Bridgehead Hydrogen Abstraction from 1-Substituted Adamantanes by the Trichloromethyl Radical
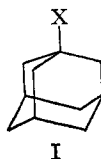
Peter H. Owens,[1] Gerald Jay Gleicher,[2] and Lawrence M. Smith, Jr.

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received February 19, 1968

Abstract: The reaction of the trichloromethyl radical with seven 1-substituted adamantanes was studied at 40°. The principle reaction observed was abstraction of bridgehead hydrogen atom. The relative rates of reaction have been correlated *via* use of the Taft equation. Correlation has also been possible using the Kirkwood–Westheimer model.

It has been pointed out that effective use may be made of the relatively rigid geometries present in alicyclic molecules to elucidate the importance of substituent effects in saturated compounds.[3] We have begun a program to determine such factors as they influence the course of free-radical reactions.

Despite the general fruitfulness of the Taft modifications of the Hammett equation,[4] there are few examples of linear free energy correlations for free-radical reactions of aliphatic systems to be found in the literature. Martin and Gleicher have obtained excellent correlations for the addition of the trichloromethyl radical to ω-substituted terminal alkenes.[5] It must be pointed out, however, that the lack of constraint found in such acyclic systems makes it impossible to definitely assess the mechanism by which the electronic effect is being transmitted. Patmore and Gritter attempted to examine the relative rates of hydrogen atom abstraction from monosubstituted cyclohexanes.[6] In spite of the presence of a fairly rigid system, a poor linear free energy correlation was obtained. This may be entirely due to the possibility of forming several different substituted cyclohexyl radicals upon hydrogen abstraction. Also, the presence of a hydrogen directly attached to the substituent bearing carbon atom allows for some radicals to be resonance stabilized. Use of 1-substituted adamantanes I obviates these difficulties.

I

There is a limited number of different abstractable hydrogens. Of the four types of hydrogen, the three bridgehead atoms should be most readily removed.[7]

Precedents for this claim are to be found not only in ionic brominations which occur exclusively at the bridgehead,[9] but also in the free-radical chlorination of adamantane[10,11] and the corresponding halogenations of bicyclo[2.2.2]octane.[12] The possibility of direct resonance interaction between the radical and the substituent is structurally precluded. A Taft study utilizing adamantanes can be already found in the literature. Thus, Fort and Schleyer[13] have obtained a reasonable correlation using the data of Stetter and Mayer for the dissociation of 3-substituted 1-adamantanecarboxylic acids.[14]

Experimental Section

Materials. Bromotrichloromethane and *o*-dichlorobenzene were purified according to standard procedure.[5,15] Adamantane was commercially obtained (Aldrich, mp 268–269°) and used without further purification.

1-Bromoadamantane was prepared *via* the direct bromination of the hydrocarbon according to the method of Stetter and coworkers,[16] mp 116.0–116.5° (lit.[16] mp 118°).

1-Hydroxyadamantane was prepared from the bromo compound by treating with basic aqueous silver nitrate under refluxing conditions,[16] mp 280–285° (sealed tube) (lit.[16] mp 288.5–290°).

1-Chloroadamantane was obtained from the reaction of alcohol and thionyl chloride,[16] mp 159–160° (lit.[16] mp 165°).

1-Iodoadamantane was also prepared from the alcohol by reaction with concentrated (48%) hydrogen iodide,[17] mp 76–76.5° (lit.[17] mp 75.3–76.4°).

1-Fluoroadamantane was obtained by treating the bromide with anhydrous silver fluoride in hexane under reflux,[18] mp 240–250° dec (lit.[19] mp 260°). A 2% impurity identified as 1-hydroxyadamantane was present. Attempts to purify the fluoro compound *via* sublimation were unsuccessful.

1-Carbomethoxyadamantane was prepared *via* Fisher esterification of the acid which was generated from the bromide by a Koch–Haaf carboxylation,[20] mp 39–39.5° (lit.[20] mp 38–39°).

1,1′-Biadamantane was prepared in a Wurtz-type coupling of 1-bromoadamantane,[21] mp 280–283° (lit.[21] 288–290°).

(1) Taken in part from the M.S. thesis of P. H. O.

(2) To whom inquiries should be addressed.

(3) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.,* 1, 284 (1966).

(4) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 226, and references cited therein.

(5) M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.,* 86, 244 (1964).

(6) E. L. Patmore and R. J. Gritter, *J. Org. Chem.,* 27, 4196 (1962).

(7) The hydrogen atoms on carbons 2, 8, and 9 are chemically equivalent. Those on atoms 4, 6, and 10, however, may be thought of as belonging to axial or equatorial sets. It is difficult to assess whether abstraction of the latter hydrogens will give rise to the same radical or whether some memory effect, due to a preferred pyramidal structure of the radical, exists.[8]

(8) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.,* 87, 2590 (1965).

(9) H. Stetter and C. Wulff, *Ber.,* 93, 1366 (1960).

(10) G. W. Smith and H. D. Williams, *J. Org. Chem.,* 26, 2207 (1961).

(11) The bridgehead radical is preferentially formed only in complexing solvents.

(12) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and C. G. Vegter, *Tetrahedron,* 9, 230 (1960).

(13) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.,* 64, 277 (1964).

(14) H. Stetter and J. Mayer, *Ber.,* 95, 667 (1962).

(15) G. J. Gleicher, *J. Org. Chem.,* 33, 332 (1968).

(16) H. Stetter, M. Schwartz, and A. Hirschborn, *Ber.,* 92, 1629 (1959).

(17) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.,* 83, 2700 (1961).

(18) R. C. Fort and P. von R. Schleyer, *J. Org. Chem.,* 30, 789 (1965).

(19) P. von R. Schleyer, personal communication.

(20) H. Koch and W. Haaf, *Org. Syn.,* 44, 1 (1964).

(21) H. F. Reinhardt, *J. Org. Chem.,* 27, 3258 (1962).

1-Methyladamantane was obtained via an aluminum chloride isomerization of exo-tetramethylenenorbornane,[22] mp 97–100° (lit.[16] mp 103°). A 2% impurity, believed to be 2-methyladamantane, could not be removed.

The procedure of Stetter and Mayer[14] for the preparation of 3-methoxyadamantane-1-carboxylic acid was adapted to the preparation of 1-methoxyadamantane. 1-Bromoadamantane (15 g, 0.070 mol), 150 ml of methanol (dried by refluxing over iodine and magnesium and distilling), and 15 g of silver oxide were added to a 250-ml, three-necked flask equipped with a mechanical stirrer and reflux condenser with drying tube. The mixture was refluxed for 15 hr with constant stirring, cooled, filtered, and concentrated on a rotary evaporator. The residue was chromatographed on an alumina column using petroleum ether (bp 30–60°) and ethyl ether as eluents. Evaporation of the solvent yielded 10.5 g of a clear liquid identified as 1-methoxyadamantane (91% yield), bp 232°, $n^{25}D$ 1.4958. The nmr spectrum in CCl$_4$ showed three peaks at δ 3.12 (ringing), 2.12 (broad), and 1.68 (doublet) having areas of 3:3:12. The ir spectrum showed prominent peaks at the following values of μ: 3.42, 3.48, 3.53, 6.88, 7.38, 7.65, 8.49, 8.93, 9.16, 9.50, and 11.20.

Anal. Calcd for C$_{11}$H$_{18}$O: C, 79.46; H, 10.91. Found: C, 79.53; H, 10.90.

An attempt to prepare 1-methoxyadamantane by forming sodium adamantoxide and treating it with dimethyl sulfate gave only unreacted 1-hydroxyadamantane.

The procedure of Reinhardt[21] for the preparation of 3,3'-dicyano-1,1'-biadamantane was modified for the preparation of cyanoadamantane. Bromoadamantane (10.8 g, 0.050 mol), 15 g of CuCN, and 75 ml of pyridine were placed in a three-necked, 250-ml flask fitted with mechanical stirrer, thermometer, and distillation head and condenser. The solid complex formed was broken up and stirred vigorously. The mixture was heated slowly to 230° and maintained at this temperature until all the pyridine had distilled over. The residue was cooled to room temperature and refluxed 6 hr with 100 ml of benzene. The benzene solution was decanted and the black tar residue refluxed twice more with 100-ml portions of benzene. The benzene solutions were combined, filtered, and concentrated on a rotary evaporator. The light brown solid remaining was recrystallized from petroleum ether at Dry Ice–acetone temperature yielding 3.98 g of a white powder identified as 1-cyanoadamantane (50% yield), mp 193–194°. The nmr spectrum in CCl$_4$ showed peaks at δ 7.95 and 8.25 having areas of 3:2, respectively. The ir spectrum (Nujol mull) revealed a peak at 4.5 μ characteristic of cyano groups.

Anal. Calcd for C$_{11}$H$_{15}$N: C, 81.94; H, 9.38; N, 8.69. Found: C, 82.07; H, 9.48; N, 8.54.

With the exception of the two cases cited, all materials showed no contaminents by gas–liquid partition chromatography.

Procedure for Product Studies of the Reaction of 1-Substituted Adamantanes and Bromotrichloromethane. Solutions of the substituted adamantane, bromotrichloromethane, and o-dichlorobenzene were prepared in the approximate molar ratio 2:9:1. In the case of adamantane, 1,1'-biadamantane, and 1-hydroxyadamantane, the ratio was approximately 2:20:1 necessitated by solubility restrictions. Approximately 0.75 ml of the solution was placed in each of several Pyrex ampoules. The ampoules were evacuated at 10–15 mm and flushed with dry nitrogen five times at Dry Ice–acetone temperature, then sealed. One ampoule was reserved for analysis of starting material; the remainder were placed horizontally just under the surface of a mineral oil constant temperature bath maintained at 40.0 ± 0.5°. Energy was provided by a Sylvania 275-W sunlamp placed 15 cm from the surface of the oil. Reaction times varied from 18 to 95 hr by which time 8 to 60% of the adamantanes had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after reaction, was carried out via gas–liquid partition chromatography. Areas of the reactants and products relative to the internal standard, o-dichlorobenzene, were determined and converted to millimoles.

Products of the Reaction of Bromotrichloromethane and Adamantane. Five grams of adamantane and 20 g of bromotrichloromethane were placed in a 50-ml flask. A nitrogen gas atmosphere was provided, and the solution was heated directly from below with a 275-W sunlamp for 2 hr. The solution was kept just below its boiling point. After cooling gas–liquid partition chromatography

showed that approximately 60% of the adamantane had reacted giving two major products of similar retention time. The major product, with the lesser retention time, had a retention time identical with 1-bromoadamantane's. There were also two small peaks before the two major ones, the first one having the same retention time as 1-hydroxyadamantane. The solution was chromatographed on an alumina column using petroleum ether (bp 30–60°) as eluent yielding in one fraction a solid residue containing only the two major products. Pure samples of the two products were obtained via preperative gas–liquid partition chromatography. The major product having the shortest retention time was identified as 1-bromoadamantane; mp 117–118°. The nmr spectrum in CCl$_4$ was identical with a sample of 1-bromoadamantane prepared by the method of Stetter, et al.,[16] and with that reported in the literature.[18] The ir spectrum (CCl$_4$ solution) corresponded to that of a known sample of 1-bromoadamantane. The major product having a slightly longer retention time than 1-bromoadamantane was identified as 2-bromoadamantane, mp 133–134°. The nmr spectrum in CCl$_4$ showed a peak at δ 4.62 and a complex set of unresolved peaks centered at δ 1.80 having areas of 1:14, respectively. This spectrum is almost identical with the reported spectrum of 2-hydroxyadamantane[18] excluding the hydroxyl proton. The ir spectrum (CCl$_4$ solution) is more complex than that of 1-bromoadamantane and does not contain an absorption between 9.5 and 10.0 μ. Landa and Hála[23] have pointed out that an absorption in this region may be characteristic of most 1-substituted adamantanes; 1-bromoadamantane displays such an absorption.

Anal. Calcd for C$_{10}$H$_{15}$Br (2-bromoadamantane): C, 55.82; H, 7.03. Found: C, 55.94; H, 6.99.

Products of the Reaction of Bromotrichloromethane and 1-Bromoadamantane. One gram of 1-bromoadamantane and 5 g of bromotrichloromethane were treated as above for 12 hr. After chromatographing on an alumina column and preparative gas–liquid partition chromatography, a compound identified as 1,3-dibromoadamantane was isolated, mp 111–112° (lit.[24] mp 112°). The nmr spectrum in CCl$_4$ was identical with that reported in the literature.[18] Several minor products having retention times in excess of 1,3-dibromoadamantane could not be isolated. It was felt safe to assume that the major product obtained in the reactions of 1-substituted adamantanes would be the bridgehead bromide unless specific reaction with the substituent were taking place. Because of symmetry these products all had shorter retention times than their isomers.

Products of the Reaction of 1-Fluoroadamantane and Bromotrichloromethane. 1-Fluoroadamantane (0.5 g) and 2 g of bromotrichloromethane were treated as above for 3 hr. After chromatographing on an alumina column and preparative gas–liquid partition chromatography, a substance was obtained that showed no detectable impurities and having the same retention time as 1-bromoadamantane, via glpc. The nmr spectrum in CCl$_4$ and the ir spectrum (KBr pellet) appeared almost identical with that of 1-bromoadamantane, as did the melting point of 115–116°. The substance was tentatively identified as a mixture of 1-bromoadamantane and 1-fluoro-3-bromoadamantane.

Anal. Calcd for C$_{10}$H$_{15}$Br: C, 55.82; H, 7.03; Br, 37.15. Calcd for C$_{10}$H$_{14}$BrF: C, 51.52; H, 6.05; Br, 34.28, F, 8.15. Found: C, 54.18; H, 6.82; Br, 35.28; F, 3.86.

Products of the Reaction of 1-Fluoroadamantane and Cumene. 1-Fluoroadamantane (0.5 g) and 5 g of cumene were treated as above for 12 hr. Glpc revealed besides the starting materials a small peak having the same retention time as adamantane and a large peak having the same retention time as 1-hydroxyadamantane. After chromatographing on an alumina column using petroleum ether and ethyl ether as eluents, a compound was isolated from the fraction eluted with pure ethyl ether. The compound was identified as 1-hydroxyadamantane, and its nmr spectrum in CCl$_4$ and ir spectrum (KBr pellet) corresponded to that of a known sample made by the method of Stetter.[16]

Anal. Calculated for C$_{10}$H$_{16}$O: C, 78.90; H, 10.60; F, 0.00. Found: C, 78.71; H, 10.76; F, 0.00.

Procedure for Kinetic Runs. Solutions of two adamantanes, bromotrichloromethane, and o-dichlorobenzene were prepared in the approximate molar ratio of 2:2:10:1. Ampoules were filled, sealed, and irradiated in a manner analogous to that described previously for product studies. All determinations were run in replicate. The procedure was to have some substituted adamantane

(22) P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, 305 (1961).

(23) S. Landa and S. Hála, *Collection Czech. Chem. Commun.*, **24**, 93 (1959).

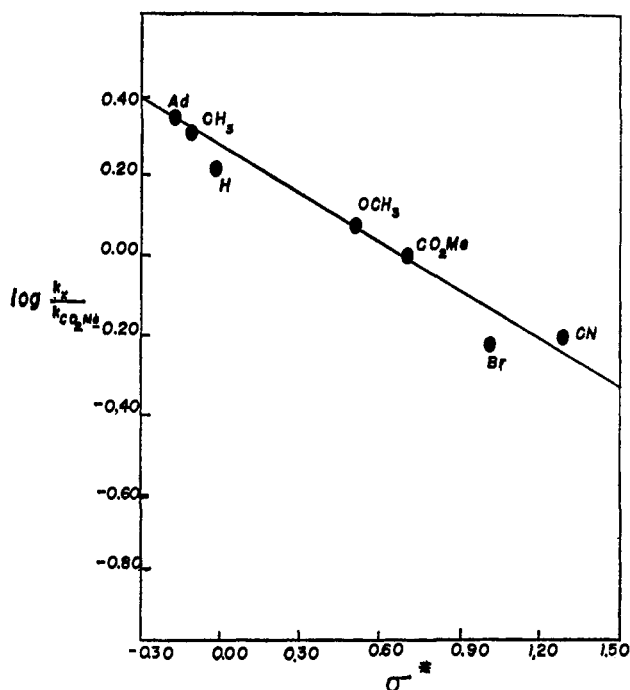(24) V. Prelog and R. Seiwerth, *Ber.*, **74**, 1769 (1941).

Figure 1. Correlation of log k_X/k_{CO_2Me} and σ^* for bridgehead hydrogen abstraction from 1-substituted admanatanes by trichloromethyl radicals.

compete directly with 1-carbomethoxyadamantane for the attacking radical. In the case of the methoxy and adamantyl derivatives, however, it was necessary to determine the reactivity relative to adamantane. The rate constants thereby obtained were converted to the desired form through the expression

$$k_X/k_{COOMe} = (k_X/k_H)(k_H/k_{COOMe})$$

Determination of k_X/k_{COOMe}. The ratios of relative rate constants were all obtained using the usual competitive procedures.[5,15]

Results and Discussion

Of the original series of compounds certain 1-substituted adamantanes were eliminated from this kinetic study. This was a result of their undergoing other, often unknown, reactions. Thus, 1-adamantanol yielded four major products. It seems probable that part of these arise from abstraction of the hydroxyl hydrogen possibly followed by rearrangement. In the reaction of the trifluoromethyl radical with methanol both types of hydrogens appear equally labile.[25]

The 1-haloadamantanes also behaved in atypical manner. 1-Iodoadamantane underwent reactions with bromotrichloromethane to generate eight products of which only 1-bromoadamantane was definitely identified. Purple solutions indicative of formation of molecular iodine were noted. A probable photolytic dissociation of the carbon–iodine bond is taking place. When mixtures of 1-iodoadamantane and cumene were irradiated, adamantane was formed in 50% yield, lending substance to this view.

1-Bromoadamantane was also formed in appreciable yield in the reactions of 1-fluoro- and 1-chloroadamantanes with the trichloromethyl radical. When these two compounds were treated with cumene, however, almost no adamantane was formed. This

suggests that what was observed was abstraction of a halogen atom by the trichloromethyl radical. Relatively large amounts of 1-adamantanol were formed in the reactions of 1-fluoroadamantane both in reactions with bromotrichloromethane and with cumene. The possibility of reaction with the oxygen in the Pyrex ampoules may account for this, considering the precautions taken to eliminate air. Until these reactions have been studied in detail only 1-bromoadamantane of the haloadamantanes was utilized.

Table I presents the relative rates of disappearance of these compounds. By correcting with the percentage of bridgehead reaction one can convert this into relative rates of bridgehead hydrogen abstraction. As may be seen in the table, reaction takes place preferentially at the tertiary site. These results differ significantly from those recently reported for adamantane by Tabushi, Hamuro, and Oda.[26] In that study, the reaction of adamantane with bromotrichloromethane showed only 56% of the reaction occurring at the bridgehead position. Also, in contrast to those workers, no evidence was found that chlorinated products were formed. The side products appear to be two oxygenated materials whose concentration was a function of the care taken to exclude air from the system. The total amount of these side products could usually be kept to less than 10% of the brominated products.

Table I. Relative Rates of Bridgehead Hydrogen Abstraction from Ad–X by the Trichloromethyl Radical at 40°

X	σ^* [a]	% bridgehead H abstn	k_X/k_{COOMe} Rel rate of disapp	k_X/k_{COOMe} Rel rate of bridgehead H abstn
Ad	−0.16[b]	87[c]	2.28 ± 0.12	2.38 ± 0.13
CH₃	−0.10	87	1.98 ± 0.09	2.08 ± 0.09
H	0.00	86	1.55 ± 0.09	1.61 ± 0.09
OCH₃	0.52	85	1.42 ± 0.08	1.21 ± 0.06
CO₂CH₃	0.71	83	1.00	1.00
Br	1.00	85	0.58 ± 0.08	0.59 ± 0.02
CN	1.30	74	0.67 ± 0.05	0.60 ± 0.04

[a] Taken from ref 2. [b] Presumed equal to the σ^* for t-Bu. [c] Estimated as equal to methyladamantane.

A ρ^* value of -0.40 ± 0.04 was obtained with a correlation coefficient of -0.980. This precision is good. As might be expected the presence of electron-donating groups facilitates reaction. In this regard the methyl substituent appears to be electron donating in character. This stands in contrast to the work of Fort and Schleyer who found the bridgehead alkyl substituents increase the strength of 1-adamantanecarboxylic acid.[27] The effects of methyl groups on reactivity are usually small, however, and may be extremely dependent upon slight changes in hybridization or solvation. A plot of the logs of the relative rates vs. σ^* is given in Figure 1.

Recent studies by several groups have shown the possibility of correlating reactions in bicyclic systems

(25) T. S. Carlton, J. R. Steeper, and R. L. Christensen, J. Phys. Chem., 70, 3222 (1966).

(26) I. Tabushi, J. Hamuro, and R. Oda, J. Am. Chem. Soc., 89, 7127 (1967).

(27) R. C. Fort, Jr., and P. von R. Schleyer, ibid., 86, 4194 (1964).

with a field-effect model.[28,29] Application of the Kirkwood–Westheimer[30] approach has proven equally useful in this study. The relative rates were calculated by presuming a unit of positive charge to be formed in the transition state and determining the interactions with the dipole of the substituent utilizing the following form of the Kirkwood–Westheimer equation

$$\log \left(\frac{k_X}{k_{COOMe}} \right) = \frac{Ae}{2.3kT} \left\{ \left[\frac{\mu \cos \theta}{R^2 D_E} \right]_X - \left[\frac{\mu \cos \theta}{R^2 D_E} \right]_{COOMe} \right\} \quad (1)$$

where A represents the actual fraction of positive charge formed, μ is the group dipole of the substituent, θ the angle between the direction of the group dipole and the extension of the carbon–substituent bond, and R the distance between the center of the dipole and the center of the carbon–hydrogen bond being broken. The effective dielectric constant, D_E, is given by the relationship

$$\frac{1}{D_E R^2} = \frac{x}{Dbr} \left\{ - \frac{2[x - \cos \alpha]}{[1 - 2x \cos \alpha + x^2]^{3/2}} - \frac{1}{x} \left[\frac{1 + \frac{[x - \cos \alpha]}{[1 - 2x \cos \alpha + x^2]^{1/2}}}{[1 - 2x \cos \alpha + x^2]^{1/2} + x - \cos \alpha} \right] + x^{1/2} \ln \left[\frac{[1 - 2x \cos \alpha + x^2]^{1/2} + x - \cos \alpha}{1 - \cos \alpha} \right] \right\} + \frac{1}{bD_i r} \left[\frac{[x - \cos \alpha]}{[1 - 2x \cos \alpha + x^2]^{3/2}} \right] + \frac{[d \cos \alpha - r]}{D_i R^3} \quad (2)$$

where R maintains the definition already given, r is the distance from the center of the adamantane skeleton to the midpoint of the projection of the dipole on the carbon–substituent bond extension, d is the invariant distance from the center of the molecule to the midpoint of the carbon–hydrogen bond to be broken, b is equal to $r + 1.5$ Å (this is the Tanford modification which defines the actual size of the cavity in which the molecule exists),[31] and α is the angle between r and d which should be a constant in any rigid polycyclic system and was given the tetrahedral value in this study. x is given by the expression

$$x = (rd/b^2)^{1/2} \quad (3)$$

and may be considered as a measure of the depth of penetration of the dipole and the removable hydrogen below the interphase of the cavity. D and D_i are respectively the dielectric constants of the solvent and the cavity. The latter was given a value of 2.0, approximately equal to that of parafin hydrocarbons. D was estimated as 3.0. Table II presents values of terms needed to evaluate D_E for the substituted adamantanes. Biadamantyl was omitted from this portion of the study due to difficulty in assessing these

values. Table III presents the values of $1/R^2 D_E$ and the calculated relative rates.

Table II. Values of R, r, d, b, x, and α for 1-Substituted Adamantanes[a]

Compound	d^b	r^c	a, deg	R	b	$x = [rd/b^2]^{1/2}$
AdMe	2.09	3.26	109.5	4.42	4.76	0.549
AdH	2.09	2.09	109.5	3.42	3.59	0.583
AdOMe	2.09	2.54	109.5	3.79	4.04	0.570
AdCOOMe	2.09	3.52	109.5	4.66	5.02	0.541
AdBr	2.09	2.51	109.5	3.76	4.01	0.571
AdCN	2.09	3.58	109.5	4.71	5.08	0.538

[a] Distances are in ångstroms. [b] This is the distance from the center of an adamantane molecule to a bridgehead carbon plus one-half the carbon–hydrogen bond length. [c] Distances obtained following the method of Kilpatrick and Morse [M. Kilpatrick and J. G. Morse, *J. Am. Chem. Soc.*, 75, 1846 (1953)].

Table III. Experimental and Calculated Values for $\log (k_X/k_{COOMe})$

Compound	$\mu \cos \theta$, ^{a} D	$(1/R^2 D_E) \times 10^2$, $1/\text{Å}^2$	$\log (k_X/k_{COOMe})$ Calcd	Exptl
AdMe	−0.4	2.24	2.251	0.3181
AdH	0.4	3.51	1.148	0.2068
AdOMe	1.2	2.98	0.092	0.0828
AdCOOMe	1.8	2.09	0.000	0.0000
AdBr	2.4	3.01	−1.683	−0.2291
AdCN	4.4	2.98	−2.532	−0.2218

[a] Taken from C. P. Smythe, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 441.

In the case of the H, OMe, and Br substituents the distance r is the distance from the center of the adamantane molecule to the bridgehead carbon plus one-half the distance from the bridgehead carbon to the end of the substituent as projected on the bridgehead carbon–substituent bond. In the case of the Me, COOMe, and CN substituents the distance r is the distance from the center of the adamantane molecule to the first carbon in the substituent plus one-half the length of the substituent as projected on the bridgehead carbon–substituent bond. Bond lengths were taken from the tables of Bowden[32] and Sutton.[33]

As can be seen, the predicted rate ratios were much too large as a full unit of charge is not formed in the transition state. When, however, the calculated rate ratios were plotted against their experimentally obtained counterparts, an excellent correlation was noted. The slope of this line, which corresponds to A in eq 1, was 0.12 ± 0.03. The correlation coefficient was 0.981.[34] This value of A may be taken as the amount of charge developed in the transition state. This may be thought of as arising from the contribution of the carbonium

(28) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, 89, 5677 (1967), and references cited therein.

(29) G. F. Wilcox and C. Leung, *ibid.*, 90, 336 (1968).

(30) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 503 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, 6, 513 (1938).

(31) C. Tanford, *J. Am. Chem. Soc.*, 79, 5348 (1957).

(32) H. M. J. Bowden, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(33) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965.

(34) Utilizing the programs of Wilcox,[29] P. H. O. has subsequently shown that within our experimental uncertainty the calculated value of A is largely independent of the choice of values for D, D_i, and the Tanford parameter. P. H. O. extends his thanks to Professor Wilcox and Professor A. Streitwieser, Jr., for making these programs available.

ion canonical structure, II_c, to the over-all resonance hybrid of the transition state.

$$R\text{—H} \cdot CCl_3 \longleftrightarrow R \cdot \ H\text{—}CCl_3 \longleftrightarrow R^+ \ H \ ^-CCl_3$$
$$II_a \qquad\qquad II_b \qquad\qquad II_c$$
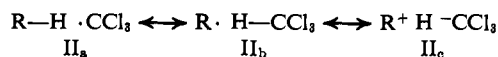
The results already obtained suggest that studies involving hydrogen abstraction from other substituted rigid systems may prove capable of assessing the mode of transmission of electronic effects in radical reactions. Work has already begun on the 1-substituted bicyclo-[2.2.2]octane system.[35]
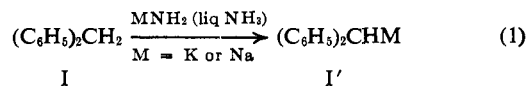
Displacement on Halogen *vs.* Carbon and on Halogen *vs.* Hydrogen of Certain Polyhalides by Diphenylmethide Ion in Liquid Ammonia

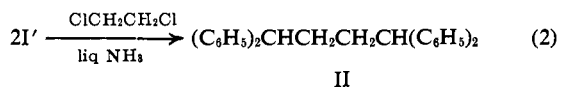**William G. Kofron and Charles R. Hauser**

Contribution from the Departments of Chemistry, University of Akron, Akron, Ohio 44304, and Duke University, Durham, North Carolina 27706. Received January 31, 1968

Abstract: Sodium and potassium diphenylmethide (I′), prepared from diphenylmethane (I) and the corresponding alkali amide in liquid ammonia, underwent displacement on halogen with ethylene bromide and iodide to form the dimer, 1,1,2,2-tetraphenylethane (III), and presumably ethylene; in contrast, I′ underwent displacement on carbon (SN2) with ethylene chloride to give the twofold alkylation product. Similarly, potassio salt I′ underwent displacement on halogen with 2,3-dibromo-2,3-dimethylbutane, 1,1,2,2-tetrabromoethane, and hexachloroethane to form dimer III and an olefinic product. The olefinic products from the tetrabromo- and hexachloroethanes were dibromoethylene and tetrachloroethylene, respectively; potassio salt I′ also underwent displacement on halogen with these olefinic halides to afford apparently acetylene. Potassio salt I′ underwent displacement on hydrogen with 1,1-dichloroethane to regenerate I, and displacement on halogen with 1,1,1-trichloroethane and benzotrichloride to form a mixture of I and III; in these cases the halide was converted to an aldimine. Potassio salt I′ underwent displacement on halogen with N-bromosuccinimide to give dimer III and succinimide.

The diphenylmethide ion I′, which is readily prepared from sodium amide or potassium amide in liquid ammonia (eq 1), has previously been shown to undergo displacement on carbon with alkyl halides[1] and certain dihalides,[2] displacement on halogen with carbon tetrachloride and bromotrichloromethane,[3] and displacement on hydrogen with chloroform.[3] In order to ascertain the influence of the structure of the halide on the course of reaction, a study of the reactions of various other halides with anion I′ was made.
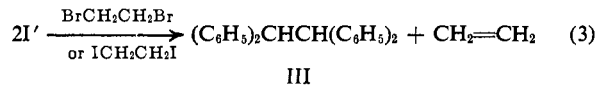
$$(C_6H_5)_2CH_2 \xrightarrow[\text{M = K or Na}]{\text{MNH}_2 \text{ (liq NH}_3)} (C_6H_5)_2CHM \qquad (1)$$
$$\text{I} \qquad\qquad\qquad \text{I}′$$

Results with Vicinal Dihalides. Sodium diphenylmethide (I′, M = Na) has been shown[2] to undergo twofold alkylation with ethylene chloride to form hydrocarbon II in excellent yield (eq 2, M = Na).

$$2\text{I}′ \xrightarrow[\text{liq NH}_3]{\text{ClCH}_2\text{CH}_2\text{Cl}} (C_6H_5)_2CHCH_2CH_2CH(C_6H_5)_2 \qquad (2)$$
$$\text{II}$$

We have found that potassium diphenylmethide (I′, M = K) similarly reacts with ethylene chloride to af-

ford hydrocarbon II, but, more significantly, that both sodium and potassium diphenylmethides react with ethylene bromide or iodide under similar conditions to produce little if any of hydrocarbon II. Instead, the dimeric product, 1,1,2,2-tetraphenylethane (III), was isolated in yields of 60–67%. Presumably ethylene was also produced (eq 3).

$$2\text{I}′ \xrightarrow[\text{or ICH}_2\text{CH}_2\text{I}]{\text{BrCH}_2\text{CH}_2\text{Br}} (C_6H_5)_2CHCH(C_6H_5)_2 + CH_2\text{=}CH_2 \qquad (3)$$
$$\text{III}$$

This complete change in the course of the reaction brought about merely by changing the halogen from chlorine to bromine or iodine is rather remarkable, and represents one of the first such changes reported. The mechanism of the twofold alkylation (eq 2) presumably involves displacement on carbon (SN2), and that of the dimerization (eq 3) displacement on halogen accompanied by β elimination of halide ion, followed by alkylation of unchanged diphenylmethide ion by the resulting benzhydryl bromide or iodide (eq 4).[4]

$$(C_6H_5)_2\bar{C}H_2 \cdots \text{Br—CH}_2\text{—CH}_2\text{—Br} \longrightarrow (C_6H_5)_2CHBr \xrightarrow{\text{I}′} \text{III}$$
$$(4)$$
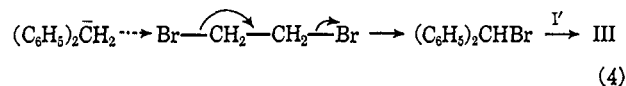
(1) C. R. Hauser and P. J. Hamrick, *J. Am. Chem. Soc.*, 79, 3142 (1957).

(2) C. R. Hauser, C. F. Hauser, and P. J. Hamrick, *J. Org. Chem.*, 24, 397 (1959).

(3) C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *ibid.*, 26, 2627 (1961).

(4) The intermediate benzhydryl halide has been isolated in the related coupling of diphenylmethide ion with carbon tetrachloride: W. G. Kofron and C. R. Hauser, *ibid.*, 28, 577 (1963).