Analyses of solvolysis products have been run on 0.1 *M* solutions heated during some ten half-lives in a stoppered flask, in the presence of more than 1 equiv of sodium acetate or sodium hydrogen carbonate to minimize secondary, acid-catalyzed reactions.

Table V summarizes the physical data of the solvolysis products.

Solvolysis of 4b ($Z = CO_2CH_3$). In 20 ml of 80% ethanol was dissolved 0.4 g of the bromo ester **4b** ($Z = CO_2CH_3$). Sodium acetate (0.24 g) was added. The sealed ampoule was heated at 110° for 5 hr. The solvent was removed under reduced pressure and the product isolated in the usual way. Of the colorless, viscous oil obtained (0.295 g) one part (0.245 g) was chromatographed over silica gel (10 g; dry column technique). Four fractions homogeneous in tlc have been obtained, of which two have been identified.

Fraction 1 (0.10 g) is eluted with 5% ether in petroleum ether. It is a *mixture* of the two ring-contracted esters obtained previously by acetolysis of **4b**[11] (*cf.* Figure 2). Quantitative evaluation of the 100-MHz nmr spectrum of the *crude reaction product* shows that this mixture of two esters makes up to 45–50% total product.

Fraction 4 (0.025 g) is eluted with 25% ether in petroleum ether. It is the methyl ester of a hydroxy acid obtained previously by saponification of the acetate[11] described in Figure 2 (route a). Methylation of this hydroxy acid with diazomethane gave an authentic comparison material.

In the present case, we have not been able to develop conditions for vpc analysis of the reaction mixture, and have not been able to deduce plausible structures for the other two products isolated.

Solvolysis of 4a (Z = CN). The same procedure was used with the bromonitrile **4a** (0.10 g). The crude product (0.073 g) gave an nmr spectrum compatible with a 1:1 mixture of the two ring-contracted nitriles described in Table V, and forming at least 70% total reaction product. The crude product (0.073 g) was chromatographed on silica gel. Ether (10%) in petroleum ether eluted the mixture of the two nitriles (0.053 g), homogeneous in tlc.

Solvolysis of 4h ($Z = CH_3$). 3α-Bromolongifolane **4h** ($Z = CH_3$) (0.057 g) was heated in 80% ethanol at reflux during 6 hr, in the presence of sodium hydrogen carbonate (0.10 g). The solvent was removed under reduced pressure and the product was extracted in the usual way. The crude oily product (0.032 g) was analyzed by vpc (140°, 5% OV-17 on Aeropak). Beside longifolene (80%), four more polar products are present (*ca.* 5% each); they appear to be alcohols or ethers, as judged by their retention times. This evaluation is confirmed by nmr. Longifolene had already been isolated from a similar reaction.[11]

Solvolysis of 4i ($Z = CH_2CH_3$). The bromide **4i** ($Z = CH_2CH_3$) (0.070 g) was treated by the preceding procedure. The crude product, by vpc in the same conditions, is shown to contain one major product (90%) and three more polar products (2, 5, and 3%). This is confirmed by nmr. The major product is purified by chromatography on silica gel, to give methyl-15 longifolene.

Free-Radical Hydrogen Abstraction from Polycyclic Aliphatic Hydrocarbons[1]

Victor R. Koch[2a] and Gerald Jay Gleicher*[2b]

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received August 26, 1970*

Abstract: Six polycyclic aliphatic hydrocarbons were allowed to react with the trichloromethyl radical photolytically generated from bromotrichloromethane at 40°. Relative rates of hydrogen abstraction were correlated with a computer analysis of the change in strain energy in going from the ground state to the intermediate. A good correlation between the log of the relative rates and the calculated changes in strain energy was obtained.

The problem of bridgehead free-radical reactivity has been under investigation for the last 30 years. Recent work has engendered conflicting data concerning the relative stabilities of certain of these species. Applequist and Kaplan studied the decarbonylation of polycyclic aldehydes.[3] They found that the 1-adamantyl radical was formed 2.50 times as fast as the *tert*-butyl radical indicating that the bridgehead adamantyl radical is the more stable species. In the decomposition of *tert*-butyl peresters Fort and Franklin and Lorand and coworkers[4] observed that the 1-adamantyl radical is formed about 1.2 times as fast as the *tert*-butyl radical indicating both radicals to be of roughly equivalent stability. Chick and Ong[5] found that the 1-adamantyl radical is formed only 0.137 times as rapidly as the *tert*-butyl radical in hydrogen abstraction from the appropriate alkyl benzyl ethers. This result stands in marked contrast to the other examples cited.

The mechanism and thermochemistry of hydrogen abstraction by the trichloromethyl radical is well documented.[6–8] Since the abstraction of the alkyl hydrogen is endothermic it follows by the Hammond postulate[9] that the intermediate alkyl radical resembles the transition state. It was felt that an examination of the relative rates of hydrogen abstraction from a series of saturated polycyclic systems might yield insight as to the comparative stabilities of bridgehead radicals. Unlike the studies of Applequist and Kaplan[3] or Chick and Ong,[5] relative rates may be directly obtained. A problem associated with both systems involves the expression of the rates of radical formation with regard to some common reaction, the rate of which is assumed independent of structure. The validity of this assumption, however, is open to question.[4] A serious problem is also present in the studies on perester decomposition. It has recently been shown that loss of carbon dioxide from the possible intermediate acyloxy radical may be

---

(1) Presented at the Northwest Regional Meeting of the American Chemical Society, June 18, 1970.

(2) (a) Taken in part from the M.S. Thesis of V. R. Koch. (b) Alfred P. Sloan Fellow (1969–1971).

(3) D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965).

(4) (a) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968); (b) John Lorand, S. D. Chodroff, and R. W. Walker, *ibid.*, **90**, 5266 (1968).

(5) W. H. Chick and S. H. Ong, *Chem. Commun.*, 216 (1969).

(6) B. P. McGrath and J. M. Tedder, *Bull. Soc. Chim. Belg.*, **71**, 772 (1962).

(7) E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 391 (1960).

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

(9) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

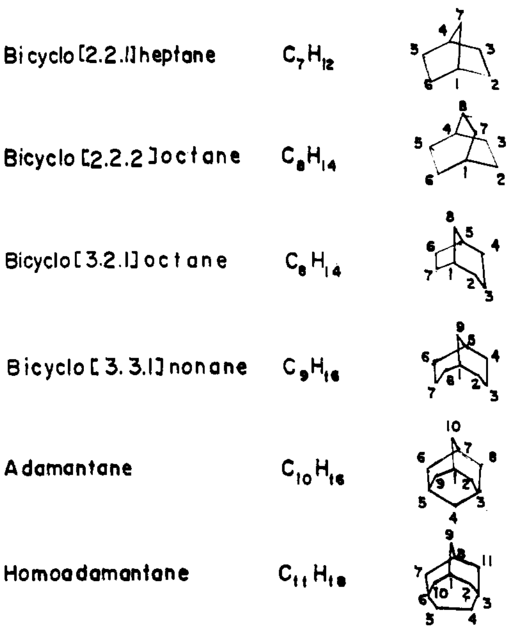

Figure 1. Polycyclic aliphatic hydrocarbons.

very dependent on the nature of the organic moiety.[10] It was also felt that, in such a study of the formation of radicals directly from the parent hydrocarbons, the results could be readily correlated with calculated strain energy differences between the starting material and transition state.[11]

Results and Discussion

The series of compounds used in this study is shown in Figure 1. This study was limited to polycyclic hydrocarbons because their relative rigidity assures a transition state free of variable interactions arising from rotations about carbon–carbon bonds. Furthermore, a similar electronic environment should be provided at the bridgehead positions throughout this series.

Kinetic Studies. The hydrogen abstraction reactions were run in replicate relative to adamantane. Reactions were carried out in sealed ampoules under nitrogen at 40.0 ± 0.5°. Solutions of adamantane, the substrate under study, bromotrichloromethane, and either chlorobenzene, bromobenzene, or *o*-dichlorobenzene as an internal standard were prepared in the approximate molar ratio of 2:2:20:1. An aliquot was reserved for analysis of starting material. The relative rates of disappearance of starting materials were determined by gas–liquid chromatography. The reaction sequence is shown as follows (eq 1–4).

$$\mathrm{BrCCl_3} \xrightarrow{h\nu} \mathrm{Br\cdot} + \mathrm{\cdot CCl_3} \quad (1)$$

$$\mathrm{R{-}H} + \mathrm{\cdot CCl_3} \xrightarrow{\text{slow}} \mathrm{R\cdot} + \mathrm{HCCl_3} \quad (2)$$

$$\mathrm{R\cdot} + \mathrm{BrCCl_3} \longrightarrow \mathrm{R{-}Br} + \mathrm{\cdot CCl_3} \quad (3)$$

$$2\dot{\mathrm{C}}\mathrm{Cl_3} \longrightarrow \mathrm{C_2Cl_6} \quad (4)$$

To account for differences in bridgehead selectivity, studies were undertaken which determined the percentage of bridgehead and, in some cases, secondary products for each hydrocarbon. These percentages, along with the appropriate statistical corrections for the number of bridgehead and secondary hydrogens, allowed the relative rates of disappearance to be converted to relative rates of abstraction for different hydrogens in these molecules. Table I lists the percentages of bridgehead reaction and the corresponding relative rates of disappearance.

Table I. Rates of Disappearance Relative to 1-Adamantane

Substrate	% bridgehead reaction	$k_X/k_{1\text{-Ad}}$ disappearance
Bicyclo[2.2.1]heptane	0	1.15 ± 0.13
Bicyclo[2.2.2]octane	8.8 ± 2	5.43 ± 0.28
Bicyclo[3.2.1]octane	Indeterminable	1.00 ± 0.10
Bicyclo[3.3.1]nonane	100	6.87 ± 0.22
Adamantane	86.0 ± 2	1.00
Homoadamantane[a]	73.5 ± 2	22.05 ± 0.88

[a] Only the 3 (bridgehead) position of homoadamantane reacted with the trichloromethyl radical. No reaction at the 1 (bridgehead) position was detected.

Determination of Strain Energies. Strain energies for the ground-state hydrocarbon and free-radical intermediates were calculated using a computer program similar to the one used by Gleicher and Schleyer in their study of bridgehead carbonium ions.[11] The ground states were constructed from the bond lengths, force constants, torsional potentials, and bond angles determined from the parent hydrocarbons. This initial geometry served as input data. A strain energy was calculated for this geometry, and the coordinates of each atom were altered until an energy minimum was reached. An energy minimum was likewise determined for the free-radical intermediate. A preferred planar configuration[12] was assumed for the free-radical intermediate and from the Hammond postulate it follows that the transition state should also be essentially planar. It must be admitted, however, that recent theoretical[13] and experimental[14] results indicate a nonplanar secondary radical site to be not infrequent. Of most concern to the present study is the possibility that angle strain may cause a preferred pyramidal radical.[13,15] Of the secondary radicals encountered in this study, however, symmetry demands that the 2-adamantyl and 2-bicyclo[2.2.2]octyl systems be planar in accord with the original assumption. Other specific assumptions for the radical intermediate initial geometry are as follows: angles about the reaction site were taken to be 120°; bending force constants were taken to be the same as in the hydrocarbon; sp^2–sp^3 carbon–carbon bonds were set at 1.515 Å; sp^2 carbon–hydrogen bonds were set at 1.075 Å. Stretching force constants were evaluated from the Tractrix equation in which the magnitude of the force constant is a function of the bond length.[16] Although reasonable correlations of bridgehead-radical reactivities have been obtained using a carbonium ion model,[17] it is strongly felt that

---

(10) T. G. Traylor, A. Sieber, H. Kiefer, and N. Clinton, *Intra-Sci. Chem. Rep.*, **3**, 289 (1969).

(11) G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(12) G. Herzberg, *Proc. Roy. Soc., Ser. A*, 262, 291 (1961).

(13) V. Buss, P. von R. Schleyer, and L. C. Allen, *J. Amer. Chem. Soc.*, in press.

(14) (a) J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969); (b) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3652 (1969).

(15) P. Bakuzes, J. K. Kochi, and P. J. Krusic, *ibid.*, **92**, 1434 (1970).

(16) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(17) R. C. Bingham and P. von R. Schleyer, *J. Amer. Chem. Soc.*, in press.

differences in preferred planarity and bond lengths require the use of a model with radical character.

The results of the strain-energy calculations and the relative rates of reaction at bridgehead and secondary positions are compared in Table II.

Table II. Relative Rates of Reaction and Corresponding Change in Strain Energy

	Bridgehead positions		Secondary positions	
Substrate	$k_X/k_{1\text{-Ad}}$	$\Delta\Delta H$,[a] kcal/mol	$k_X/k_{1\text{-Ad}}$	$\Delta\Delta H$,[a] kcal/mol
Bicyclo[2.2.1]heptane		+6.032	0.668	−2.417[b]
Bicyclo[2.2.2]octane	1.112	+0.487	1.919	−4.042
Bicyclo[3.2.1]octane				−4.683[b]
Bicyclo[3.3.1]nonane	15.976	−3.696		−4.022[b]
Adamantane	1.000	0	0.049	−1.139
Homoadamantane	40.306	−4.367[c]		

[a] $\Delta\Delta H = \Delta H_{\text{substrate}} - \Delta H_{1\text{-adamantane}}$ where $\Delta H = H_{\text{tss}} - H_{\text{gss}}$, where tss is transition-state strain and gss is ground-state strain. [b] Position 2. [c] Position 3.

Correlation of Kinetic Data with Strain Energies. The changes in strain energy, $\Delta\Delta H$, were calculated relative to adamantane as essentially strain free due to its "ideal" ground-state geometry, *i.e.*, tetrahedral bond angles, normal bond lengths, and no unfavorable torsional interactions. The value of 1.66 kcal/mol "total strain" was originally calculated by the computer analysis.[11] Recently, Schleyer and coworkers[18] have reported that current thermochemical data indicate that adamantane has 6.48 kcal/mol of strain and have modified certain of their parameters accordingly. The new findings do not, however, invalidate the calculated strain energy data in Table II. The strain energy of each of the compounds was calculated on the same basis as adamantane and the relative differences should be small.

The 3 (bridgehead) position of homoadamantane reacted some 40 times faster than adamantane. The driving force is a relative relief of approximately 4.3 kcal/mol of strain. In the ground state, homoadamantane is distorted from the "strain free" adamantane structure by the ethylene bridge. While C–C–C angles in ground-state adamantane are approximately tetrahedral, the angles in homoadamantane range from 109.1 to 117.8°.[11] On going to the near-planar free-radical intermediate, angle strain can be appreciably decreased.

The bridgehead position of bicyclo[3.3.1]nonane reacted about 16 times faster than adamantane. Because this system lacks the extra one-carbon bridge found in adamantane the bicyclo[3.3.1]nonane molecule is much more flexible. The bridgehead position can, therefore, more readily adjust its structure to accommodate a planar or near-planar free radical than can adamantane. Indeed, Schleyer and coworkers[19] have brominated the bridgehead position of bicyclo[3.3.1]nonane at room temperature by stirring the hydrocarbon in bromine. Since this reaction presumably goes by way of a carbonium ion intermediate which demands a planar conformation the free-radical reactivity at this position is not surprising.

Bicyclo[3.2.1]octane affords no utilizable kinetic data. The four products which arose from the reaction of bromotrichloromethane and this hydrocarbon could not be separated for identification.

The bridgehead position of bicyclo[2.2.2]octane reacted at about the same rate as adamantane. This was not unexpected since the change in angle strain on going to the intermediates is nearly identical for both molecules. Both adamantane and bicyclo[2.2.2]octane have equivalent geometries around the bridgehead positions in the ground state with angles of 109.5 and 109.0° respectively, and bond lengths of 1.537 and 1.540 Å, respectively.[11]

A comparison of these results with carbonium ion data of Gleicher and Schleyer[11] for the bicyclo[2.2.2]-octyl system is in order. Gleicher and Schleyer commented on a 5000-fold rate difference between the solvolyses of the bridgehead adamantyl and bicyclo[2.2.2]-octyl bromides. They felt that a large portion of this was caused by an increase in strain due to the C_1–C_4 nonbonded interaction for the bicyclo[2.2.2]octyl system. An important distinction involving the corresponding radicals concerns the decreased importance of this factor. It is known that out-of-plane bending force constants are small for free radicals.[20,21] It is also reasonable to suppose that these force constants for carbonium ions are much larger since the neighboring bonding electrons should be strongly attracted to a cationic center.[11,17,22] The free-radical species should, therefore, be able to easily lessen this interaction. For the bicyclo[2.2.2]octane system there is calculated only a small strain energy change of +0.487 kcal/mol relative to adamantane. This is directly attributable to an increase in nonbonded repulsion between C_1 and C_4 as the bridgehead "flattens out" on going to the free-radical intermediate. For the corresponding carbonium ions the relative strain energy difference is +2.671 kcal/mol as caused by this nonbonded repulsion.

The secondary position of bicyclo[2.2.2]octane reacted about twice as fast as did bridgehead adamantane. Though a secondary position should be electronically less favorable than a tertiary position for supporting a free radical, a loss of approximately 4 kcal/mol of strain makes for a facile reaction at the 2 position. The bulk of the change in strain on going from ground state to the planar intermediate is due to the relief of eclipsing interactions between hydrogens on C_2 and C_3. Though one unfavorable torsional interaction between hydrogens on C_1 and C_2 is formed, the net change is favorable.

A similar situation holds for reaction at the 2 position of bicyclo[2.2.1]heptane. However, a C_1–C_2–C_3 bond angle of 102.9° in norborane (compared to 109.9° for the bicyclo[2.2.2]octane) would mitigate against a facile formation of a trigonal center at this site. A relative rate of 0.668, some three times slower than the 2 position of bicyclo[2.2.2]octane, bears this out.

No reaction at the bridgehead site of norbornane was detected in accordance with the observation of Koo-

---

(18) P. von R. Schleyer, J. E. Williams, and K. B. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(19) P. von R. Schleyer, P. R. Isele, and R. C. Bingham, *J. Org. Chem.*, **33**, 1239 (1968).

(20) F. D. Greene and N. N. Lowry, *ibid.*, **32**, 875 (1967).

(21) P. T. Lansbury and J. D. Sidler, *Chem. Commun.*, 373 (1965).

(22) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968).

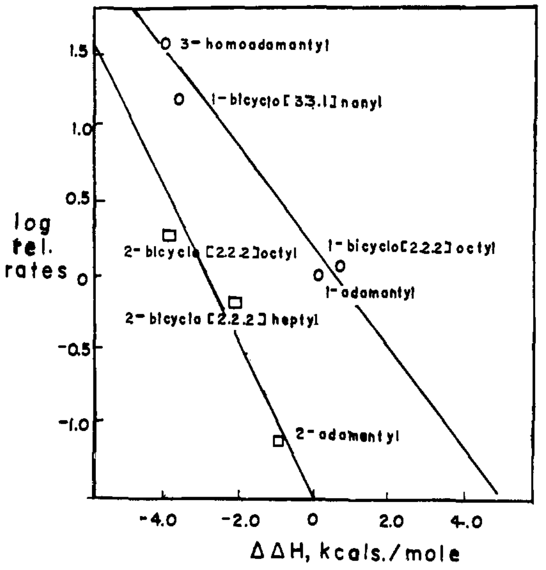

Figure 2. Correlation of relative rates of secondary sites with changes in strain energy; correlation of relative rates of bridgehead sites with changes in strain energy.

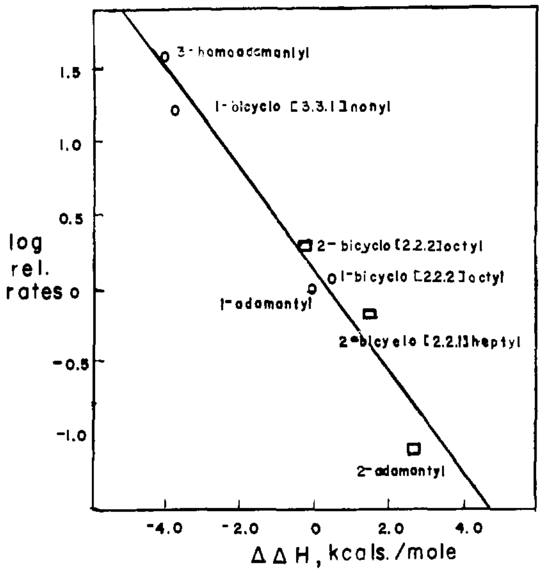

Figure 3. Correlation of relative rates of secondary and bridgehead sites with changes in strain energy.

yman and Vegter.[23] This is in keeping with calculated strain energy data which indicate an increase of 6.032 kcal/mol on going to a bridgehead free-radical intermediate.

Finally, the secondary position of adamantane reacted about 20 times slower than did the bridgehead site. Not only is an electronic factor operative, but, two unfavorable torsional interactions come into play. The hydrocarbon allows a staggered conformation between all methylene and bridgehead hydrogens. In the planar intermediate, the hydrogen at the radical site is eclipsed with those at the two adjacent bridgehead positions.

Figure 2 presents the logs of the relative rates of reaction plotted against the calculated changes in strain energy in a dual correlation. Correlations were determined using the least-squares method. The slope for the bridgehead points is −0.327 with a correlation coefficient of 0.989. The slope for the secondary points is −0.537 with a correlation coefficient of 0.953. An iterative least-squares calculation was undertaken to "fit" all of the points within a single correlation. It was determined that the secondary points could be best accommodated in a single correlation if each secondary point was adjusted by 3.70 kcal/mol. The results of this calculation are shown in Figure 3. A slope of −0.362 with a correlation coefficient of 0.970 was obtained. The empirical value of 3.70 kcal/mol can be treated as a measure of the difference between secondary and tertiary carbon–hydrogen bond dissociation energies. Hay[24] reports a 5.6-kcal/mol difference in energy between secondary and tertiary carbon–hydrogen homolytic bond dissociation. Vedeneyev and coauthors[25] indicate that the difference between a secondary and tertiary carbon–hydrogen bond strength is 5 ± 2 kcal/mol. It should be mentioned that these values are based on experimental measurements performed on acyclic, unstrained, model compounds. In any case, however, the empirical value of 3.70 kcal/mol appears to be a reasonable measure of energy differences for the bonds in question.

Table III summarizes the slopes and correlation coefficients for the dual correlation, the single correlation, and the bridgehead carbonium correlation using data from Gleicher and Schleyer.[11]

Table III. Correlation of Rates of Formation of Reactive Intermediates from Polycyclic Molecules with Calculated Strain-Energy Differences

System	Slope	Corr coeff
Bridgehead radicals	−0.327	0.989
Secondary radicals	−0.537	0.953
All radicals[a]	−0.362	0.970
Bridgehead carbonium ions[b]	−0.529	0.953

[a] Based upon a bond dissociation energy difference of 3.7 kcal/mol. [b] Reference 11.

When compared to the slope of −0.529 for the bridgehead carbonium ions, the slope of −0.327 for the bridgehead radicals reflects the diminished steric dependence for formation of free-radical intermediates. While carbonium ions demand a planar conformation, a free radical can assume a pyramidal configuration with little expense of energy even though a planar configuration may be preferred. This is most dramatically demonstrated when the relative rates of bridgehead carbonium ion formation are compared to those for the bridgehead free radicals. The carbonium ion rates are spread over six powers of ten—from 4.65 for 3-homoadamantyl to 1.8×10^{-6} for 1-bicyclo[2.2.2]octyl.[11] The rates for the same bridgehead free radicals are spread only over two powers of ten—from 40.306 to 1.112.

Experimental Section

Melting points were taken in sealed capillary tubes. Melting and boiling points were uncorrected. Nmr spectra were taken on Varian A-60 and HA-100 instruments using spectroquality carbon tetrachloride as the solvent and TMS as a reference.

---

(23) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 4, 382 (1958).
(24) J. M. Hay, *J. Chem. Soc. B*, 45 (1970).
(25) V. I. Vedeneyev, L. V. Gurvich, V. N. Kendrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," St. Martins Press, New York, N. Y., 1966, p 56.

Materials. Bromotrichloromethane, chlorobenzene, bromobenzene, *o*-dichlorobenzene, and adamantane were either purified by standard techniques or used as commercially obtained.

Bicyclo[2.2.1]heptane was prepared by hydrogenating bicyclo[2.2.1]hepta-2,5-diene. The hydrocarbon was sublimed at 50° (1 mm) and gave a melting point of 85–86° (lit.[26] 86–87°).

Bicyclo[2.2.2]octane was prepared by hydrogenation of bicyclo[2.2.2]oct-2-ene (Columbia Organic Chemical Co.) according to the procedure of Grob and coworkers.[27] Sublimation at 50° (1 mm) gave the hydrocarbon, mp 169–170° (lit.[28] 171–173°). The nmr spectrum corresponded to that reported in the literature.[28]

Bicyclo[3.2.1]octane and bicyclo[3.3.1]nonane were prepared by the same route. 2-*N*-Morpholinobicyclo[3.2.1]octan-8-one and 2-*N*-morpholinobicyclo[3.3.1]nonan-9-one were prepared by the method of Foote and Woodward.[29] The bicyclo[3.2.1]octyl amino ketone (55%) had bp 110–130° (0.3 mm) [lit.[29] 127–140° (0.2 mm)], and the bicyclo[3.3.1]nonyl amino ketone (57%) had bp 130–147° (0.3 mm) [lit.[29] 141–147° (1 mm)]. The amino ketones were reduced *via* a Wolff–Kischner reduction[30] giving 32%, bp 80–110° (0.3 mm) and 50%, bp 90–120° (0.3 mm) [lit.[31] 158–160° (15 mm)], yields, respectively. The morpholino functions were eliminated according to the procedure of Hartmann[31] yielding bicyclo[3.2.1]octan-2-one (54%), mp 122–124° (lit.[32] 123.0–126.5°), and bicyclo[3.3.1]nonan-2-one (56%), mp 134–137° (lit.[31] 135–137°). The ketones were converted to the hydrocarbons by way of another Wolff–Kischner reduction and were purified by sublimation at 55° (1 mm); bicyclo[3.2.1]octane (50%), mp 132–134° (lit.[33] 136–137.5°), and bicyclo[3.3.1]nonane (80%), mp 143–145° (lit.[34] 145–146°). The nmr of bicyclo[3.2.1]octane gave sharp absorptions at δ 1.42, 1.51, and a broad band at 2.13. The nmr spectrum of bicyclo[3.3.1]nonane was identical with the one reported by Schleyer and coworkers.[19]

Homoadamantane was prepared as follows: 1-adamantylcarboxylic acid (Aldrich) was reduced with lithium aluminum hydride in ether by the procedure of Nordlander and coworkers.[35] The resulting 1-adamantylcarbinol (80%), mp 115–116° (lit.[36] 115°) was converted to 1-adamantylcarbinyl tosylate as in the procedure of Stetter and coworkers.[36] The tosylate (90%), mp 76–77° (lit.[36] 76–78°), was converted to 3-homoadamantol by the procedure of Nordlander and coworkers.[35] 3-Homoadamantol (90%), mp 275–276° (lit.[35] 274–275.5°), was brominated with phosphorus tribromide according to the procedure of Stetter and Goebel[37] yielding 75% 3-homoadamantyl bromide, mp 124–125° (lit.[37] 124.5–125.5°). The 3-homoadamantyl bromide was converted to the hydrocarbon by the procedure of Stetter and Goebel[37] yielding 70% homoadamantane. Recrystallization from acetic acid gave white crystals, mp 262–263° (lit.[37] 258–259°). The nmr spectrum showed a multiplet between δ 2.40 and 1.10 (lit.[38] 2.4–1.0). Major absorptions were at δ 1.85, 1.74, 1.47, and 1.35.

All of the polycyclic aliphatic hydrocarbons had purities in excess of 99%.

Product Studies. Solutions of substrate, bromotrichloromethane, and chlorobenzene as an internal standard were prepared in the approximate molar rates of 2:20:1. Approximately 0.75 ml of the solution was placed in each of several KIMAX ampoules. The ampoules were sealed under a reduced pressure of nitrogen and one was reserved for analysis of unreacted starting materials. The remainder was allowed to react at 40 ± 0.5° for from 4 to 28 hr. Analysis of the mixtures was carried out *via* gas–liquid chromatography. In all cases the bridgehead bromides were observed to elute prior to the secondary bromides. Dibromides had a much longer retention time than either bridgehead or secondary bromides. In most cases only one or, at most, two monobrominated products were formed. Identification was carried out by comparison with known compounds prepared *via* standard synthetic means.

Reaction of Bromotrichloromethane with Homoadamantane. A solution of homoadamantane, bromotrichloromethane, and chlorobenzene as an internal standard was prepared in the approximate molar ratio of 1:30:1. The mixture was allowed to react in a sealed ampoule under a reduced pressure of nitrogen for 4 hr. Glc analysis showed three products were formed. The major product (73.5 ± 2%) eluted first and had the same retention time as 3-bromohomoadamantane. The other two products eluted close together and were collected as a mixture. Nmr analysis showed absorptions between δ 1.2 and 2.5 and at 3.0. A downfield absorption at δ 4.85 indicated secondary bromides.

The nmr spectrum of the glc collected material having the same retention time as 3-bromohomoadamantane was found to be identical with that of adamantyl carbinyl bromide as reported by Fort and Schleyer.[39] It was later shown that 3-bromohomoadamantane rearranged quantitatively to adamantyl carbinyl bromide at 270° on the SE-30 column used in all these studies.

Kinetic Studies. Solutions of adamantane, substrate, bromotrichloromethane, and the internal standard were prepared. Kinetic data were determined by having substrate compete directly for the trichloromethyl radical. In the case of homoadamantane it was necessary to determine the reactivity relative to bicyclo[3.3.1]nonane. The rate constant thereby obtained was converted to the desired form through the expression

$$k_{\mathrm{X}}/k_{1\text{-Ad}} = \left[\frac{k_{\mathrm{X}}}{k_{[3.3.1]}}\right]\left[\frac{k_{[3.3.1]}}{k_{1\text{-Ad}}}\right]$$

The ratios were determined by using established procedures.[8,40]

Acknowledgments. We wish to thank Professor Paul von R. Schleyer of Princeton University for providing us with information prior to publication. Appreciation is also expressed to the Oregon Computer Center for providing the necessary computing time for this project.

---

(26) G. Komppa and S. Beckmann, *Justus Liebigs Ann. Chem.*, **512**, 172 (1936).

(27) C. A. Grob, M. Otah, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(28) D. S. Breslow, E. I. Edwards, R. Leone, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **90**, 7097 (1968).

(29) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(30) A. C. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1959, p 510.

(31) M. Hartmann, *Z. Chem.*, 6, 182 (1966).

(32) K. Alder and E. Windemuth, *Chem. Ber.*, **71**, 2404 (1938).

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

(34) E. Buchta and S. Billenstein, *Justus Liebigs Ann. Chem.*, **692**, 42 (1966).

(35) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, 88, 4475 (1966).

(36) H. Stetter, M. Schwartz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1620 (1959).

(37) H. Stetter and P. Goebel, *ibid.*, 96, 550 (1963).

(38) B. R. Vogt, *Tetrahedron Lett.*, 1579 (1968).

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

(40) E. S. Huyser, *J. Amer. Chem. Soc.*, 82, 394 (1960).