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REACTION OF 1-SUBSTITUTED ADAMANTANES WITH BROMINE ATOMS

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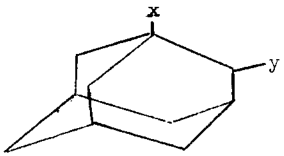
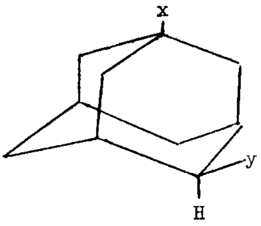
A recent investigation of hydrogen abstraction by the trichloromethyl radical from 1-substituted adamantanes has been reported by us (1). It was observed that appreciable halogen abstraction by the radical occurred for 1-fluoroadamantane and 1-chloroadamantane. Similar halogen abstraction from adamantanes has been also observed using other carbon radicals (2). In order to re-examine the results of our previous study, we have repeated our experiments using bromine generated photolytically from N-bromosuccinimide as the abstracting agent.

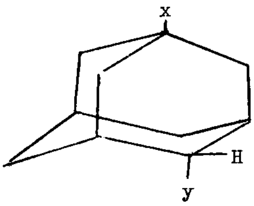
The reactions are carried out competitively in carbon tetrachloride. Four products are obtained from adamantane. These are, in order of elution from a 5% SE 30 gas chromatographic column, 1-chloroadamantane, 2-chloroadamantane, 1-bromoadamantane and 2-bromoadamantane. The first two products are formed by reaction of the adamantyl radical with solvent. Examples of such reactions for alicyclic radicals exist (3,4). Each 1-substituted adamantane also yields



I



II



III

y = Cl or Br

four products. This is somewhat surprising. Each of these compounds could yield six nonbridgehead substitution products (I, II and III) as well as the two bridgehead substituted compounds.

While complete identification of all compounds has not been carried out, we believe the order of elution for bridgehead and nonbridgehead chlorides and bromides to be the same as for the parent compound. Isomeric halides of structural type II and III could conceivably elute from the column together. Type I halides may be formed less readily due to both possible steric and electronic interactions with the substituent. In those cases examined to date, the bridgehead substituted compounds appear uncontaminated giving pmr spectra in agreement with the literature (5). The percentage of each product, based on the chromatographic peak areas, are shown in Table I. The product percentages for the parent compound agree with those reported in the literature (4). Despite the abstraction of chlorine from solvent we do not believe that the trichloromethyl radical functioned as an abstracting agent. No chloroform is formed and hexachloroethane is found in the reaction mixtures. No evidence for any halogen abstraction from 1-haloadamantanes is found.

TABLE I

Products of the Reaction of Ad-x with NBS in CCl_4 at 40°

x	Number of Runs	Bridgehead Chloride	% Nonbridgehead Chloride	Bridgehead Bromide	Nonbridgehead Bromide
CH_3	4	58.4 ± 2.8	4.2 ± 2.9	8.7 ± 2.7	28.8 ± 2.2
H	4	48.7 ± 2.1	8.7 ± 2.2	10.9 ± 2.2	31.7 ± 0.4
CO_2CH_3	4	54.9 ± 2.5	12.6 ± 2.6	13.3 ± 1.6	19.2 ± 1.3
Br	4	36.3 ± 0.8	21.4 ± 1.7	8.9 ± 0.8	33.5 ± 0.8
Cl	3	38.1 ± 1.3	20.0 ± 0.6	9.0 ± 0.7	33.1 ± 1.6
F	4	41.4 ± 1.9	17.1 ± 1.2	11.5 ± 0.7	30.1 ± 2.5
CN	4	37.5 ± 1.8	28.1 ± 2.2	9.0 ± 0.9	25.1 ± 1.1

Table II presents the relative rates of hydrogen abstraction. These data yield a ρ^* value of -0.59 ± 0.04 with a correlation coefficient of -0.992. The substituent dependence for this reaction is appreciably larger than that observed when the trichloromethyl radical is the abstracting agent. A correlation with the Kirkwood-Westheimer charge-dipole model has been carried out (1,6). The relative rates of hydrogen abstraction are calculated for a model in which a unit of positive charge is developed at the bridgehead in the transition state. These are found in Table II. A plot of the logs of the experimental relative rates against the log of their calculated counterparts yields a straight line. The slope, A, is equal to the amount

TABLE II

Relative Rates of Bridgehead Hydrogen Abstraction From Ad-x by Bromine Atoms at 40°

x	σ*	% Bridgehead Reaction	Number of Runs	$^{k_x}/_{k_{CO_2Me}}$		
					Bridgehead Reaction	
				Disappearance	Experimental	Calculated
Ad	-0.16[a]	67.1[b]	4	4.43 ± 0.13[c]	4.39	
CH_3	-0.10	67.1	6	2.74 ± 0.37	2.69	1.79×10^2
H	0.00	59.6	6	3.64 ± 0.30[c]	3.19	9.40×10^1
CO_2Me	0.71	68.2	-	1.00	1.00	1.000
Br	1.00	45.2	8	1.04 ± 0.05	0.68	2.08×10^{-2}
Cl	1.05	47.1	6	1.07 ± 0.07	0.76	4.79×10^{-2}
F	1.10	52.9	3	0.97 ± 0.05	0.68	2.75×10^{-2}
CN	1.30	46.5	5	0.64 ± 0.07	0.43	2.95×10^{-3}

[a] Taken equal to σ* for t-Bu
[b] Assumed equal to the methyl substituent
[c] Statistically corrected

of positive charge developed in the transition state. It was found in this study to be 0.17 ± 0.03 with a correlation coefficient of 0.988. This value is appreciably larger than that found with the trichloromethyl radical. It is possible that the greater electronegativity of bromine relative to trichloromethyl leads to a greater amount of carbonium ion character in the radical (7). It has been observed that the A value for a reaction which generates primary radicals is much smaller than those observed for the tertiary adamantyl system in keeping with the high energy of primary carbonium ions (8).

It has been pointed out that this approach may be extended to evaluate the amount of charge developed in any reaction (9). Schleyer and Woodworth have recently reported the rates of solvolysis for 4-substituted 1-bicyclo[2.2.2]octyl brorylates and 3-substituted 1-adamantyl bromides (10). Application of the Kirkwood-Westheimer equation to these systems leads to suspect results. It might be expected that appreciable positive charge is developed in the transition states of these molecules. The calculated A values, however, have impossible values of 1.16 ± .12 for the bicyclo[2.2.2]octyl series and 1.37 ± .21 for the adamantyl compounds. The transition state structures of the bicyclo[2.2.2]octanes and adamantanes may involve appreciable "flattening out" of the bridgehead. Even a small amount of such planarity will decrease the distance between reaction site and substituent and substantially increase the calculated relative rates of reaction. Schleyer and Woodworth have also pointed out the possible high sensitivity of these reactions to small structural deformations (10). Specific solvation effects may also account for the greater than expected solvolysis rates.

It is unfortunate that this simple Kirkwood-Westheimer treatment may apparently be unsuccesful at correlating bridgehead solvolyses. We feel, however, that this approach is very sound for systems whose rigid geometries undergo only slight changes on reaction.

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