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THE DECOMPOSITION OF TRIARYLMETHYL AZIDES UPON ELECTRON IMPACT

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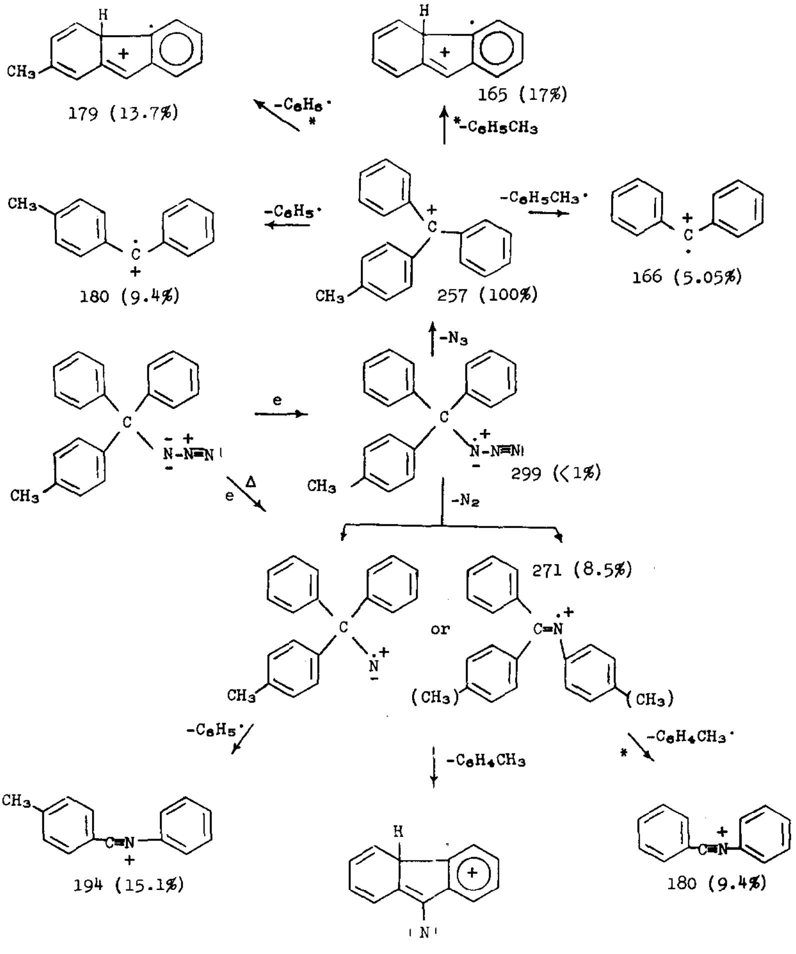
The thermal[1] and photochemical decomposition[2] of triarylmethyl azides has been studied by Saunders and co-workers. Both modes of decomposition proceed via loss of molecular nitrogen and migration of an aryl group from the carbon to nitrogen to yield the corresponding Schiff's base. The thermal reaction is characterized by a more pronounced selectivity in the migratory aptitudes of the aryl groups relative to the almost statistical migration observed in the photochemical reaction.

It appeared of interest to study the decomposition of triarylmethyl azides upon electron impact, since this process may be regarded as a third distinct way of supplying energy to the molecule for the initiation of its decomposition. Basically we wished to determine whether the reaction pattern established for the thermolytic and photolytic reactions would prevail in the case of $R_3C\text{-}N_3^+$.

Table 1 presents the masses and abundances of the principal fragments observed for p-methyl, p-chloro and p-nitro triphenylmethyl azides. The obvious trend discernible from these results is that, invariably, the most intense peak is the one due to the triarylmethyl carbonium ion. This behavior is in marked contrast to the pathway followed in the thermolytic and photolytic reactions in which the primary process is loss of molecular nitrogen to yield the nitrene.

A further point of interest in the mass spectra of the triarylmethyl azides is the detection of the P-N_2 ion. The intensity of this fragment varies from 1% to 10% for the various azides. Mass measurements on p-$CH_3C_6H_4(C_6H_5)_2CN_3$-N_2 yielded a value of 271.1358 (calc. 271.1360). This result confirms the composition of the ion; however, the structure of the ion remains unresolved. Two possible structures for this ion are the positively charged nitrene, $(Ar)_3C-\overset{+}{\bar{N}}.$, or the rearranged arylimino positive ion, $(Ar)_2C=\overset{+}{\dot{N}}-Ar$. Furthermore, this fragment may arise from an initial thermal reaction rather than by direct electron impact upon the parent azide. Lowering of the ionizing voltage from 70 e.v. to 50 e.v. in the case of p-tolyldiphenylmethyl azide caused proportionately little change in the abundance of the azide-N_2 positive ion. This result agrees with a primary thermal loss of molecular nitrogen followed by ionization of the nitrene or imine. Some thermal decomposition of triarylmethyl azides as pure solids does occur at 120°, although higher temperatures are required for substantial evolution of nitrogen. *The fragmentation pattern for p-tolydiphenylmethyl azide may be represented* by the following reactions:



* supported by metastable transition

TABLE 1

Principal Fragments Observed in the Mass Spectra of p-Substituted Triarylmethyl Azides

	$X\text{-}C_6H_4(C_6H_5)_2C\text{-}N_3$		
Transitions	$X{=}CH_3$	$X{=}Cl$	$X{=}NO_2$
$P\text{-}N_3$	257 (100%)	277 (100%)	288 (100%)
$P\text{-}N_3\text{-}X$		242 (8%)	242 (9%)
$P\text{-}N_3\text{-}HX$	241 (11.7%)	241 (5.72%)	
$P\text{-}N_3\text{-}C_6H_4X$	166 (5.05%)		166 (2.6%)
$P\text{-}N_3\text{-}C_6H_5X$	165 (17%)	165 (27%)	165 (14.9%)
$P\text{-}N_3\text{-}C_6H_5$	180 (9.4%)		
$P\text{-}N_3\text{-}C_6H_6$	179 (13.7%)	199 (14%)	
$P\text{-}N_2$	271 (8.5%)	291 (10%)	302 (4.5%)
$P\text{-}N_2\text{-}C_6H_4X$	180 (9.4%)	180 (12%)	180 (10%)
$P\text{-}N_2\text{-}C_6H_5X$	179 (13%)		179 (8.7%)
$P\text{-}N_2\text{-}C_6H_5$	194 (15.1%)	214 (17.8%)	225 (5.5%)
HN_3	43 (7.28%)	43 (9.4%)	43 (1.9%)

TABLE 2

Metastable Transitions for the p-Substituted Triarylmethyl Azides

Compounds	Observed	Calculated	Transition	
R-CH_3	129.0	129.0	179^+	$152^+ + 27$
	124.5	124.7	257^+	$179^+ + 78$
	46.5*	46.3	91^+	$65^+ + 26$
	33.8*	33.78	77^+	$51^+ + 26$
	33*	32.90	76^+	$50^+ + 26$
	30.	30.55	271^+	$91^+ + 180$
R=Cl	211.5	211.42	277^+	$242^+ + 35$
	143	143.0	277^+	$199^+ + 78$
	98.5	98.29	277^+	$165^+ + 112$
	33.8*	33.78	77^+	$51^+ + 26$
	33*	32.90	76	$50^+ + 26$
R=NO_2	203.5	203.4	288^+	$242^+ + 26$
	33.8*	37.78	77^+	$51^+ + 26$
	33*	32.90	76^+	$50^+ + 26$
R-Cl	27.8	27.71	214^+	$77^+ + 137$
	97.2	97.09	199^+	$139^+ + 60$

*The peaks marked with an asterisk are not characteristic for the molecule.

Two sets of transformations are seen to occur; one set derives from the triarylmethylcarbonium ion, and the second results from P-N_2. Again the structure of the fragments derived from the P-N_2 ion may be rearranged. Table 2 lists metastable transitions which support several of the postulated ionic reactions.

Some similarities exist between the fragmentation pattern observed for benzophenone N-phenylimine and the course of electron impact reactions of the triarylmethyl azides discussed above. For example, a strong peak (58%) at mass 180 in the spectrum of benzophenone N-phenylimine probably corresponds to the ion $C_6H_5C=N^+C_6H_5$. This suggests that the peak at mass 180 in the triarylmethyl azide decompositions may also be attributed to this fragment.

The high stability of the triarylmethyl carbonium appears to be the determinative factor in controlling the course of the electron impact decomposition. In order to gain further information to this point, the mass spectrum of azidodiphenylacetic acid was determined. In this system the carbonium analogous to the triarylmethyl ion is less stable due to the carboxyl group, i.e. $(C_6H_5)_2\overset{+}{C}COOH$ compared to $(C_6H_5)_3C^+$. In this case the base peak corresponds to $(C_6H_5)_2CN_3COOH-N_2-CO_2$. This is precisely the mode of decomposition observed in the solution photolysis of azidodiphenyl acetic acid[4].

In conclusion we wish to emphasize the point that analogies between photochemical and electron impact reactions depend greatly upon the nature of the specific compounds under consideration. Thus, in the case of the triarylmethyl azides, the course of the photolysis relative to the electron impact decomposition differs considerably.[5]

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2. W. H. Saunders, Jr., and E. A. Caress, J. Am. Chem. Soc., 86, 861 (1964).
3. Spectra were obtained using an A.E.I. MS-9 spectrometer. Samples were introduced on the probe at temperature from 120-180°. The ionizing voltage was varied from 55-70 e.v.
4. Robert M. Moriarty and M. Rahman, J. Am. Chem. Soc., 87, 2519 (1965).
5. This conclusion would be invalid if the ionization efficiency of the nitrene were very low. In other words, it might be formed in high yield, but simply go undetected. There is, however, no strong reason to believe that this situation obtains in the present case.