In conclusion, the present work affords an impressive illustration of how a minor molecular change (absence or presence of C-17 alkyl substituent: I and II *vs.* III) can have a major effect on the mass spectral fragmentation and how indispensable deuterium labeling is for a proper mechanistic interpretation of the results.

Experimental Section[21]

Reduction of Labeled Androstanones. The reduction of the various labeled androstanones (1.9–10-mg samples) was carried out by using a previously reported general procedure.[4] The products were purified by thin layer chromatography (tlc) on silica gel H, followed by recrystallization from methanol, yielding the following labeled 5α-androstane samples (the position of the keto function in the starting materials is indicated in parentheses): 3α-d_1 (XVI, from 17-one[10] XIV), mp 51–52°; 5α-d_1 (VIII, from 3-one[8] IV), mp 52°; 6,6-d_2 (IX, from 3-one[8] V), mp 51–52°; 8β-d_1 (XIII, from 12-one[9] XII), mp 50–50.5°; 9α-d_1 (X, from 3-one[8] VI), mp 52–53°; 18,18,18-d_3-*dl* (XVII, from *dl*-17-one[10] XV), mp 77–79°; 19,19,19-d_3 (XI, from 3-one[8] VII), mp 51–52°.

14α-d_1-5α-Androstane (XIX). A mixture of 14α-d_1-5α-androstane-3,17-dione[11] (XVIII, 5 mg), 2 ml of diethylene glycol, and 1 ml of 85% hydrazine hydrate was heated under reflux for 1.5 hr, then cooled to 100°. One pellet (~150 mg) of potassium hydroxide was added and the temperature was raised gradually, boiling off the hydrazine hydrate. The heating was continued for 11 hr at 205–210°, then the resulting brown solution was cooled and diluted with water. Ether extraction, washing the ether phase with water, and drying over anhydrous sodium sulfate gave a glassy product (5 mg). Purification by tlc on silica gel H in hexane yielded the pure, partially crystalline 14α-d_1-5α-androstane (XIX, 2 mg) which exhibited a mass spectrum identical with that of an authentic unlabeled sample with the exception of mass shifts of the deuterium containing peaks.

Reduction of an unlabeled sample (15 mg) under identical conditions, followed by recrystallization from methanol, gave 5α-androstane (III, 8 mg), mp 51–52°.

5α-Androstan-12-one Ethylene Thioketal (XXI). Boron trifluoride etherate (0.1 ml) was added to a solution of 5α-androstan-12-one[9] (XX, 20 mg) in ethanedithiol (0.1 ml). After storing at room temperature for 10 min, the reaction mixture was diluted with ether, washed with plenty of dilute sodium hydroxide solution, and dried over anhydrous magnesium sulfate. Evaporation of the ether gave the crude mercaptal which was purified by tlc on silica gel H in benzene–ether (9:1), yielding the pure 5α-androstan-12-one ethylene thioketal (XXI, 20 mg, 79%), mp 110–111° (methanol).

Anal. Calcd for $C_{21}H_{34}S_2$: C, 71.93; H, 9.77. Found: C, 71.91; H, 9.79.

12,12-d_2-5α-Androstane (XXII). Freshly prepared[22] deuterium-containing Raney nickel (from 0.4 g of alloy) was added to a solution of 5α-androstan-12-one ethylene thioketal (XXI, 7 mg) in d_1-methanol (3 ml). The resulting suspension was stirred and heated under reflux for 4 hr, then the nickel was removed by filtration and the solvent was evaporated. The residue was purified by tlc on 10% silver nitrate containing silica gel H in hexane, yielding pure 12,12-d_2-5α-androstane (XXII, 5 mg, 95%), mp 53–54° (methanol); the melting point showed no depression when mixed with authentic unlabeled 5α-androstane. For isotopic purity see Table I.

5α-Androstan-16-one Tosylhydrazone (XXIV). A solution of 5α-androstan-16-one[15] (XXIII, 20 mg) and *p*-toluenesulfonylhydrazide (20 mg) in methanol (1.5 ml), containing a microdrop of concentrated sulfuric acid, was heated under reflux for 2 hr. A few drops of water were added and the solution was cooled in an ice bath. The crystalline precipitate after filtration and drying under reduced pressure (0.1 mm) provided 5α-androstan-16-one tosylhydrazone (XXIV, 27 mg, 84%), mp 188–190°; ν_{max} 3290, 3210 (N—H), 1660 (C=C), and 1160 (S=O) cm^{-1}, but no carbonyl absorption.

Anal. Calcd for $C_{26}H_{38}N_2O_2S$: C, 70.55; H, 8.65. Found: C, 71.00; H, 8.60.

5α-Androstan-17-one Tosylhydrazone (XXVII). Conversion of 5α-androstan-17-one (XXVI, 25 mg) by the same procedure as described above for the preparation of XXIV gave the crystalline tosylhydrazone derivative XXVII, mp 200–202° (lit.[14b] 201–202°), which was used in the next step without further purification.

16,16-d_2-5α-Androstane (XXV). A suspension of 5α-androstan-16-one tosylhydrazone (XXIV, 14 mg) and lithium aluminum deuteride (20 mg) in dry dioxane (2 ml, reagent grade) was heated under reflux for 15 hr, and the excess deuteride decomposed by the addition of a few drops of deuterium oxide. After cooling, the inorganic salts were removed by filtration, the solvent was evaporated under reduced pressure, and the residue was subjected to tlc analysis on 10% silver nitrate containing silica gel H in hexane. The resulting olefin-free 16,16-d_2-5α-androstane (XXV) amounted to 4.5 mg (45%), mp 53–54° (methanol). For isotopic purity see Table I.

17,17-d_2-5α-Androstane (XXVIII). The preparation and purification of 17,17-d_2-5α-androstane (XXVIII) were performed as described above for the 16-labeled analog XXV, starting with 34 mg of the tosylhydrazone XXVII. The yield of the olefin-free product was 6.5 mg (32%), mp 52–54° (methanol).

(21) Melting points (uncorrected) were determined on a Kofler block and the infrared spectra were measured in chloroform solution on a Perkin-Elmer Model 137 Infracord spectrophotometer. The mass spectra were measured by Mr. J. W. Smith and Dr. A. M. Duffield on a CEC 21-103C and Atlas CH-4 (with TO-4 ion source) mass spectrometers at 70 eV unless otherwise indicated. The elemental analyses are due to Messrs. E. Meier and J. Consul.

(22) D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 85, 2091 (1963).

Some "Steric Effects" of Methyl in Mass Spectral Fragmentations

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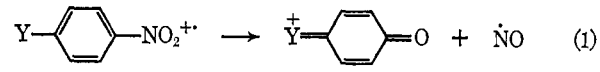
Abstract: Substituent effects of methyl groups *ortho* to resonance donors were studied for the loss of NO by substituted nitrobenzene ions in the mass spectrometer. The results were found to be consistent with an interpretation as simple steric effects at high voltages. *o*-Methyl groups seem to prevent coplanarity of the dimethylamino group in this system, but not of the methoxy group. Both peak intensity comparisons and metastable ion characteristics support this conclusion. At low voltage an additional complication, possibly associated with ring expansion, appears. Methyl is not completely inert as a hindering group for this reaction, especially at low voltage, and it may be preferable to use halogen substituents for studies of steric effects.

The interpretation of steric effects in mass spectrometry must be made with caution. Interesting parallels between mass spectral substituent effects and Hammett substituent constants suggest that the electronic effects of substituents in mass spectral decompositions resemble those of solution chemistry in some

cases.[1] Because of the uncertainty in establishing structures of gaseous ions, characterization of an effect such as "steric inhibition of resonance" is tenuous except in the most thoroughly studied cases.

The effect of a single substituent on the loss of NO from nitrobenzene radical ions in the mass spectrometer has been reported.[2] This study indicated that there was no loss of positional identity between *meta* and *para* positions, and further that a special resonance effect could be observed for electron-donating substituents in the *para* position, as structure I would indicate (eq 1). Later work demonstrated a distinction between *ortho*

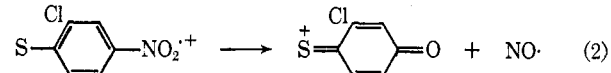


(1)

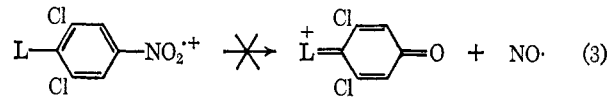
I

and *para* positions.[3] The quinonoid structure I for the product is consonant with all of these data, and emphasizes the distinction of position.

The case for this structure is further supported by observation of large reductions of the intensities of the "quinonoid" product ion when substituents assumed not to cause confusing alterations of the structure (for example, ring expansion) prevent the *para* substituent from lying in the same plane as the ring in the ground state.[4] The substituents chosen for this study were chlorine and bromine, which so far have not been demonstrated to induce isomerization of aromatic rings. They retain positional identity in the loss of NO from nitrobenzene ions, in particular.[2,3] Their effect in modifying the rate of this reaction may be demonstrated by consideration of eq 2 and 3. Let the small group S



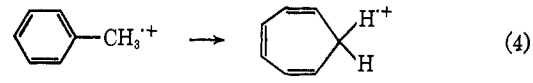
(2)



(3)

be hydroxy or amino; then the intensity of the $(M - NO)^+$ ion with respect to that of the $M\cdot^+$ ion defines[1,2,5] an expected value, Z, for substituents of similar electronic character in the absence of interfering phenomena.[6] When the *para* substituent is methoxy or dimethylamino, it is apparently "large" (L), for the corresponding relative intensity ($[(M - NO)^+]/[M\cdot^+]$) of the fragment ion is reduced by a factor of 23 or 21, respectively. The reduction in intensity is most simply explained by the inability of the lone pairs on O and N in the large substituents to overlap effectively with the π system of the ring, so that the quinonoid form I is not attained. Formation of this system, as noted above, has been cited as a possible reason for the stabilization by $-R$ groups in the *para* position, and so the results are consistent with an explanation based on steric inhibition of resonance resembling that advanced[7-9] for ground-state systems.

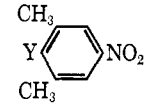
Since the methyl group is so commonly employed as a hindering substituent in solution chemistry,[7-9] we thought it advisable to begin a study of its utility for similar purposes in interpreting mass spectral decompositions. In many cases,[10,11] but not all studied so far,[12-14] the methyl substituent seems to be consumed in a ring expansion (*e.g.*, eq 4) before decomposition. While most of these scrambling reactions have been



(4)

noted in hydrocarbons where other low-energy decomposition pathways might not be available to the molecule, ring expansions are apparently rapid enough to compete with simple fragmentation in other kinds of systems as well, such as substituted ferrocenes.[15] It would therefore be inadvisable to use the methyl group to demonstrate steric inhibition of resonance for the first time, but the effects of the methyl group might be compared with those of the chloro and bromo substituents, whose documentation and interpretation are more secure.

Effects on the Intensities of Normal Ions. The compounds II–V, analogous to those chosen for the study[4]



II, Y = OH
III, Y = NH_2
IV, Y = OCH_3
V, Y = $N(CH_3)_2$

with chloro and bromo substituents, were used for this study. If the Z value ($[(M - NO)^+]/[M\cdot^+]$) for the hydroxy compound is again used as the standard, the Z/Z_0 values at 75 eV are: *p*-OH, 1.00; *p*-NH_2, 1.25; *p*-OCH_3, 0.73; *p*-$N(CH_3)_2$, 0.11. For "hindering" methyl substituents, then, only the dimethylamino substituent appears to be affected in such a way that the intensity of the daughter ion is greatly reduced; even so, it is not as reduced as it is when the dimethylamino substituent is hindered by halo substituents. The results may be interpreted in terms of reduced efficiency at stabilizing the quinonoid form only for the dimethylamino group. To call this a steric effect, one would argue that only this group is twisted out of the plane of the ring by two *o*-methyl groups, with the assumption that the original six-membered ring has not expanded for the great majority of ions which lose NO. On the other hand, the methoxy group appears to be accommodated by two flanking methyl groups, for the $(M - NO)^+$ ion is stabilized almost as well as the $(M - NO)^+$ ions in the spectra of the hydroxy- and amino-substituted compounds II and III. In the latter, of course, the OH and NH_2 groups can easily fit between two methyl groups

(1) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).
(2) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 5023 (1966).
(3) M. M. Bursey, *Org. Mass Spectrom.*, in press.
(4) M. M. Bursey, *J. Am. Chem. Soc.*, **91**, 1861 (1969).
(5) M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967).
(6) In monosubstituted nitrobenzenes the Z values relative to the Z value of *p*-OH at 75 eV are[2]: *p*-OH, 1.00; *p*-NH_2, 1.18; *p*-OCH_3, 1.34; *p*-$(CH_3)_2N$, 0.83.
(7) A review: G. S. Hammond and M. F. Hawthorne, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 164.
(8) A review: R. W. Taft, Jr., ref 7, p 556.
(9) A. van Loon, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **79**, 977 (1960), and previous papers in this series.
(10) P. N. Rylander S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).
(11) F. Meyer and A. G. Harrison, *ibid.*, **86**, 4757 (1964).
(12) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, **84**, 4 (1962).
(13) P. Brown, *ibid.*, **90**, 2694 (1968).
(14) F. W. McLafferty and M. M. Bursey, *ibid.*, **90**, 5299 (1968).
(15) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *ibid.*, **90**, 973 (1968).

in the ground state, as space-filling Catalin molecular models indicate.

In distinction, the methoxy group seems to be very poorly accommodated between two chloro or bromo substituents. It would appear, therefore, that as a hindering group *ortho* to a large substituent which must become planar for resonance interaction, the methyl substituent is smaller than the chloro or bromo substituent in some mass spectral reactions. In solution chemistry, it has been estimated that the steric effects of the methyl and chloro groups are of similar magnitude and parallel the van der Waals radii of these groups.[16] There are of course many factors which would differ in determining the electronic distributions which are called "size" in solution chemistry and the chemistry of gaseous ions. Not the least of these, presumably, is a variable response of a substituent, particularly a *para* substituent, to resonance demand.[17] In gaseous ions, it is impossible for solvent orientation to affect charge distribution, so that the demand must be satisfied totally within the molecule; this greater demand on the *para* group may appear as a greater deformability of the substituents next to it. The deformability may be altered from solution affects in different amounts for different substituents. In addition, the demand may vary considerably in different mass spectral reactions. The nitrobenzene system is an example of a reaction where the demand for resonance is very high in the product. Other well-studied cases may provide examples where the demand is lower (for example, formation of acyl ions from acylbenzenes[1]) and should provide an interesting set of data for comparison with these.

Effects on Kinetic Energy Released with the Loss of NO. Results of substituent eflects on "flat-topped metastables" support the interpretation above. In general these effects provide a subject for controversy. One of the earliest papers to deal with nitrobenzenes in the mass spectrometer noted the existence of "flat-topped metastables" in their spectra,[19] and the original illustrations of correlations with kinetic energy release used them as examples.[20] Parallelism between resonance parameters such as σ_R^0 [21] and the kinetic energy release, determined from the width of the metastable, has been noted.[2] For substituents which release electrons to stabilize the quinonoid form I by development of charge on O or N, the metastable peak is flat topped; for all others, it has the usual "Gaussian" shape. This correspondence of kinetic energy release with σ_R^0 is not universal, for apparently some cases exist in which the kinetic energy released is independent of the substituent, in spite of the fact that quinonoid forms may be drawn on paper for the products.[22] It is difficult to find sufficiently analogous compounds to test whether this difference in behavior may be ascribed to difference in stereochemistry in the two cases, as was suggested. A recent, very general study indicated that reliable structural information could not generally be gained from kinetic energy release correlations.[23] Presumably, then, if information is to be extracted at all from these metastable characteristics, the systems must be narrowly defined.

Because of isotopic distributions the dichloro and dibromo compounds examined previously yielded very poor information about metastable widths, and then only with great difficulty. The present series is free of this complication, however, and provides a helpful extension of the data for the singly substituted nitrobenzenes already reported. The three compounds of the dimethyl series (II–IV) whose normal $(M - NO)^+$ peaks are of comparable relative intensities display flat-topped metastable peaks for the transition to $(M - NO)^+$: the kinetic energy release is calculated to be 0.76 ± 0.05 eV for the *p*-amino substituent, 0.65 ± 0.08 eV for the *p*-hydroxy, and 0.58 ± 0.07 eV for the *p*-methoxy substituent. The values in the unhindered, monosubstituted nitrobenzenes were found to be 0.85 ± 0.04 eV, 0.74 ± 0.06 eV, and 0.56 ± 0.06 eV, respectively.[2] There is considerable similarity between the trends for the unhindered and the hindered series. It is questionable whether the apparently sharper decrease as one proceeds to the methoxy compound in the unhindered series is meaningful, because of the large error associated with the data. In fact they are consistent with the data above for the normal peaks, where a slight decrease of the intensity of the $(M - NO)^+$ peak might possibly indicate some slight destabilization of the quinonoid form for the hindered methoxy compound, only within the large error quoted. It seems of little value to treat them further.

The more interesting case is that of the hindered dimethylamino compound. In the unhindered parent, the loss of NO is characterized by a flat-topped metastable indicating an energy release of 0.84 ± 0.02 eV. In the hindered compound, there is an important process for the loss of NO from the (M − 1) ion[24] with an intense metastable peak, which partially obscures the *m/e* region where the expected metastable peak for $M\cdot^+ \rightarrow (M - NO)^+$ should be found. Examination of the spectra of this region at very high sensitivity indicates that the *maximum* width of the flat-topped peak (if indeed it is flat topped) corresponds to an energy release of 0.05 eV. A dramatic reduction in the amount of kinetic energy released is thus observed, a fact that is consistent with the hypothesis that stability of ionic products is related to kinetic energy, particularly in those cases where resonance effects dominate. Apparently stereoelectronic effects do influence the width of flat-topped metastables, at least in the nitrobenzene system.

Of course we have no evidence that the structure of the dimethylamino $(M - NO)^+$ ion is really a "twisted quinonoid" type whose only difference from the true quinonoid type I is the large deviation of the dihedral angle of the substituent's and the ring's planes from 0°. We know only that this ion differs in energetics from all models for it. Perhaps the inability of the *para* group to stabilize the product so slows the loss of NO that competing ring expansion processes involving the

(16) R. W. Taft, Jr., ref 7, footnote 5, Table XVI, p 650.

(17) Such a response has been noted even in solution chemistry for the phenyl substituent.[18]

(18) (a) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1242 (1962); (b) H. C. Brown and L. M. Stock, *ibid.*, **84**, 3298 (1962).

(19) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964).

(20) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 180 (1965).

(21) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960); R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(22) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967).

(23) D. H. Williams, R. G. Cooks, and I. Howe, *J. Am. Chem. Soc.*, **90**, 6759 (1968).

(24) This process is also important in the dichloro and dibromo compounds.

methyl groups are important. Irrespective of the detailed nature of the product, however, all the details of the chemistry explored so far are readily explained as "steric effects" of the blocking methyls.

Low-Voltage Phenomena. Ordinarily low-voltage data, where the product ion no longer decomposes, may be used as a measure of relative rates of formation of an ion.[25] In the nitrobenzenes, this interpretation is weakened by the fact that an ionizing voltage cannot be found where the $(M - NO)^+$ ion is both reasonably intense and free from further decomposition; in general, if the $(M - NO)^+$ peak is large enough to measure, there is a peak of mass 28 amu less than it, corresponding to the loss of CO from $(M - NO)^{+}$.[2,4] This peak is generally small, and so the interpretation of the intensity of $(M - NO)^+$ as a fairly accurate reflection of its rate of formation is not unreasonable. For the monosubstituted nitrobenzenes[2] and the dihalonitro compounds[4] the data from low-voltage spectra strongly resemble those at high voltage and reinforce the interpretation assigned the high-voltage spectra. An unexpected result was obtained for the dimethylnitro compounds, however.

The spectra were recorded at voltages corresponding to an increment of 3.0 V above the ionization potential, as was done for the model[4] dihalonitro systems. This ensures that the internal energy distributions of the ions are as similar as they can be made in a conventional electron-impact system by external influence.[26,27] In stark contrast to the predictable values of Z/Z_0 found for the dihalonitro compounds at 3.0 V above the ionization potential, the Z/Z_0 values found for the loss of NO from the dimethylnitro molecular ions (relative to the *p*-hydroxy compound) at 3.0 V above the ionization potential were: *p*-hydroxy, 1.00; *p*-amino, 0.5; *p*-methoxy, 0.8; *p*-dimethylamino, 0.7. Thus at low voltage a steric effect is not discerned: the small substituents OH and NH_2 give Z/Z_0 values which actually bracket those of the larger substituents. An argument based on generally lower energy content of the ions as the ionizing voltage is reduced would have predicted an even more pronounced steric substituent effect as less energy becomes available for vibrations and internal rotations. This lack of similarity of results to predictions suggests a deep-seated source of structural modification to explain the energetics of the system.

The explanation for this unexpected behavior may well lie in the nature of unimolecular reaction kinetics. The earliest acceptable theory of unimolecular reaction rates[28,29] derived an expression for the rate constant of such a process

$$k(E) = A\left(\frac{E - E^0}{E}\right)^{n-1}$$

where E^0 is the activation energy for decomposition, n the effective number of harmonic oscillators,[30] and A a type of frequency factor. This was incorporated into the quasi-equilibrium theory of mass spectra[31] and has recently been interpreted[32] to explain the increase of intensities of ions resulting from rearrangements, particularly hydrogen rearrangements, at low ionizing voltages. This evidence[32] suggests that at low voltage more complex rearrangements (with lower frequency factors) compete even more effectively than less complex ones with simple cleavage processes. In the context of the dimethylnitrobenzenes, the data might indicate that ring expansion (a more complex process, with a lower frequency factor) competes effectively with rearrangement of the nitro group before fragmentation. Consequently, a large fraction of the decomposing ions at low voltages (but not at high voltage) might have ring expanded, so that the observed substituent effects can no longer be correlated with effects in six-membered rings.

Even this unusual observation is, then, consistent with theory. The complication of ring expansion by methyl groups at low voltage negates the simple interpretation that one wishes to attach to substituent effects, and consequently the methyl group seems slightly less desirable as a blocking substituent than the "unreactive" halogen atoms studied previously. In the present case, the competing ring expansion affects a small enough percentage of reacting ions at high voltage to have little effect on the interpretation of results; but this need not generally be the case. For example, rearrangement of a blocking methyl substituent may compete even more effectively with the rate of a simple cleavage than the rate of a three-center rearrangement such as this one at low internal energy. Methyl may still be found to be a suitable hindering group *a posteriori*. But it would appear more promising in general to investigate the characteristics of the methyl group itself as a hindering substituent, rather than to use it as a convenient tool for studying other types of reactions.

Experimental Section

Chemicals. All of the compounds have been previously reported in the literature. Melting points (uncorrected) obtained on a Thomas-Kofler apparatus agreed to within 2° of reported values.

The phenol II, 2,6-dimethyl-4-nitrophenol, was a commercial sample (Aldrich Chemical Co., Inc.), mp 169–171° dec, lit.[33] 170–170.5°. It was converted to the anisole,[34] mp 90–91°, lit.[33,34] 92°, by refluxing with CH_3I in acetone in the presence of fresh Ag_2O.[35] The aniline III, 2,6-dimethyl-4-nitroaniline, mp 158–160°, lit. 158°,[33] was prepared by a three-step procedure[36] from commercial (Aldrich) 2,6-dimethylaniline. It was methylated with methyl sulfate to give V,[37] mp 65–67°, lit.[37] 67–68°.

Mass Spectra. The spectra were recorded on a single-focusing Hitachi Perkin-Elmer RMU-6E instrument with sample introduction through the heated inlet system (inlet, 190°; source, 170°) using conditions identical with those for previous studies.[2,4] The resolution for all spectra was near 450, as defined by a 100% valley. As a result, reproducibility was good for normal peaks (*ca.* 3–4%) for duplicate scans; the ratios reported ($Z = [(M - NO)^+]/[M\cdot^+]$ with no corrections) are accurate to 6–8% by definition. The significant feature of the data, therefore, lies in the abnormality of Z for the dimethylamino substituent, not in trends in the other cases.

Specific values of Z (within the errors noted above) were: II, 0.29; III, 0.36; IV, 0.21; V, 0.032. The ion current carried by the molecular ion as a fraction of the total current was 0.25 for II, 0.40 for III, 0.25 for IV, and 0.20 for V. Ionizing voltage was 75 V; emission current, 80 μA.

(25) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 4484 (1966).
(26) F. W. McLafferty and M. M. Bursey, *J. Org. Chem.*, **33**, 124 (1968).
(27) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **90**, 5461 (1968).
(28) O. K. Rice and H. C. Ramsperger, *ibid.*, **49**, 1617 (1927).
(29) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928).
(30) Not the number of effective harmonic oscillators.
(31) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).
(32) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).
(33) "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965.
(34) A. W. Baldwin and Sir R. Robinson, *J. Chem. Soc.*, 1264 (1934).
(35) *Cf.* W. Koerner, *Gazz. Chim. Ital.*, **4**, 305 (1874).
(36) B. M. Wepster, *Rec. Trav. Chim.*, **73**, 809 (1954).
(37) B. M. Wepster, *ibid.*, **76**, 335 (1957).

We repeat our earlier[1, 5, 25, 38] statement that these simple Z values cannot be equated to simple rates of formation, because the ions retain the substituent and decompose further. An approximation to rates of formation may sometimes be gained from low-voltage studies where intensities are no longer altered by further decomposition of the daughter ion of interest. This is not possible in the nitrobenzenes,[2, 4] and the low-voltage data presented serve only to suggest a rough order of stability with respect both to formation and decomposition.

Kinetic energy release was calculated from the usual formula,[20] using data obtained at several accelerating voltages. The quoted error reflects not only the deviation of these different data, but also the error in estimating the width of the flat top of the metastable because of interference by the finite width of the normal peaks in some cases and difficulty in assigning the correct slope to the sides of the peak. The resolution of 450 used was a compromise between a low value, which would spread the normal peaks over the metastable to an unacceptable extent, and a high value, which would reduce the intensity of the metastable so much that analysis of its shape would have been very difficult.

The low-voltage data were obtained 3.0 V above the vanishing-current ionization potentials of each compound, *i.e.*, at nominal voltages of 12.22 V for II, 11.80 V for III, 12.44 V for IV, and 11.40 V for V. The reproducibility of the nominal ionization potential in a single set of three experiments was ±0.04. We emphasize that the vanishing-current method is not an elegant method for determining ionization potentials for future reference, and deliberately omit nominal ionization potentials obtained lest they be quoted. The merit of the vanishing-current method for this study is in the ability to arrive at a number representing a voltage 3.0 V higher than the potential of vanishing current without reference to an arbitrary fractional intensity at some point; practically all other methods of determining ionization potentials which are available to us demand this arbitrary assignment explicitly or implicitly, and render the final voltage used significant within only a narrow interpretation. We have commented on this before.[38]

The Z values for the low-voltage experiments described above, not corrected for further decomposition of the $(M - NO)^+$ ion,[39] were 0.06 for II, 0.03 for III, 0.045 for IV, and 0.04 for V. The fraction of the ion current carried by the molecular ion in these cases was 92% for II, 96% for III, 93% for IV, and 93% for V. The spectra were measured at high amplification with source conditions as for ionization-potential determinations (trap current, *ca.* 3 μA; other parameters adjusted to minimize fields in the source). A digitital voltmeter (United Systems Corporation, Dayton, Ohio) was used for the assignment of precise potentials.

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(38) M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

(39) Peaks indicating further decomposition of the $(M - NO)^+$ ions were those corresponding to a loss of CO, that is, the $(M - NO - CO)^+$ ions. They ranged in intensity from 2 to 8% of the $(M - NO)^+$ ions, and thus any correction of the Z values for them would be so slight that the interpretation would not change.

Halomethyl–Metal Compounds. XXX. CH_2 Transfer to Olefins Using Monohalomethylmercury Compounds[1]

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Abstract: The reaction of bis(bromomethyl)mercury with olefins at temperatures of 80° or above in inert solvents results in the formation of cyclopropanes *via* CH_2 transfer from the mercurial to the olefin. Bromomethylmercuric bromide is inert under these reaction conditions, but it can be brought into reaction by admixture of 1 molar equiv of diphenylmercury. The latter reacts with $BrCH_2HgBr$ to give the reactive bis(bromomethyl)mercury and possibly $PhHgCH_2Br$. Iodomethylmercuric iodide also transfers CH_2 to olefins and it also is "activated" by added diphenylmercury. The yields of cyclopropanes and their rates of production are variable, depending on the structure of the olefin. Olefins with electron-attracting substituents and hindered olefins react more slowly than simple alkyl-substituted olefins. The available evidence is against a free carbene mechanism and in favor of a direct reaction between the organomercury reagent and the olefin. Relative reactivity determinations show that electrophilic attack at the C=C bond is taking place and that steric factors are less important than electronic factors.

The preparation of cyclopropanes by divalent carbon transfer from an organometallic reagent, iodomethylzinc iodide, was first reported in 1958,[4] and in 1961, bis(iodomethyl)zinc was shown to react with olefins in similar fashion.[5] Extension of this organometallic cyclopropane synthesis to other halomethyl–metal compounds was of interest, but according to reports by Wittig and Schwarzenbach[5] and Simmons and his coworkers,[6] halomethylmercurials of type $Hg(CH_2X)_2$ and $XHgCH_2X$ were unreactive as reagents for cyclopropane synthesis.[7] It was difficult to assess the work of either group on these mercury compounds since experimental details were not provided.

(1) (a) Part XXIX: D. Seyferth, R. Damrauer, R. M. Turkel, and L. J. Todd, *J. Organometal. Chem.* (Amsterdam), in press; (b) preliminary communication: D. Seyferth, M. A. Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 121 (1964).

(2) Postdoctoral Research Associate, 1962–1963.

(3) Postdoctoral Research Associate, 1963–1964.

(4) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959).

(5) G. Wittig and K. Schwarzenbach, *Ann. Chem.*, **650**, 1 (1961).

(6) H. E. Simmons, E. P. Blanchard, Jr., and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964).

(7) Monohalomethyl derivatives of various other metals, *e.g.*, lithium, sodium, magnesium, cadmium, aluminum, indium, iron, and iridium, were found to be active as CH_2 transfer agents. For leading references see ref 6 and 8.

(8) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 4953 (1967).