquad (1)$$

$$\underset{m/e\ 92}{C_7H_8\cdot^+} \xrightarrow{-H\cdot} \underset{m/e\ 91}{C_7H_7^+} \xrightarrow{-C_2H_2} \underset{m/e\ 65}{C_5H_5^+} \qquad (2)$$

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(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11–15, 1967, Paper No. S-85.

(2) J. Momigny, *Bull. Soc. Roy. Sci. Liege*, **22**, 541 (1953).

(3) P. N. Rylander, S. Meyerson, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **85**, 2723 (1963).

(4) P. N. Rylander, S. Meyerson, and H. M. Grubb, *ibid.*, **79**, 842 (1957).

(5) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., p 516.

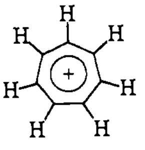
(6) Rylander, *et al.*, found "a proposal of ring expansion less attractive in aniline than in toluene."[3] However, thiepinium, oxepinium, and azatropylium ions have been postulated as intermediates in the mass spectral fragmentation of thiophenol,[7] *meta*- and *para*-substituted phenetoles,[8] picolines,[9] and methylquinolines and -isoquinolines.[10]

Table I. Mass Spectral Peaks (Low Resolution)

	Relative abundance[a–c]		
m/e	Aniline-^{15}N[d–f]	Aniline[d] (unlabeled)	Aniline-1-^{13}C[e,g]
61	0.018	0.021	0.020
62	0.026	0.032	0.033
63	0.047	0.063	0.055
64	0.030	0.040	0.034
65	0.246	0.280	0.232
66	0.572	0.524	0.533
67	0.025	0.040	0.056
68	0.036	0.000	0.037

[a] Σ_{61-68} = 1.000. [b] Corrected for naturally abundant ^{13}C. [c] Average of at least three runs. [d] Commercial sample, purified by glpc. [e] Calculated for 100% isotopic enrichment. [f] Sample contained 94.7% excess ^{15}N. [g] Sample contained 56.3% excess ^{13}C.

aniline-1-^{13}C. Loss of HCN from an unrearranged intermediate (IIb) would proceed with total loss of ^{13}C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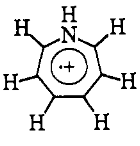
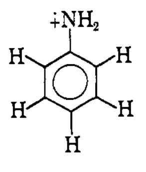

IIa



IIb

label, while the HCN lost from IIa would remove only a portion of the isotopic label.[11] The synthetic sequence proceeded from toluene-1-^{13}C[1] to benzoic acid-1-^{13}C to aniline-1-^{13}C.[12]

Low-resolution mass spectra were determined with an Atlas CH4 mass spectrometer; employing wide slits, flat-topped peaks were measured (Table I). Comparison of the peaks at m/e 65, 66, and 67 indicates that nitrogen[3] and the aniline carbon atom (1-^{13}C) bearing the amino group are both mostly lost.

However, from the slight decrease in the m/e 65 ion and the slight increase of the m/e 67 ion, some ions must contain ^{13}C. Quantitative interpretation of the spectrum in this region is complicated by the alternative, less important fragmentation pathway shown in eq 3;[3] in the unlabeled spectrum all nominal masses

$$\underset{m/e\ 93}{C_6H_7N\cdot^+} \xrightarrow{-C_2H_2} \underset{m/e\ 67}{C_4H_5N\cdot^+} \qquad (3)$$

near m/e 65 are C_5H_n–$C_4H_{n-2}N$ doublets and the aniline-1-^{13}C spectrum is complicated by the occurrence of up to four isobaric ions at each nominal mass, *viz.* C_5H_n, $^{13}CC_4H_{n-1}$, $C_4H_{n-2}N$, and $^{13}CC_4H_{n-3}N$. The relative abundances of the isobaric peaks were measured in the high-resolution spectrum of aniline-1-^{13}C (CEC 21-110B mass spectrometer at a resolution of 20,000). The peak intensity ratios for each isobaric set were averaged for 20–30 repetitive scans (Table II).

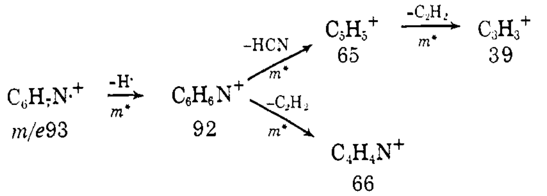
Table II. Mass Spectral Peaks for Aniline-1-^{13}C (High Resolution)

m/e	Composition	Relative abundance[a–d]	Abundance ratios
65	C_5H_5	0.458 (0.490)	$C_5H_5/(C_5H_5 + {}^{13}CC_4H_5)$ = 0.74
	C_4H_3N	0.003	
66	C_5H_6	1.000 (1.000)	$^{13}CC_3H_3N/(C_4H_3N + {}^{13}CC_3H_3N)$ = 0.97
	$^{13}CC_4H_5$	0.163	
	C_4H_4N	0.022	$C_5H_6/(C_5H_6 + {}^{13}CC_4H_6)$ = 0.93
	$^{13}CC_3H_3N$	0.099 (0.108)	
67	$^{13}CC_4H_6$	0.081	$^{13}CC_3H_4N/(C_4H_4N + {}^{13}CC_3H_4N)$ = 0.73
	C_4H_5N	0.003	
	$^{13}CC_3H_4N$	0.058 (0.082)	
68	$^{13}CC_3H_5N$	0.096 (0.099)	$^{13}CC_3H_5N/(C_4H_5N + {}^{13}CC_3H_5N)$ = 0.97

[a] Abundance of C_5H_6 defined as 1.000. [b] Corrected for naturally abundant ^{13}C. [c] Calculated for 100% isotopic enrichment; sample contained 56.3% excess ^{13}C. [d] Relative abundances in the high-resolution spectrum of unlabeled aniline given (in parentheses) for comparison beside the most abundant isotopic species.

From the data in Table II it is again clear that most of the ions which have lost nitrogen have also lost ^{13}C and most of those that retain nitrogen retain ^{13}C—*but not all.* For the ions C_5H_6 (M − HCN) and C_4H_5N (M − C_2H_2), as well as C_4H_3N (reasonably formed from C_4H_5N by loss of molecular hydrogen), more than 90% of the ions arise from an unrearranged parent ion.

For the ions C_5H_5 and C_4H_4N, however, a much higher proportion of the ions (at least one-third of C_5H_5, nearly all of C_4H_4N) must arise from a rearranged ion.[11,13] Since the isotopic figures of Table II belie the formation of C_5H_5 exclusively from C_5H_6[14] and C_4H_4N from C_4H_5N, an alternative pathway must exist, namely formation from C_6H_6N, as shown in eq 4. These fragmentations are, in fact, supported by



(4)

metastable ion peaks at m/e 91.1 (93 → 92),[3] 45.9 (92 → 65),[15] 47.4 (92 → 66),[15] and 23.4 (65 → 39).[15]

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(7) D. G. Earnshaw, G. L. Cook, and G. U. Dinneen, *J. Phys. Chem.*, **68**, 296 (1964).

(8) F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Am. Chem. Soc.*, **88**, 5022 (1966).

(9) T. F. Palmer and F. P. Lossing, *ibid.*, **85**, 1733 (1963).

(10) S. D. Sample, D. A. Lightner, O. Burchardt, and C. Djerassi, *J. Org. Chem.*, **32**, 997 (1967).

(11) The precise amount of ^{13}C lost would depend on the route followed in forming the azepinium ion. If the nitrogen atom were inserted between C-1 and C-2, one-half the ^{13}C would be retained in C_5H_6; if the nitrogen atom were inserted randomly (as is the methyl carbon in forming the tropylium ion),[1] five-sixths of the ^{13}C would be retained.

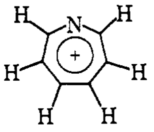
(12) Pure by glpc analysis.

(13) From azepinium-2-^{13}C, statistical loss of acetylene would give four-fifths $^{13}CC_3H_5N$ and one-fifth C_4H_5N; azepinium-U-^{13}C would give two-thirds $^{13}CC_3H_5N$ and one-third C_4H_5N.

(14) Although we did not observe a metastable ion peak for the 66 → 65 transition, this was reported by earlier authors.[3] Our data suggest one-half to two-thirds of C_5H_5 may come from C_5H_6.

(15) Metastable ion peaks not reported previously.

From our data we conclude that, while the C_6H_7N ion is nearly entirely unrearranged, the C_6H_6N ion is largely, at least, rearranged. This result is entirely reasonable since it is, of course, the C_6H_6N ion, an even-electron ion (III),[16] which would correspond to the tropylium ion. The parent ion C_6H_7N is an odd-electron ion[16] which can either lose HCN and C_2H_2 directly or can rearrange to an even-electron ion while losing a hydrogen atom.



III

Acknowledgment. This research was supported by a grant (No. AI 04769) from the National Institute of Allergy and Infectious Diseases. We thank Dr. M. F. Grostic, The Upjohn Co., for assistance in determining the high-resolution mass spectra.

(16) F. W. McLafferty, in ref 5, p 313 ff. Appropriate symbolism is employed in the present formulas and equations indicating ions as even or odd electron.

(17) National Institutes of Health Predoctoral Fellow, Allied Chemical Co. Fellow.

(18) National Institutes of Health Postdoctoral Trainee in Biophysical Chemistry (Training Grant No. 2TI GM722).

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Received November 22, 1967

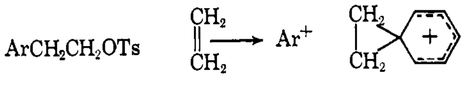
The Solvolysis of Arylethyl *p*-Toluenesulfonates[1]

Sir:

The question of aryl participation[2] has been the subject of recent controversy.[3] We wish to report some studies which have a bearing on this problem, and which also seem to suggest a novel procedure for measuring the nucleophilic activity of nucleophiles.

The idea behind this work was that information can frequently be gained concerning the mechanism of a reaction by comparing the observed relative rates for a number of reactants with those calculated by MO theory, assuming different possible mechanisms. In a study of this kind, it is advisable to use hydrocarbons as reactants, if at all possible, for two reasons: firstly, one avoids in this way the disturbing influence of field and inductive effects which are hard to calculate theoretically, and, secondly, because MO calculations are much easier for hydrocarbons than for molecules containing heteroatoms. This procedure was used very successfully some years ago in studies of aromatic substitution[4] and the solvolysis of arylmethyl chlorides,[5] using a simple perturbational MO approach.

In the case of the assisted solvolysis of a 2-arylethyl tosylate (I), the intermediate ion can be written either as a π complex (II) or a spirocyclopropanoarenonium ion (III).[6] In II the transition state has a structure in which the π MO's of aryl are conjugated with an additional orbital, and which is consequently isoconjugate with the arylmethyl cation, $ArCH_2^+$. The rate of such a reaction should therefore correlate[7] with the difference (δE_π) in π-binding energy between the aryl system Ar and the cation $ArCH_2^+$. In III, one orbital is removed from conjugation, and the rates should correlate with the difference ($\delta E_\pi'$) between Ar and the arenonium ion. Since δE_π and $\delta E_\pi'$ are linearly related, however, the two are indistinguishable by this method. If on the other hand the reaction is not assisted, the rate should be independent of Ar, for Ar is insulated from the reaction center by a methylene group, and any inductive or field effects will be similar for different aryl groups,[8] given that we are concerned only with cases where Ar is a radical derived from a neutral aromatic hydrocarbon.



I II III

A plot of log *k* *vs.* δE_π for such a reaction should therefore be a horizontal straight line if the reactions are all unassisted and a straight line of finite slope if they are all assisted. In the intermediate case, where only the most active aryl groups can participate, the plot should consist of two intersecting straight lines, the value of δE_π at the intersection serving as a measure of the competition between nucleophilic participation by the solvent in a normal SN2-type displacement and participation by aryl in the assisted SN1 reaction.

Winstein and his collaborators[10] have reported an example of the first of these situations: the rates of ethanolysis of 2-phenylethyl (I, Ar = Ph) and 2-(9-anthryl)ethyl (I, Ar = 9-anthryl) tosylates were almost identical. They also showed that in less nucleophilic solvents (acetic and formic acids) the anthryl derivative reacted much faster, implying that the solvolysis must have been assisted. We have now measured the rates of solvolysis of several other 2-arylethyl tosylates[11] in acetic and formic acids, the rate constants being listed in Table I.

Figure 1 shows plots of log *k* *vs.* the NBMO coefficient, a_{0r} (proportional to δE_π),[5] for solvolysis in the two

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(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) See, *e.g.*, H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965).

(4) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

(5) M. J. S. Dewar and R. Sampson, *ibid.*, 2789 (1956); 2946 (1957).

(6) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1966).

(7) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1964).

(8) A referee has claimed that this may be a poor assumption, although it seems to us inherent in the current picture of inductive and field effects. It is generally accepted that the atoms in an alternant hydrocarbon are essentially neutral; such a group could not then exert any field or inductive effects, other than those associated with the polar sp^3–sp^2 bond linking it to an adjacent saturated carbon atom, and these should be similar for different groups of this kind. In any case it is known[9] that an excellent correlation exists between SCF MO delocalization energies and rates of solvolysis for arylmethyl chlorides, a reaction which involves a situation primarily analogous to that in the assisted solvolysis of β-arylethyl derivatives. This result implies very strongly that differential field and/or inductive effects do not interfere with correlations of this kind indicated in the present communication, and also that steric effects due to *peri* hydrogen atoms are likely to be unimportant.

(9) M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

(10) S. Winstein, *et al.*, *ibid.*, **87**, 3504 (1965).

(11) All new compounds gave satisfactory analyses, etc.