Mass Spectrometry of Aryl Azides[1]

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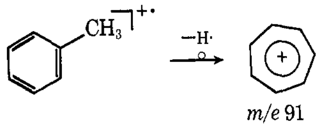
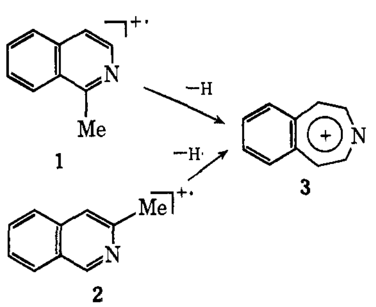
The mass spectra of 18 monosubstituted (Cl, CN, NO_2, MeO, Ph, Me) and two disubstituted phenyl azides are reported. The fragmentations of eight of the azides were found to fit a general or "normal" pattern, which is described. The fragmentation patterns of the other azides are described and discussed with respect to the "normal" fragmentations, supported in a number of cases with accurate mass determinations. The mass spectra of the three tolyl azides are discussed in particular, supported by accurate mass determinations and by a partial analysis of the low-resolution spectrum of *o*-tolyl azide-α-^{13}C.

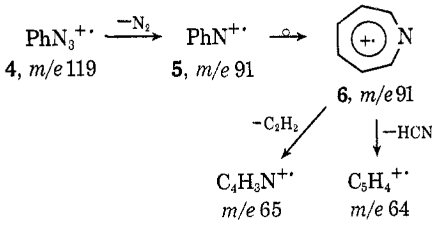
One of the more interesting areas of the mass spectrometry of organic molecules has been the study of the formation of the tropylium ion (*m/e* 91) from toluene, other C_7H_8 isomers, and from various benzylic compounds.[2-4] Similar ring-expansion pathways have been shown to best rationalize the mass spectral data from 1- and 2-methylisoquinolines 1 and 2, respectively), in which a benzazatropylium (benzazepinium) ion **3** was postulated,[5] and for the even electron ion $C_6H_6N^+$ from aniline and derivatives thereof.[6,7]





Another route to a ring-expanded ion is *via* the nitrenium ion **5** [from phenyl azide (**4**)] which could give the H_5-azepinium ion **6**[8] (Scheme I). Loss of acetylene and hydrogen cyanide from **6** would give the fragment ions *m/e* 65 and 64, respectively. Evidence has been presented to show that **6** is indeed formed: measurement of the mass spectrum of phenyl azide-*1*-^{13}C showed that randomization of C-1 occurred prior to expulsion of HCN.[9] It was estimated that between one-half to five-sixths of **5** rearranged to **6**. It has also been found by deuterium labeling that the hydrogen atoms in **6** are completely randomized prior to any further fragmentation.[10] There is no other information concerning the mass spectrometry of aryl azides. It was felt that it would be of interest to study the electron impact induced decomposition of a series of ortho, meta, and para X-substituted aryl azides to determine the effect that these substituents might have on the fragmentation patterns. To this end 21 substituted aryl azides were synthesized and subjected to mass spectral analysis.

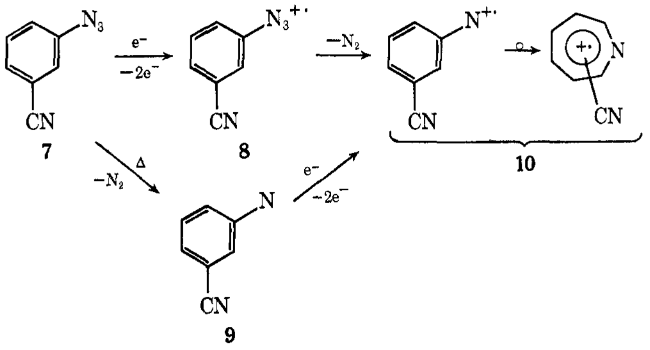
SCHEME I



Results and Discussion

Since aryl azides readily undergo thermolysis in the temperature range 140–170°,[11] the effect of variation of ion source temperature was studied for a model azide, *m*-cyanophenyl azide (**7**) (Scheme II).

SCHEME II



The spectra determined at various temperatures between 165 and 250° were identical except for a change in the ratio of the molecular ion **8** to $M^+ - N_2$ (**10**) peaks as illustrated in Figure 1. Since other than for this ratio the spectra were identical within experimental error, the most reasonable explanation for this behavior is that all of the fragmentation is derived from **10** and that it does not matter whether

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[1] Presented in part at the Southeast-Southwest Combined Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970.

[2] (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden Day, San Francisco, Calif., 1967, pp 76–81. (b) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, pp 516–519.

[3] A. S. Siegel, *J. Amer. Chem. Soc.*, **92**, 5277 (1970).

[4] I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

[5] M. Marx and C. Djerassi, *ibid.*, **90**, 678 (1968).

[6] K. L. Rinehart, Jr., A. C. Buchholz, and G. E. Van Lear, *ibid.*, **90**, 1073 (1963).

[7] A. V. Robertson and C. Djerassi, *ibid.*, **90**, 6992 (1968).

[8] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).

[9] P. D. Woodgate and C. Djerassi, *ibid.*, 1875 (1970).

[10] D. G. I. Kingston and J. D. Henion, *Org. Mass Spectrom.*, **3**, 413 (1970).

[11] R. A. Abramovitch and E. P. Kyba, "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, London, 1971.

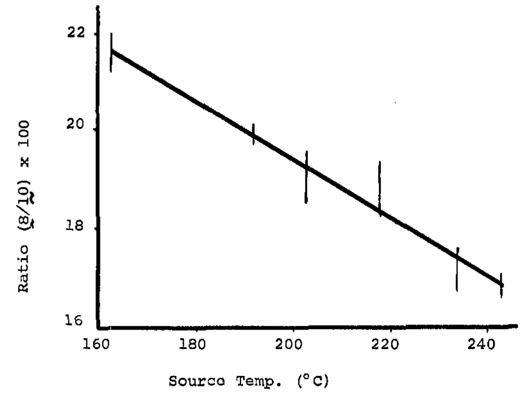


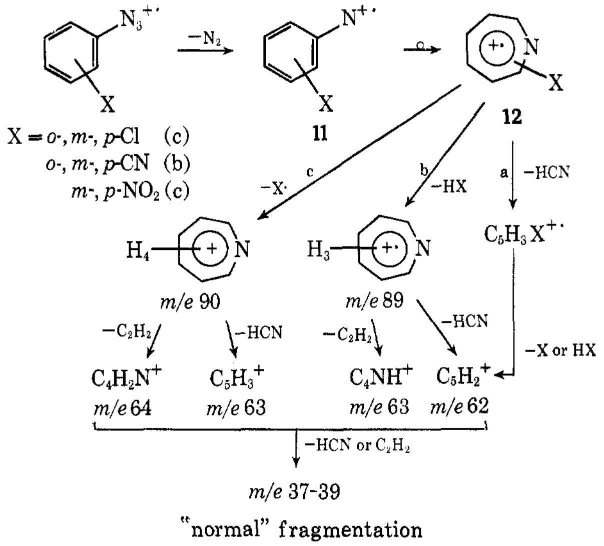
Figure 1.—Plot of the ratio of the relative abundance of **8**/**10** *vs.* source temperature. The uncertainties at each temperature are the average deviations in five scans.

this arises from **8** or from the electron-impact ionization of the arylnitrene **9** formed by thermolysis of the azide **7**.

The effect of the variation of ionizing potential on the ratio **8**/**10** was studied also and the results are illustrated in Figure 2. As expected, the fragmentation pattern became simpler at lower ionizing voltages, but the ratio of **8**/**10** was not markedly affected until the ionizing voltage was taken below about 11 eV. The standard conditions used for the other azides unless otherwise stated were source temperature 250° and ionizing voltage 70 eV.

It has been found that eight of the aryl azides studied could be adequately described by a fragmentation pattern (Scheme III) quite analogous to that of phenyl azide (Scheme I), except that the unsubstituted azepinium ions were either one or two mass units lower than that from the unsubstituted azide. Table I presents the relative abundances of the major peaks for the three chloro-, three cyano-, and *m*- and *p*-nitrophenyl azides. These give rise to what will be referred to as "normal fragmentation," the chief characteristics of which are a relatively high ion current at *m/e* $M^+ - 28$, and/or 90 or 89, 63 and 62, and 39–37. In addition, there is only low ion current at *m/e* 77, 76, and 52–50 with these azides. The loss of hydrogen cyanide from the substituted azepinium ion **12** is usually negligible (path a, Scheme III), but a 10–13% relative abundance was observed with the chlorophenyl azides (*m/e* 98, Table I). (The fragmentation will be written as occurring *via* the azepinium ion **12**, instead of the nitrenium ion **11**, by analogy with phenyl azide. It is realized, of course, that only labeling experiments can establish whether the ring expansion does indeed occur with each azide.) Path b (loss of HX) is followed predominantly by the three cyano derivatives, path c (loss of X) mainly by the three chloro- and *m*-nitrophenyl azides, and an appreciable amount of path b was followed by *p*-nitrophenyl azide.

SCHEME III



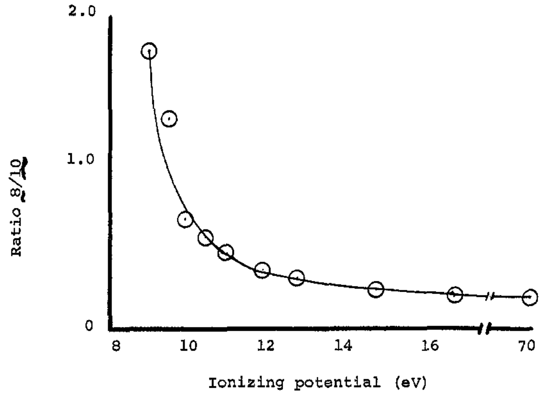


Figure 2.—Plot of the ratio of the relative abundance of **8**/**10** *vs.* ionizing voltage.

Exceptions to the "normal fragmentation" pattern will now be discussed. Figure 3 shows the mass spectrum of *o*-nitrophenyl azide (**13**), run at the source temperature of 170°. Although a part of the spectrum can be rationalized on the basis of a "normal fragmentation" (*m/e* 90, 63, and 39), there are major peaks at *m/e* 120, 78, 76, and 51. Scheme IV illustrates the proposed fragmentation pattern to give the *m/e* 76 and 78 peaks. The composition of these fragments as $C_5H_4N^+$ and $C_6H_4^{\cdot +}$ (and not $C_6H_6^{+\cdot}$ or $C_5H_2O^+$, and $C_5H_2N^+$, respectively) was established

SCHEME IV

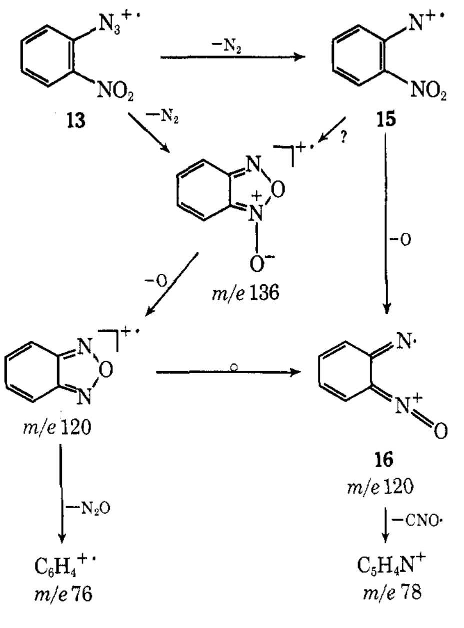


TABLE I

RELATIVE ABUNDANCES OF THE MAJOR FRAGMENTS IN THE MASS SPECTRA OF EIGHT r-X-SUBSTITUTED PHENYL AZIDES

m/e	*o*-CN[a]	*m*-CN[b]	*p*-CN[c]	*o*-^{35}Cl[d]	*m*-^{35}Cl[e]	*p*-^{35}Cl[f]	*m*-NO$_2$[g]	*p*-NO$_2$[h]
M^+	21	15	17	18	22	22	12	24
$M^+ - 26$	20	16	15	*i*	*i*	*i*		4
$M^+ - 27$	12	10	11	8	8	8		6
$M^+ - 28$	100	100	100	89	100	100	19	52
98				11	13	10		
91	7	4	4	12	10	10	9	9
90	9	9	7	100	98	94	100	79
89	53	61	45	21	23	23		35
80								14
76	11	10	8					6
75	7	8	6	11	9	10		5
74				7	8	7		8
73				12	9	10		
65	24	17	13	10	9	10		8
64	19	16	16	32	30	32	36	54
63	25	23	24	82	88	85	83	100
62	37	44	39	29	35	32	13	49
61	9	8	7	14	16	16	7	13
52	14	12	13	10	8	6	6	27
51	13	12	10	12	10	7	12	14
50	13	12	9	19	22	22	18	32
41	9	9	7					
40				12	14	10	12	9
39	15	19	9	44	44	32	64	92
38	34	36	22	34	35	30	18	42
37	21	20	18	32	27	30	17	34

[a] Registry no. are given as follows: 31656-77-6; [b] 31656-78-7; [c] 18523-41-6; [d] 31656-80-1; [e] 31656-81-2; [f] 31656-82-3; [g] 1516-59-2; [h] 1516-60-5. [i] Same peak as the ^{37}Cl isotope $M^+ - 28$ peak.

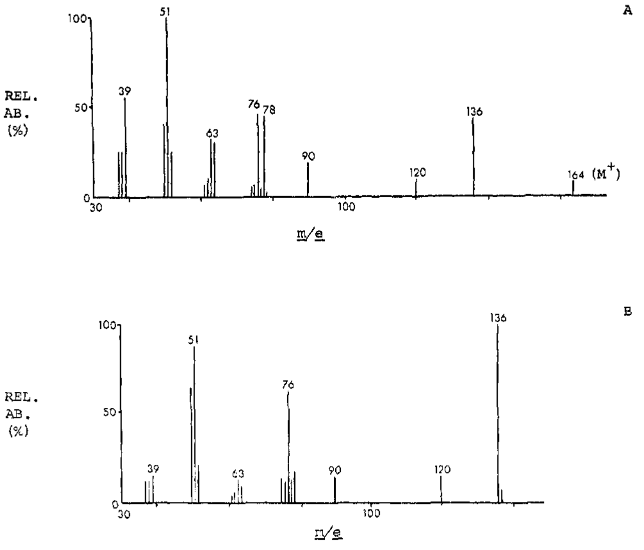


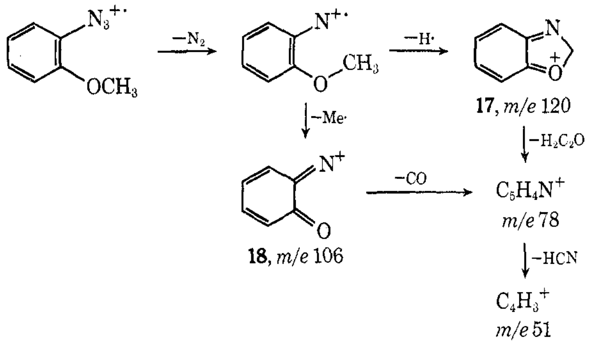
Figure 3.—Mass spectra of A, *o*-nitrophenyl azide (**13**); B, benzofuroxan (**14**).

by high-resolution mass spectrometry. The most likely source of the *m/e* 51 peak is the *m/e* 78 fragment which can lose HCN, although the *m/e* 76 fragment could presumably also yield it by loss of C_2H. Since it is known that benzofuroxan (**14**) is formed readily on thermolysis (>70°) of **13**, the mass spectrum of **14** was determined (Figure 3B). Although qualitatively the spectra are similar, there are some large quantitative differences, particularly in the fact that the molecular ion is the base peak with benzofuroxan and that the *m/e* 78 peak is considerably smaller than the *m/e* 76 peak. Thus, the azide must offer a pathway to *m/e* 78 that is not as readily available to **14**. It is suggested that this might be the sequence **13** → **15** → **16** (Scheme IV).

The three methoxyphenyl azides show pronounced "abnormal" fragmentation and exhibit major differences among themselves. The spectra of the three isomers are shown in Figure 4A–C. The spectrum of the meta isomer is relatively easy to rationalize *via* the methoxyazepinium ions (*m/e* 121), which may then lose a methyl radical to give the azepinone ions (*m/e* 106). Loss of CO and then HCN would give the other two major peaks in the spectrum, *m/e* 78 and 51, respectively. A small amount of normal fragmentation could be initiated by the loss of formaldehyde[12] from the methoxyazepinium ions to give the azepinium ion *m/e* 91.

The *o*-methoxy isomer has an additional mode of reaction, leading to the benzofurazan species **17** as shown in Scheme V. The elemental composition of

SCHEME V



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(12) See ref 1b, pp 237–248.

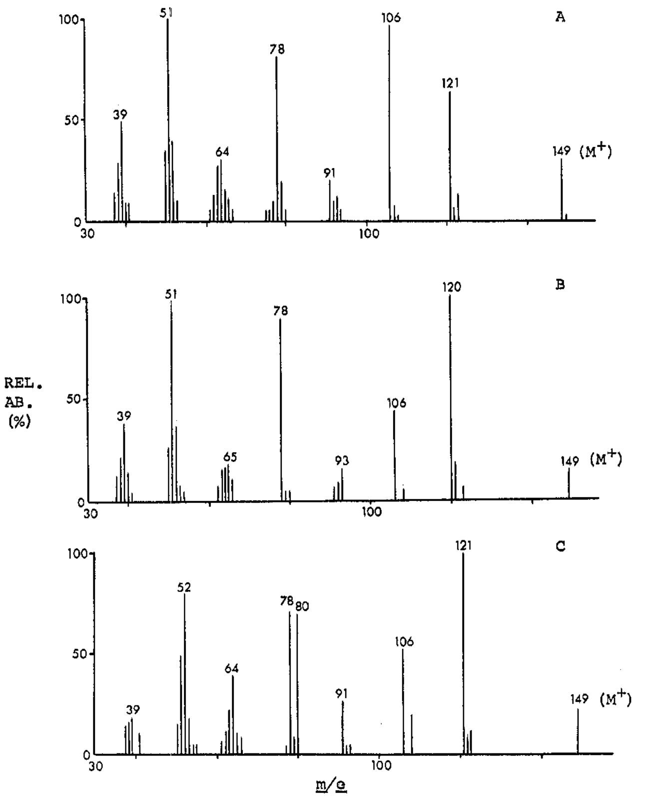
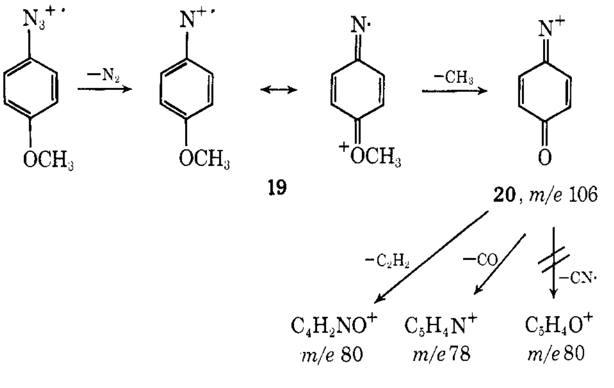


Figure 4.—Mass spectrum of A, *m*-methoxyphenyl azide; B, *o*-methoxyphenyl azide; and C, *p*-methoxyphenyl azide.

the ions shown in Scheme V were confirmed by accurate mass determination. The *m/e* 106 fragment ion might be **18** as shown in Scheme V or an azepinone ion. Loss of H· from $M^+ - 28$ appears very facile and still occurs at low ionization voltages. The peak at *m/e* 93 (Figure 4B) was found by high-resolution mass spectrometry to be composed of both $C_6H_7N^{+\cdot}$ and $C_6H_5O^+$, the latter perhaps arising *via* the loss of HCN from **17**. $C_6H_7N^{+\cdot}$ could arise from uncyclized nitrenium ion, with the ultimate expulsion of CO.

The most striking differences in the mass spectrum of *p*-methoxyphenyl azide (Figure 4C) and those of the ortho and meta isomers are the large peaks at *m/e* 80 and 52 in the spectrum of the former. The fragmentation pattern accounting for these differences is best rationalized on the basis of the resonance stabilized nitrenium ion **19** (Scheme VI), which can lose a methyl radical to give the *p*-quinone–imino ion **20**. An analogous pathway has been described for the mass spectral fragmentation of *p*-anisidine.[13] Loss of carbon monoxide from **20** would give $C_5H_4N^+$, *m/e* 78. *A priori,* loss of CN· or C_2H_2 would give rise to the *m/e* 80 peak, but it was found by accurate mass determination that the peak was in fact monobaric, with the composition C_4H_2NO (loss of C_2H_2). Loss of carbon monoxide from this fragment would give the $C_3H_2N^+$ fragment at *m/e* 52.

SCHEME VI



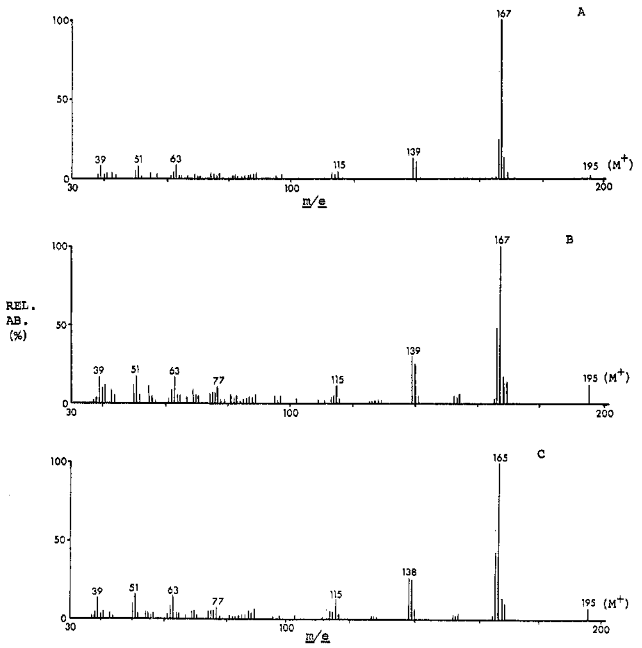
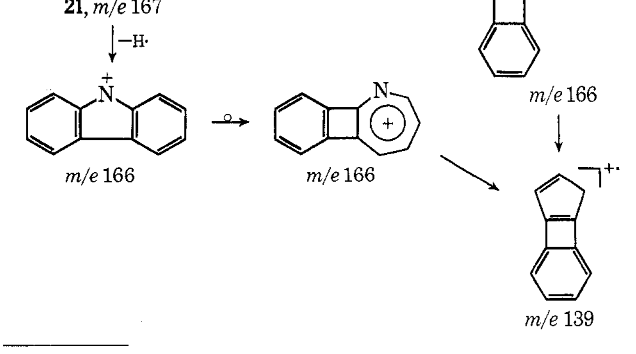


Figure 5.—Mass spectra of A, 2-azidobiphenyl; B, 3-azidobiphenyl; and C, 4-azidobiphenyl.

The mass spectra of the three azidobiphenyls are given in Figure 5A–C. These are typical of biphenylyl types of fragmentations[14] in which very little ion current is observed at low *m/e* values. Scheme VII illustrates the proposed fragmentation pattern

SCHEME VII



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[13] G. Spiteller and M. Spiteller-Friedmann, *Monatsh. Chem.*, **93**, 1395 (1962).

[14] See ref 1b, pp 86–88.

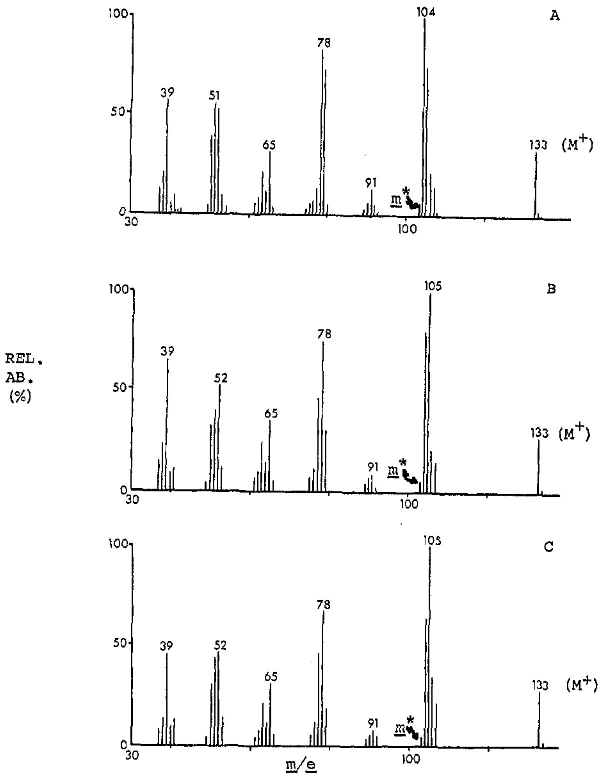


Figure 6.—Mass spectra of A, *o*-tolyl azide; B, *m*-tolyl azide; and C, *p*-tolyl azide.

for these molecules. It is possible that cyclization to the carbazole **21** is occurring with the ortho isomer, but there is no evidence in support of this.

The tolyl azides represent a very interesting class of compounds for mass spectral study in that they may lead to two different ring-expanded products, **22** and **23** (Scheme VIII). The mass spectra of the three isomeric tolyl azides are given in Figure 6A–C. Qualitatively, the spectra are similar and are all "abnormal" as defined above. They exhibit a metastable transition m* 103.1 corresponding to *m/e* 105 → 104 (calcd m* 103.0). Whereas the meta and para isomers give a base peak at *m/e* 105, the ortho isomer gives as the base peak *m/e* 104. In addition, the *m/e* 79 peak is much larger with the ortho isomer than from the other two (Table II). The ortho isomer also gives rise to a very weak diffuse metastable peak m* 76 (*m/e* 78 → 77) when the spectrum is determined on an MS-9 double focusing instrument; this was not observed in the low-resolution spectra determined on the CEC-21-104 using an accelerating potential of 1.2 kV. Again in the ortho isomer, an accurate mass determination indicates that *m/e* 107 is at least in part due to ($M^+ - C_2H_2$) (obsd, 107.0494; calcd for $C_5N_5N_3$, 107.0483). This process was not examined further here but, since all our azides show an $M^+ - 26$ peak (previously thought to be due exclusively to the primary amine cation), a more detailed study would appear to be warranted.

SCHEME VIII

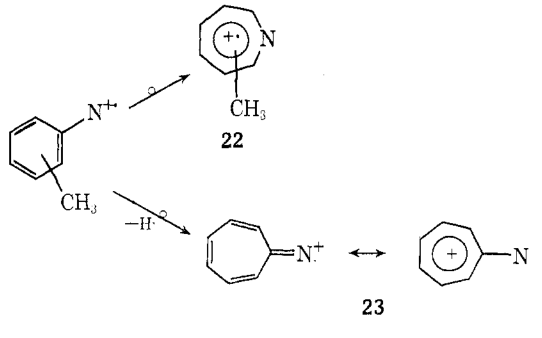


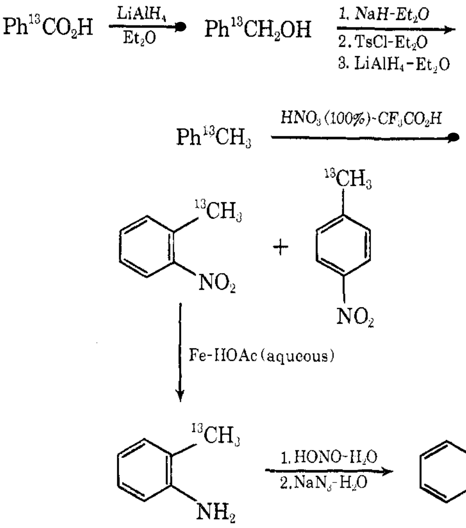
TABLE II

MASS SPECTRA OF TOLYL AZIDES.
RELATIVE ABUNDANCE OF SELECTED IONS

Isomer	50	51	52	76	77	78	79	104	105	133
	m/e									
o-Me	39	57	54	14	47	84	74	100	76	25
m-Me	34	42	54	12	47	75	32	80	100	27
p-Me	30	44	47	12	47	68	19	64	100	27

In order to investigate more fully the nature of the processes occurring in the electron impact induced decomposition of the tolyl azides, *o*-tolyl azide-α-^{13}C was synthesized starting from benzoic acid ^{13}C-carboxylate (61% enriched) as shown in Scheme IX.

SCHEME IX



The results of the mass spectral measurements on unlabeled and labeled *o*-tolyl azides are given in Table III. Slow scan rates and wide slit widths were used and for this reason the spectrum of the unlabeled azide (Table III) is not exactly the same as that presented in Table II in which a narrow slit width and fast scan rate was used. Since the conditions used for the determination of the spectra for the three isomeric tolyl azides were identical, the results given in Table II represent a valid comparison of the behavior of three isomers, but the spectrum given in Table III for *o*-tolyl azide is regarded as much more accurate.

It is easily calculated from the peak intensities at *m/e* 134 and 133 that the tolyl azide-α-^{13}C is 61% enriched in ^{13}C. One can obtain a calculated spectrum by taking 39% of the relative intensities of the unlabeled compound and adding to this 61% of the unlabeled compound *displaced upward by one mass unit.* The results are given in the sixth column in Table III. It can be seen that the agreement between the observed (column 5) and calculated abundances is good for the mass cluster *m/e* 103–108. On the other hand, SCHEME X

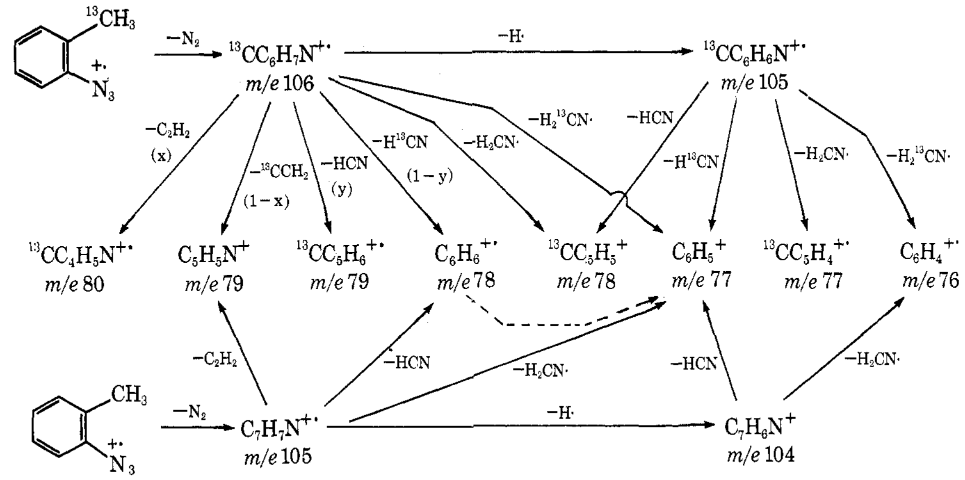


TABLE III
MASS SPECTRA OF UNLABELED AND ^{13}CH$_3$-LABELED o-TOLYL AZIDE

m/e	Unlabeled azide[a]	Unlabeled azide cor for natural abundance of ^{13}C[b]	Labeled azide[c]	Labeled azide cor for natural abundance of ^{13}C[d]	Calcd spectrum[e]
135			1.3		
134	2.3		16.7	16.5	
133	25.6	25.7	10.1	10.5	
108			7.6	6.9	7.1
107	12.2	11.0	16.4	13.3	14.4
106	20.4	15.1	54.5	49.8	48.9
105	74.7	67.0	93.2	93.6	93.6
104	100.0	100.0	44.0	45.6	45.9
103	6.5	6.5	3.9	4.1	3.4
81	1.3	1.2	1.2	0.8	1.3
80	5.0	1.2	13.4	8.2	42.1
79	68.6	63.8	100.0	100.0	77.1
78	80.1	77.6	64.5	65.3	61.4
77	45.1	44.5	27.0	27.5	29.9
76	12.4	12.0	10.0	10.0	9.0
75	6.5	6.1	6.5	6.4	6.1
74	5.4	5.4	3.6	3.7	2.2

[a] See Experimental Section for conditions used. Average of five scans, average deviation, ±0.2. [b] See F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967. [c] Average of seven scans, average deviation, ±0.2. [d] Weighted averages based on the fragments in Scheme IX were used. [e] See text for description of calculation. Spectrum is normalized so that m/e 105 peaks in observed ^{13}C and calculated spectra are of the same intensity.

there is very poor agreement between the observed and calculated spectra for the mass cluster m/e 74–81, particularly for m/e 79 and 80. This simple method of calculating the relative abundances also predicts that m/e 105 should be the base peak, whereas m/e 79 is observed to be the base peak in the spectrum of the labeled azide. Even if a statistical loss ($^1/_7$) of ^{13}C as ^{13}CCH$_2$ is assumed to occur, the relative abundances of m/e 79 and 80 would become 84.4 and 36.2, respectively, still far from agreement with the observed spectrum.

To understand the processes that give rise to the mass cluster m/e 76–80, it is necessary to consider the possible fragmentations that can occur from the labeled and unlabeled azides, and this is outlined in Scheme X. The composition of the ions for the unlabeled azide in the m/e 76–80 range was confirmed by high-resolution mass spectrometry, and ions such as $C_6H_7{}^+$ for m/e 79, $C_5H_4N^{+·}$ for m/e 78, and $C_5H_3N^+$ for m/e 77 were eliminated from consideration by the accurate mass determination. It appears that the most logical source of the fragments at m/e 79 and 78 for the unlabeled azide is $C_7H_7N^{+·}$ (m/e 105), by loss of C_2H_2 and HCN, respectively, and that of m/e 76 is $C_7H_6N^+$ (m/e 104) by loss of $H_2CN·$. The m/e 77 fragment may arise either from $C_7H_7N^{+·}$ by loss of $H_2CN·$ or from $C_7H_4N^+$ by loss of HCN.

As can be seen from Scheme X, for the labeled azide there are a number of processes which occur to unknown extents as, for example, the amount of $^{13}CCH_2$ relative to C_2H_2 being lost from $^{13}CC_6H_7N^{+·}$. If one assumes that loss of $H_2CN·$ and $H_2{}^{13}CN·$ from $^{13}CC_6N_7N^{+·}$ and of $N_2CN·$ from $C·H_7N^{+·}$ are unimportant, it is possible to calculate the extent to which the various other fragmentations are occurring to give m/e 76–80. Unfortunately, the results are not internally self-consistent, suggesting that the above assumption may not be valid. On the other hand, it can be seen that fragments m/e 80 and 79 (Scheme X) arise in a straightforward manner from m/e 106 and the proportions, x and y, in which $^{13}CC_6H_7N^+$ loses C_2H_2 and HCN, respectively [and hence $^{13}CCH_2$ (1 − x) and $H^{13}CN$ (1 − y)], can be readily determined from eq i and ii. In view of the relatively small size of the

$$m/e\ 80 \quad 0.61(63.8)x = 8.2 \qquad x = 0.21 \tag{i}$$

$$m/e\ 79 \quad 0.39(63.8) + (0.61)(63.8)(1 - x) + (0.61)(77.6)y = 100 \qquad y = 0.94 \tag{ii}$$

m/e 80 and 79 peaks, it is safer to estimate that x is in the range 0.1–0.2 and y in the range 0.8–0.9.

It can thus be seen that a large proportion (80–90%) of the acetylene lost from $^{13}CC_6H_7N^{+·}$ contains the ^{13}C label and that only a small amount of the ^{13}C label is eliminated as $H^{13}CN$ (10–20%). This accounts qualitatively for the fact that the base peak in the mass spectrum of the labeled azide is m/e 79, whereas the base peak for the unlabeled azide spectrum is m/e 104. The preferential loss of the labeled methyl carbon atom in acetylene has the effect of decreasing the relative abundance at m/e 80 and increasing the relative abun-

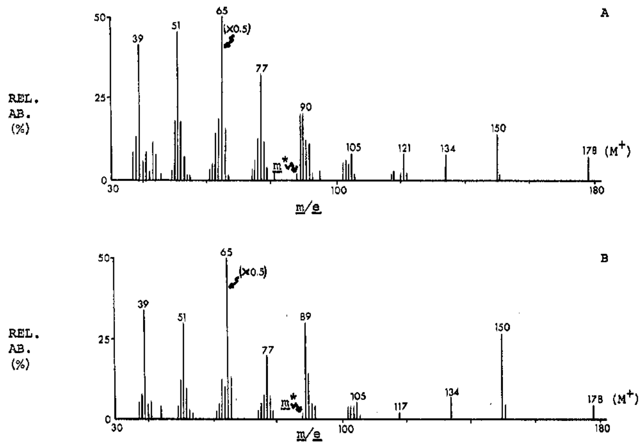
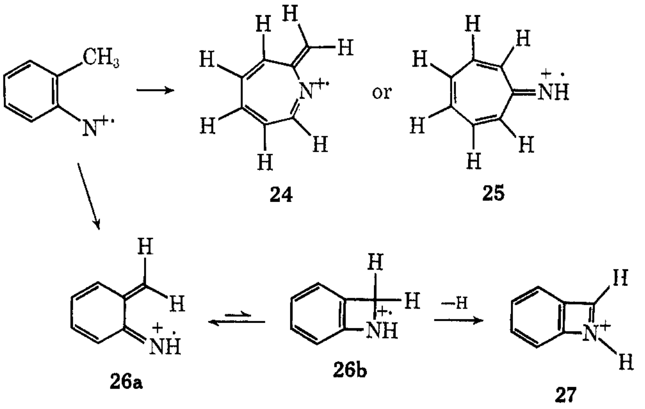


Figure 7.—Mass spectra of A, 2-azido-3-nitrotoluene; and B, 4-azido-3-nitrotoluene.

dance at *m/e* 79 to the point that the latter becomes the largest peak in the spectrum.

There are several possible structures for the $C_7N_7N^{+\cdot}$ fragment, and these are in Scheme XI. It is felt that,

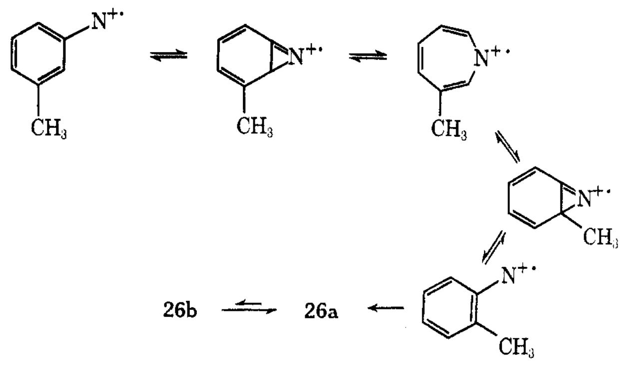
SCHEME XI



although structure **24** could account for the marked preferential loss of the methyl carbon atom as acetylene, there is no reason to expect loss of H· to give the *m/e* 104 fragment (known to occur by the observation of m* 103). Structure **25** could well give rise to the metastable transition m* 103, but it could not give the observed preferential loss of the methyl carbon atom as acetylene (at most, this would occur to the extent of 50%). Thus, neither **24** nor **25** represents a probable structure for the $C_7N_7N^+$. fragment. Structures **26a** $\rightleftharpoons$ **26b** do account for the above observations. **26a** might be expected to lose the methyl group preferentially as acetylene and also to eliminate hydrogen cyanide not containing the methyl carbon. In addition, the equilibrium with **26b** could account for the small amount of methyl carbon lost as hydrogen cyanide and for the metastable transition *m/e* 105 → 104. This then leads to the suggestion that the structure for the *m/e* 104 fragment is **27**.

An examination of Table II indicates that the loss of acetylene from *m/e* 105 in the *o*-tolyl azide is much more facile than with the meta and para isomers, and a similar situation seems to exist for the metastable transition *m/e* 105 → 104. One possible explanation for these observations is that in all three azides elimination of C_2H_2 and HCN is occurring from the *o*-quinonoid type of structure **26a** (Scheme XI) and that the ring-expanded species **24**, **25** (Scheme XI), **22**, and **23** (Scheme VIII) are not important in the *fragmentation.* Ions such as **22** would be important, however, in interconverting positional nitrenium ion isomers. Thus, in order for the meta and para isomers to lose C_2H_2 and HCN by the same mechanism as does the ortho isomer, a nitrenium azepinium ion equilibrium (Scheme XII) would have to be established,

SCHEME XII



similar to that suggested for equilibration of tolyl carbenes at 420° in the gas phase.[15] This scheme would now account for the fact that the *o*-tolyl azide gives the largest of the *m/e* 104 and 79 peaks and the para isomer the smallest. Although ^{13}C labeling experiments were not carried out on *p*-tolyl azide, high-resolution mass spectrometry showed that the composition of the ions in the mass range *m/e* 76–80 derived from the para isomer was identical with that obtained from the *o*-tolyl azide.

The mass spectra of 2-azido-3-nitrotoluene and 4-azido-3-nitrotoluene are presented in Figure 7A, 7B. They contain features of both the nitrophenyl azides ($M^+ - N_2 - O$) and tolyl azides (m* 93 → 89). It is also interesting to note that the ratio of $(M^+):(M^+ - N_2)$ is much larger in the case of the *o*-methyl group than for the *p*-methyl group. This might mean that the *o*-methyl group is sterically hindering the usually very facile concerted cyclization–elimination of nitrogen to give the benzofuroxan. Dyall and Kemp[16] found virtually no evidence of an anchimerically assisted reaction in the thermolysis of 2-azido-3-nitrotoluene, as opposed to the case of *o*-nitrophenyl azide.

The mass spectrum of ferrocenyl azide has also been determined. This will be discussed, however, in a forthcoming paper on the mass spectra of some ferrocene derivatives.[17]

Experimental Section

Low-resolution mass spectra were recorded on a CEC 21-104 spectrometer, using as standard conditions (unless otherwise stated) the source temperature at 250°, ionizing potential of 70 eV, and an accelerating potential of 1200 V. Samples were introduced with a direct probe inlet. For all the spectra except

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(15) W. T. Baron, M. Jones, Jr., and P. P. Gasper, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).

(16) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968).

(17) R. A. Abramovitch, C. I. Azogu, E. P. Kyba, and R. G. Sutherland, unpublished results.

the quantitative work on the labeled and unlabeled *o*-tolyl azides, a slit width of 5 mils was used and the magnetic scan rate was such that the entire spectrum (from m/e 160 to m/e 28 in most cases) was determined in about 30 sec. For the quantitative work on *o*-tolyl azide, the slit width was set at 20 mils and the scan rate was such that a scan from *ca.* m/e 104 to 65 required about 30 sec, and flat-topped peaks were obtained. The high-resolution mass spectra were determined on a CEC-21-110B. All of the azides were known compounds, and their physical properties were in agreement with those reported in the literature. One representative synthesis (4-methyl-2-nitroazidobenzene) is reported here, as is the synthesis of *o*-tolyl azide-$\alpha^{13}C$ in which the conditions were developed with unlabeled materials, such as to optimize the yields of the precious labeled product.

4-Methyl-2-nitroazidobenzene.—Sodium nitrite (2.8 g, 41 mmol) in water (25 ml) at 0–5° was added dropwise to a mixture of 4-methyl-2-nitroaniline (5.0 g, 33 mmol), concentrated sulfuric acid (6 ml), and water at 0–5°. Urea was added to remove the excess nitrous acid (starch–iodide paper) and the resulting solution was treated with activated charcoal for 30 min at 0°. Sodium azide (3.6 g, 55 mmol) in water (20 ml) at 5° was added slowly. The yellow precipitate which formed was filtered and dried. The solid was recrystallized from pentane to give 4-methyl-2-nitroazidobenzene (3.5 g, 60%), mp 36–38° (lit.[16] mp 35–36°).

Benzyl Alcohol-α-^{13}C.—Benzoic acid $^{13}CO_2H$ (*ca.* 62%) (3 g, 24.6 mmol) in dry ether (60 ml) was added to a 2 *M* solution of lithium aluminum hydride in ether (20 ml, 160 mmol) and the mixture was stirred and boiled under reflux for 24 hr. The cooled (0°) mixture was decomposed with 10% aqueous sodium hydroxide, filtered, dried, diluted with ether to 200 ml, and analyzed by gas chromatography using a 6 ft × $^3/_{16}$ in. column packed with SE-30 (20%) on Gas-Chrom Q (60–100 mesh) at 120° and a helium flow rate of 60 ml/min. *n*-Nonane was used as the internal standard. Yield of benzyl alcohol-α-^{13}C was 89%.

Toluene-α-^{13}C.—The above solution of benzyl alcohol (21.8 mmol) was boiled under reflux for 24 hr with sodium hydride (0.65 g, 27 mmol), cooled to −20°, and treated with *p*-toluenesulfonyl chloride (4.3 g, 22.6 mmol) in dry ether (70 ml, dried over molecular sieves) dropwise, with stirring at −20° for 2 hr and then at room temperature for 2 hr. A solution of 2 *M* lithium aluminum hydride (14 ml) in ether was added, and the mixture was stirred at room temperature for 3 hr and then boiled under reflux for 12 hr. Water (20 ml) and then 3 *N* HCl (100 ml) were added, and the ether layer was washed with water, dried, and evaporated to give toluene-α-^{13}C (67% yield).

***o*-Tolyl Azide-α-^{13}C.**—Toluene-α-^{13}C (1.0 g, 107 mmol) was added in one portion to 100% nitric acid (1 ml) in trifluoroacetic acid (25 ml) at 0°. The dark red-brown solution was allowed to stand for 1.5 hr by which time the color had almost totally disappeared. It was poured into water (250 ml) and the solution neutralized (Na_2CO_3 solid). The mixture was extracted with ether (two 150-ml portions), and the ethereal layer was washed (4% aqueous Na_2CO_3), dried, and evaporated to give a yellow oil (1.2 g) which was chromatographed on basic alumina (120 g). Elution with petroleum ether–benzene (97:3 v/v) gave pure (by glc) *o*-nitrotoluene-α-^{13}C (300 mg, 22% yield). Further elution gave a mixture of the ortho, meta, and para isomers (200 mg) and then the pure para isomer.

o-Nitrotoluene-α-^{13}C (300 mg, 2.2 mmol) was reduced with iron (3 g) in water (1.4 ml) and acetic acid (0.2 ml) to give the pure toluidine (glc) (180 mg, 76%). This was diazotized at 0°, the excess nitrous acid was destroyed with urea, and the solution was treated with ether (2 ml) and then NaN_3 (184 mg) in water (0.8 ml). Extraction with ether, washing the ethereal extract with 10% NaOH (2 × 5 ml), drying, and concentration gave the desired azide as a yellow liquid (67 mg, 30%), bp 28–30° (20 μ).

Registry No.—*o*-Nitrophenyl azide, 1516-58-1; benzofuroxan, 480-96-6; *m*-methoxyphenyl azide, 3866-16-8; *o*-methoxyphenyl azide, 20442-97-1; *p*-methoxyphenyl azide, 2101-87-3; 2-azidobiphenyl, 7599-23-7; 3-azidobiphenyl, 14213-01-5; 4-azidophenyl, 31656-91-4; *o*-tolyl azide, 31656-92-5; *m*-tolyl azide, 4113-72-8; *p*-tolyl azide, 2101-86-2.

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Notes

The Mechanism of Acid Hydrolysis of Imidazolines

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Recently Haake and Watson[1] have proposed that amidines (and related strong bases) hydrolyze by nucleophilic attack by water on the diprotonated amidines. Their proposal was based on (1) the rate of hydrolysis of the strong base lysidine, 2-methylimidazoline (pK_a = 11),[2] being linearly dependent on acid concentration with a rate maximum at 10–12 *M* sulfuric acid which suggests a transition state consisting of a lysidinium ion, a proton, and water and (2) the large downfield shift in the nmr signals of lysidinium ion in sulfuric acid more concentrated than 102%, which suggests protonation of lysidinium ion to a dication. Because of its novelty, we undertook additional experiments to test the validity of the proposed mechanism. The results, which are reported in this paper, were all consistent with the proposed mechanism.

Experimental Section

Ultraviolet spectra were determined on a Cary Model 15 recording spectrometer. Nmr spectra were determined on a Varian T-60 spectrometer. Acid solutions were standardized as previously described.[1]

2-(*m*-Nitrophenyl)imidazoline.—To 7 ml of concentrated sulfuric acid cooled by an ice bath, 1.72 g of 2-phenylimidazoline was added; 7 ml of concentrated nitric acid was added dropwise to the cooled, stirred solution. The ice bath was removed and the solution was slowly heated to 60° and its temperature maintained at 60° for 10 min. The reaction mixture was then cooled by means of an ice bath and made alkaline with 50% potassium hydroxide. The precipitate was collected and purified by recrystallization from benzene. A yield of 1.2 g, mp 155–156°, was obtained: nmr (CCl_4) τ 1.4–2.8 (4.0 H, multiplet), 5.4 (1.2 H, singlet), τ 6.2 (4.0 H, singlet). Hydrolysis of this compound

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(1) P. Haake and J. W. Watson, *J. Org. Chem.*, **35**, 4063 (1970).

(2) R. B. Martin and A. Parcell, *J. Amer. Chem. Soc.*, **83**, 4830 (1961).