A. Glendinning, D. E. Johnston, and M. A. McKervey, *Tetrahedron Lett.*, 1671 (1971); (c) M. A. McKervey, D. E. Johnston, and J. J. Rooney, *ibid.*, 1547 (1972); (d) D. E. Johnston, M. A. McKervey, and J. J. Rooney, *Chem. Commun.*, **29** (1972), and ref 48 and 49.

(14) (a) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **79**, 3292 (1957); (b) P. v. R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

(15) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

(16) E. B. Whipple and M. Ruta, *J. Amer. Chem. Soc.*, **87**, 3060 (1965).

(17) Confirmed by molecular mechanics calculations. See (a) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972); (b) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *ibid.*, in press.

(18) A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966).

(19) (a) H. Pines, C. T. Chen, and A. W. Shaw, *J. Amer. Chem. Soc.*, **80**, 1930 (1958); (b) H. Pines, F. J. Pavlick, and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

(20) For a general review of Lewis acid catalyzed hydrocarbon reactions, see H. Pines and J. Mavity in B. G. Brooks, *et al.*, Ed., "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold, New York, N. Y., 1955, Chapter 39, pp 9–58.

(21) H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, **75**, 6279 (1953); H. Pines and R. W. Meyerhalz, Jr., *ibid.*, **77**, 5392 (1955).

(22) M. Nomura, P. v. R. Schleyer, and A. A. Arz, *J. Amer. Chem. Soc.*, **89**, 3657 (1967).

(23) M. J. T. Robinson and H. J. F. Tarrat, *Tetrahedron Lett.*, 5 (1968).

(24) H. Koch and J. Franken, *Brennst.-Chem.*, **42**, 90 (1961); *Chem. Abstr.*, **55**, 21059*i* (1961).

(25) Such disproportionation reactions occur frequently in such Lewis acid catalyzed processes.[20] For example, the isomerization of *endo*-tetrahydrodicyclopentadiene to adamantane can give up to 87% disproportionation to *trans*-decalin depending on conditions.[24]

(26) (a) D. Fărcasiu, P. v. R. Schleyer, and D. Ledlie, *J. Org. Chem.*, **38**, 3455 (1973); (b) D. Fărcasiu, unpublished results.

(27) (a) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); also see ref 32; (b) H. D. Scharf, G. Weisgerber, and H. Hover, *Tetrahedron Lett.*, 4227 (1967).

(28) (a) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966); (b) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967); (c) N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 5446 (1972).

(29) C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968).

(30) Z. Majerski and P. v. R. Schleyer, *Tetrahedron Lett.*, 6195 (1968).

(31) *Cf.* J. S. Wishnok, P. v. R. Schleyer, E. Funke, G. D. Pandit, R. O. Williams, and A. Nickon, *J. Org. Chem.*, **38**, 539 (1973).

(32) (a) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966). (b) G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970). (c) The originally proposed[32a] von Baeyer IUPAC name for "Binor-S" is incorrect.[12] See, however, D. von Bimmendylo and A. C. Mackay, *Can. J. Chem.*, **51**, 718 (1973).

(33) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, pp 133–134.

(34) We thank Dr. E. Hagaman and Professor E. Wenkert for the ^{13}C spectra and spectral analyses reported in this paper.

(35) (a) P. v. R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, 2845 (1967); (b) A. Nickon, G. D. Pandit, and R. O. Williams, *ibid.*, 2851 (1967); (c) A. Nickon, H. Kwasnik, T. Schwartz, R. O. Williams, and J. B. Di Giorgio, *J. Amer. Chem. Soc.*, **87**, 1613, 1615 (1967); (d) B. R. Vogt and J. E. Hoover, *Tetrahedron Lett.*, 2841 (1967).

(36) The original colloquial "belt" designation given to the 1, 2, 6, 7, 11, and 12 positions of diamantane[3e,g] is not adjectival. We now prefer "medial," which seems to us to describe these positions better than the recently employed "zonal."[13] We thank Professor C. W. Jefford for this suggestion.

(37) S. H. Liggero, P. v. R. Schleyer, and K. C. Ramey, *Spectrosc. Lett.*, **2**, 197 (1969).

(38) The ^{13}C nmr spectrum was determined by Professor T. M. Grant, University of Utah, private communication.

(39) T. Pehk, E. Lippmaa, V. V. Sevost'janova, M. M. Krayuschkin, and A. I. Tarasova, *Org. Magn. Resonance*, **3**, 783 (1971).

(40) Z. Dolejsek, S. Hála, V. Hanuš, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966).

(41) S. T. Rao, M. Sundaralingam, E. Osawa, E. Wiscott, and P. v. R. Schleyer, *Chem. Commun.*, 861 (1970).

(42) A. G. Yurchenko, F. N. Stepanov, S. S. Isaeva, B. M. Zolotarev, V. I. Kadentsev, and O. S. Chezhov, *Org. Mass Spectrom.*, **3**, 1401 (1970).

(43) I. L. Karle and J. Karle, *J. Amer. Chem. Soc.*, **87**, 919 (1965).

(44) M. Mansson, N. Rapport, and E. F. Westrum, Jr., *J. Amer. Chem. Soc.*, **92**, 7296 (1970).

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

(46) R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys., Chem.*, **75**, 1264 (1971).

(47) S. R. Butler, A. S. Carson, P. G. Laye, and W. V. Steele, *J. Chem. Thermodyn.*, **3**, 277 (1971).

(48) A. S. Carson, P. G. Laye, W. V. Stelle, D. E. Johnston, and M. A. McKervey, *J. Chem. Thermodyn.*, **3**, 915 (1971).

(49) T. Clark, D. E. Johnston, H. Markle, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1042 (1972).

(50) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. W. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

(51) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11**, M-102 (1958); C–C bond length in graphite = 1.4210 ± 0.0001.

Diamantane. II.[1] Preparation of Derivatives of Diamantane

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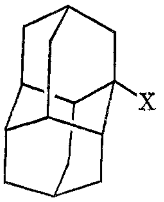
Methods have been developed for the conversion of diamantane (I) to the three possible types of monofunctional derivatives: 1- (medial), 3- (secondary), and 4- (apical). The 1-diamantyl cation is the most stable and most readily generated by hydride abstraction. Kinetically controlled nucleophilic attack on this cation can be made to give 1-bromodiamantane (III) and 1-diamantanecarboxylic acid (V) in liquid bromine and under Koch–Haaf conditions, respectively. Sulfuric acid oxidation of I affords 3-diamantanone (X), a convenient source of other 3-diamantyl derivatives. The secondary 3-diamantyl tosylate (XII) solvolyzes about 3.5 times faster than 2-adamantyl tosylate. Under equilibrium conditions apical adamantyl derivatives are favored by enthalpy over their medial isomers, but the entropy effect is opposite. The enthalpy term for relatively large groups such as methyl dominates. Thus, 4-methyldiamantane (XXIII) can be synthesized by isomerization of the other methyldiamantanes or of other pentacyclotetradecanes, such as XXII, XXV, or XXVI. The equilibrium is less one-sided for smaller substituents, *e.g.*, halide and alcohols, and preparations of apical products require chromatographic separation since they are seriously contaminated by their medial isomers. ^{1}H nmr chemical shifts of the various types of diamantane derivatives can be predicted satisfactorily by using additivity increments obtained from similarly constituted adamantanes.

The preparation of functional derivatives of diamantane (I) depended on the availability of the parent hydrocarbon.[1a] When the yield of I was improved to 10% by employing the exo-trans-exo norbornene dimer as precursor and aluminum bromide sludge catalyst,[3] the study of the chemistry of diamantane began.[3-5] The reactions employed were modeled after those which had been used successfully on the first member of the diamondoid series, adamantane (II).[6]

Bromination of diamantane by neat bromine led to bridgehead substitution, but, unlike adamantane, two isomers, medial[7] (1-) and apical[7] (4-), were possible. Nmr

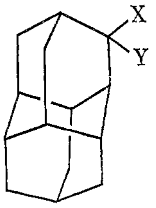
Table I
1-Substituted (Medial) Diamantanes



Compd	X	Starting material	Method	Ref	Diamantane registry no.
III	Br	X = H	Br_2 or *t*-BuBr–$AlBr_3$	1b, 12, 13b	30545-17-6
IV	Cl	X = H	CH_3COCl–$AlCl_3$ $ClSO_2Cl$–$AlCl_3$	13	32401-16-4
V	CO_2H	X = H	Koch–Haaf	9, *a*	30545-18-7
VI	OH	X = Br	Hydrolysis	1b, 9, *a*	30545-19-8
VII	CH_3	X = Br	CH_3MgBr	*b*	26460-76-4
VIII	$NHCOCH_3$	X = Br	CH_3CN–H_2SO_4 (Ritter)	9, *a*	30545-21-2
IX	$NH_3{}^+Cl^-$	X = $NHCOCH_3$	Hydrolysis	9, *a*	30545-22-3

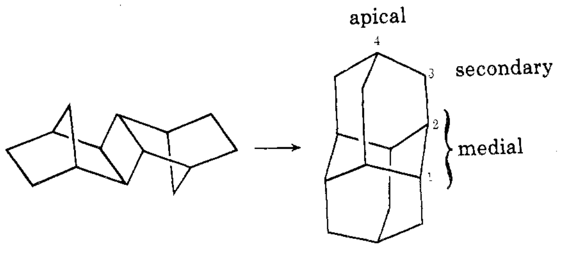
[a] This work. [b] E. Osawa, Z. Majerski, and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 205 (1971).

Table II
3-Substituted (Secondary) Diamantanes

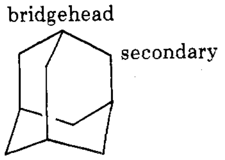


Compd	X	Y	Starting material	Method	Ref	Diamantane registry no.
X	=O		X, Y = H	H_2SO_4	9, 13, *a*	30545-23-4
XI	OH	H	X, Y = O	$LiAlH_4$	9, *a*	30545-24-5
XII	OTs	H	X = OH; Y = H	*p*-$C_7H_7SO_2Cl$	9, *a*	30651-00-4
XIII	Br	H	X = OH; Y = H	PBr_5	9, *a*	30545-25-6
XIV	Cl	H	X = OH, Y = H	$SOCl_2$	9, *a*	30651-01-5
XV	CH_3	OH	X, Y = O	CH_3MgBr	9, *a*	30545-26-7
XVI	=CH_2		X = CH_3; Y = OH	H_3PO_4	9, *a*	30545-27-8
XVII	CH_3	H	X, Y = CH_2	H_2/PtO_2	9, *a*	30545-28-9

[a] This work.



I



II

spectroscopy revealed that the product was 1-bromodiamantane (III, Table I) and this provided a synthetic entry to other medial derivatives.[3–5,6e,g]

Likewise, the discovery by Geluk and Schlatmann[8] of a convenient oxidation procedure for forming 2-adamantanone from II prompted the application of this reaction to diamantane. The 3-diamantanone (X, Table II) obtained by the action of sulfuric acid was readily converted to other 3-substituted derivatives.[6e,9]

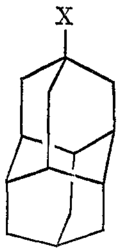
Functionalization of the 4 position (apical) was less straightforward, although 4-methyl- and 4,9-dimethyldiamantane (XXIII, Table III, and XXVII, respectively) had been prepared by rearrangement of C_{15} and C_{16} pentacyclic precursors.[6e,g,9–11] 4-Bromodiamantane (XVIII) was first synthesized as a component of a complex bromination mixture and by partial reduction of the 4,9-dibromide XXVIII.[1b,6e,12] McKervey, who independently studied the preparation and functionalization of diamantane,[13] found that 4 derivatives can be obtained more easily by equilibration, although mixtures of products result.[14] Preferential attack of the less hindered apical bridgehead has been achieved,[15] and recent improvement of this approach provides an even better entry to apical diamantanes.[16]

This paper describes the preparation and physical and nmr spectroscopic properties of the three different kinds of diamantane derivatives. A full discussion of the bromination and polybromination of diamantane is presented in the following paper.[1b]

Results and Discussion

Tables I–III summarize all of the monosubstituted diamantanes which have been prepared to date. Interchange of functional groups was generally accomplished by standard methods not requiring detailed comment. The principles involved in the direct functionalization of diamantane

Table III
4-Substituted (Apical) Diamantanes

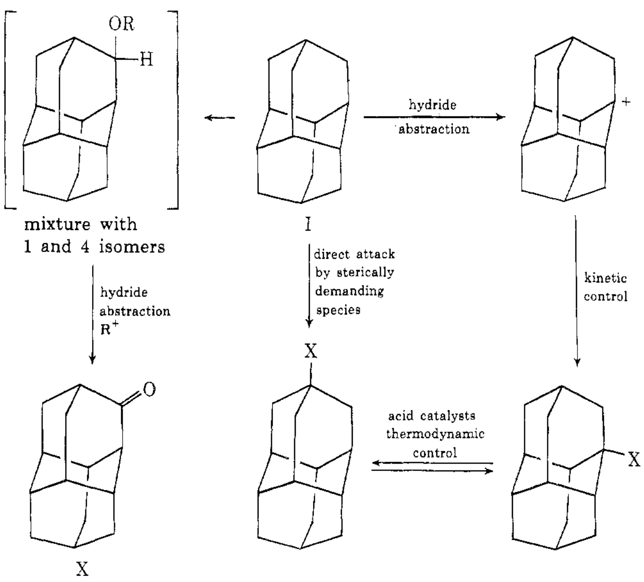


Compd	X	Starting material	Method	Ref	Diamantane registry no.
XVIII	Br	X = H	*t*-BuBr–AlBr$_3$ or Br$_2$–AlBr$_3$ or	1b	30545-30-3
		1-Bromodiamantane (III)	equilibration	12	
XIX	Cl	X = H	CH$_3$COCl–AlCl$_3$	13	32401-17-5
XX	OH	X = Br	Hydrolysis	1b, 9	30651-03-7
XXI	CO$_2$H	X = Br	Koch–Haaf	9, *a*	30651-04-8
XXIII	CH$_3$	XXII XXV	Rearrangement, AlBr$_3$ or sludge catalyst[b]	1a, 9, *a*	28375-86-2

[a] This work. [b] Prepared from *tert*-butyl bromide-aluminum bromide; *cf.* ref 1a and 3.

at the three types of positions are of greater interest and are summarized in Chart I.

Chart I



Medial Substitution. The 1 position was functionalized directly either by bromination at room temperature to form III,[12] or by the Koch-Haaf[9] reaction to give carboxylic acid V. Both these reactions depended on the greater ease of formation and greater stability of the 1-diamantyl cation over the 4 and 3 cations;[1b] the products are derived by kinetic control.

Secondary Substitution. Sulfuric acid oxidation of diamondoid hydrocarbons such as I and II involves generation of carbocations and the equilibration of alcohols or their sulfate esters.[8] Secondary alcohols, even though less stable than tertiary, can be further oxidized to ketone by hydride abstractions, and this explains the unique course of such reactions.[8] In actual fact, diamantane (I) was converted to 3-diamantanone (X) in 61% yield by 97% H_2SO_4.[9]

3-Diamantanone (X) may also be prepared by rearrangement. Treatment of Binor-S (XXIX) with concentrated sulfuric acid gave a 15% yield of X, along with some diamantane. Similar results have been obtained by McKervey from rearrangement of tetrahydro-Binor-S (XXX) in sulfuric acid.[13]

Acetolysis of 3-diamantyl tosylate (XII) gave the following rate constants and activation parameters: $k_{100°} = 3.52 \pm 0.00 \times 10^{-4}$ sec^{-1}, $k_{75.0°} = 2.20 \pm 0.08 \times 10^{-5}$ sec^{-1}, $\Delta H^* = 27.9$ kcal/mol, $\Delta S^* = 0.0$ eu. The calculated rate constant at 25°, 2.17×10^{-8} sec^{-1}, is 3.6 times faster than that observed for 2-adamantyl tosylate acetolysis at the same temperature.[17] Δ strain calculations[18] on the 2-adamantyl and the 3-diamantyl cations give essentially the same results suggesting that the origin of the enhanced 3-diamantyl rate is electronic rather than steric in origin; the γ branching afforded by the attached adamantane unit evidently is responsible.

Apical Substitution. 4-Substituted diamantanes, because of their equatorial character, have lower enthalpies than their 3 or 1 isomers.[13b,14] The degree of branching favors substitution at either bridgehead over the secondary position. While entropy disfavors apical substitution due to higher symmetry, this factor should be less important than enthalpy in magnitude unless the substituents are small. The symmetry contribution to the $T\Delta S$ term at 25° is 0.65 kcal/mol favoring apical to medial and 1.06 kcal/mol for apical to secondary isomerization. Thus, thermodynamically controlled reactions should generally favor apical substitution.

The first realization of this expectation was achieved not by direct substitution, but by isomerization of pentacyclopentadecanes and pentacyclohexadecanes. Rearrangement of *exo*-tetrahydrotricyclopentadiene (XXII) with aluminum bromide "sludge" catalyst gave a complex mixture from which 4-methyldiamantane (XXIII) was isolated in 3% yield. The other isomers, 1-methyldiamantane (VII) and 3-methyldiamantane (XVII), being of lower thermodynamic stability, were not detected in this reaction. The order of thermodynamic stability of the methyldiamantanes has been determined by empirical force field calculations[18,19] and by experiment;[14b] these results indicate that the equilibrium composition should consist of 93–98% apical (XXIII), 1.3–4.7% medial (VII), and 0.7–2.4% secondary (XVII) methyldiamantanes at 25°. Both homodiamantane isomers XXVIa and XXVIb are expected to be of considerably lower thermodynamic stability than the three methyldiamantanes, and were not observed in any of the above experiments. XXVIa, independently synthesized with aluminum bromide in refluxing cyclohexane, gave a mixture of the three methyldiamantanes, with the 4 isomer (XXIII) comprising >95% of the product mixture (Chart II).[15]

NMR of Substituted Diamantanes. In the following paper of this series[1b] we show that the ^1H-nmr spectra of diamantyl mono- and polybromides may be calculated by assuming additivity using a set of substituent parameters derived from 1- and 2-substituted adamantanes. To a first approximation, good correlation is observed, but even better agreement was obtained by using "refined" additivity increments derived from 220 MHz nmr spectra of 4- and 1-diamantane bromides.

We report here the calculation and observed nmr spectra of some 4-, 3-, and 1-substituted diamantanes, and compare shift parameters obtained from 1- and 2-adamantanes to those derived from observed spectra. Tables VI, VII, and VIII summarize the data.

4-Substituted Diamantanes. The spectra of four 4-diamantanes studied (Table VI), were relatively simple with absorptions in the δ 1.41 to 2.3 region and were predictable reasonably well using the adamantane chemical shift increments. The five types of protons give overlapping peaks; in all cases, δ, ε, and ζ proton chemical shifts vary only by 0.07 ppm, are not separable by 60 MHz nmr, and are least affected by substituents. β and γ proton chemical shifts may be shielded or deshielded and range over 0.89 and 0.20 ppm, respectively, with changes in substituents; sometimes the signals are resolved (Br, OH, CH_3) and sometimes not (COOH). The range of chemical shifts is comparable to those reported for 1-adamantanes[24] which give variations in β protons of 0.82 ppm, γ of 0.16 ppm, and δ of 0.10 ppm.

Of the four substituents, bromine exhibits the largest chemical shift differences with the β protons being most deshielded. The hydroxy group deshields the γ protons most and has only a slight effect on the others. The carboxylic acid group deshields both β and γ protons to a similar extent, while the methyl group shields the β protons (-0.27 ppm) and has relatively little effect on the other protons which appear as a singlet.

TABLE VI

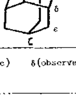
CHEMICAL SHIFTS IN 4-SUBSTITUTED DIAMANTANES[a] (δ) (cont.)

Substituent X	Proton Type	Area	δ(calc)	δ(observed)	Area	Shift from[b] Diamantane (ppm)	Increments[c] used for calculation
	δ,ε,ζ	10	1.64	1.78(s)	10	+0.10	-0.04
COOH	γ	3	1.83	1.90(s)	9	+0.22	+0.15
	β	6	1.84				+0.16
	COO<u>H</u>	1		8.96(b)	1		
	C<u>H</u>$_3$	3	0.79[e]	0.80(s)	3		
CH$_3$	β	6	1.38	1.41(d,J ≅ 3cps)	6	-0.27	-0.30
	δ,ε,ζ	10	1.58		13		-0.10
	γ	3	1.72	1.70(s)		+0.02	+0.04

[a] In $CDCl_3$ solution with TMS internal standard. [b] Positive value indicates a downfield shift and negative value an upfield shift from the diamantane resonance at δ 1.68. [c] Substituent shifts for corresponding adamantane derivatives, cf. ref 24. [d] CCl_4 solution. [e] Value for 1-adamantane derivative.

TABLE VI

CHEMICAL SHIFTS IN 4-SUBSTITUTED DIAMANTANES[a] (δ)



Substituent X	Proton Type	Area	δ(calc)	δ(observed)	Area	Shift from[b] Diamantane (ppm)	Increments[c] used for calculation
	δ,ε,ζ	10	1.63	1.73 (s)	13	+0.05	-0.05
Br[d]	γ	3	1.88	1.80 (m)		+0.12	+0.20
	β	6	2.20	2.30 (d,J≅1.5Hz)	6	+0.62	+0.52
	O<u>H</u>	1	1.3-2.0[e]				
OH	δ,ε,ζ	10	1.54	1.65(s)	17	-0.03	-0.14
	β	6	1.59	1.72(d)		+0.04	-0.09
	γ	3	1.92	1.9 (b)	3	+0.22	+0.24

TABLE VII. CHEMICAL SHIFTS IN 3-SUBSTITUTED DIAMANTANES[a] (δ)

Substituents X	Y	Proton Type	Area	δ (calcd)	δ (observed)	Area	Shift from Diamantane[b]	Increments used for calculation[b,c]
		e	1	1.55				-0.13
		i,j,m,n,o,p,q,r	8	1.63	1.72(s)	14	+0.04	-0.05
		k, l	2	1.70				+0.02
Br	H	f,g,h	3	1.84				+0.16
		a,b	2	1.96	1.95(m)	2	+0.27	+0.28
		c,d	2	2.26	2.32(AB)	2	+0.64	+0.58
		Y	1	4.58[d]	4.48(b)	1		
		e	1	1.50				-0.18
		k,l,m,n	4	1.69				+0.01
					1.75(s)	14	+0.07	
		i,j,o,p,q,r	6	1.73				+0.05
Cl	H	f,g,h	3	1.79				+0.11
		a,b	2	1.88	1.90(br)	2	+0.22	+0.20
Cl	H	c,d	2	2.20	2.25(br)	2	+0.57	+0.52
		Y	1	4.29[d]	4.25(br-s)	1		

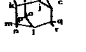


TABLE VII

CHEMICAL SHIFTS IN 3-SUBSTITUTED DIAMANTANES[a] (δ) (cont.)

Substituents X	Y	Proton Type	Area	δ (calc)	δ (observed)	Area	Shift from Diamantane[b]	Increments used for Calculation[b,c]
		e	1	1.46			-0.26	-0.22
		h	1	1.62	1.42	16		-0.06
		a,b	2	1.72	1.73		+0.05	+0.04
		i,j,m,n,o,p,q,r	8	1.73				+0.05
OH	H	f,g	2	1.75				+0.07
		k,l	2	1.78			+0.27	+0.10
		c,d	2	1.99	1.95	2		+0.31
		Y	1	3.75[d]	3.75 (b,s)	1		
		O<u>H</u>	1		1.58(s)	1		
=O		c-r	16	1.90	1.88(t)	16	+0.20	+0.22
		a,b	2	2.31	2.45(br,s)	2	+0.77	+0.65
		c-r	16	1.78	1.78(s)	16	+0.10	+0.10
=CH$_2$		a,b	2	2.28	2.30(br, s)	2	+0.62	+0.60
		-CH$_2$	2	4.38	4.42(s)	2		+2.70

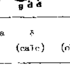
TABLE VII

CHEMICAL SHIFTS IN 3-SUBSTITUTED DIAMANTANES[a] (δ) (cont.)

Substituents X	Y	Proton Type	Area	δ (calc)	δ (observed)	Area	Shift from Diamantane[b]	Increments used for Calculation[b,c]
		C<u>H</u>$_3$	3	1.05[d]	1.0(d,J≅8Hz)	3		
		Y a,b	2	1.40[e]				
CH$_3$	H	c,d	2	1.95[e]	1.52(b)	19	-0.16	
		All others	15	1.6-1.8[f]	1.68(s)		~0	
		C<u>H</u>$_3$	3	1.3[d]	1.3(s)	4		
		O<u>H</u>	1	1.22[d]				
CH$_3$	OH		1	1.45[d]	1.5(s)			
		Others	16	1.78	1.7(b)	16	+0.02	
		e,f	2	2.22[d,g]	2.2(b)	2	+0.52	

[a] In CCl_4 solution with internal TMS. [b] Positive value indicates a downfield shift and a negative value an upfield shift from diamantane resonance of δ 1.68. [c] Substituent shifts for corresponding 2-adamantane derivatives, cf. ref 25. [d] Value for 2-adamantane derivative. [e] Calculated from 220 MHz nmr spectrum of 2,2-dimethyl adamantane. [f] Value extrapolated from 2-methyl adamantane. [g] Assignment tentative since decoupling experiments were not performed. The effect of an axial methyl on a γ-equatorial proton has not been determined.

TABLE VIII. CHEMICAL SHIFTS IN 1-SUBSTITUTED DIAMANTANES[a] (δ)



Substituent X	Proton Type	Area	δ (calc)	δ (observed)	Area	Shift from[b] Diamantane	Increments used for Calculation[c]
	d	2	1.55	1.40(AB-J≅12)	10	-0.28	-0.15
	e,g,δ	6	1.63	1.60(br-s)		-0.08	-0.05
	f	2	1.70				+0.02
Br[d]	γ(b)	3	1.88[e]	1.90(br-s)	5	+0.22	+0.20
	a	2	1.96				+0.28
	β	2	2.20	2.20(d)	4	+0.52	+0.52
	c	2	2.26	2.30(AB,J≅12)		+0.62	+0.58
	d	2	1.46	1.32(br)		-0.36	-0.22
	δ	4	1.54				-0.14
	β	2	1.59		14		-0.09
	a	2	1.72	1.68(br-s)		0	+0.04
OH	e,g	2	1.73				+0.05
	f	2	1.78			+0.32	+0.10

TABLE VIII

CHEMICAL SHIFTS IN 1-SUBSTITUTED DIAMANTANES[a] (δ) (cont.)

Substituent X	Proton Type	Area	δ (calc)	δ (observed)	Area	Shift from[b] Diamantane	Increments used for calculation[c]
	γ,b	5	1.92	2.0(br)	5		+0.24
OH	c	2	1.99	2.25(AB-J≅12)		+0.57	+0.31
	O<u>H</u>	1		1.50(s)	1		
	d	2	1.42	1.48		-0.20	-0.26
	δ	4	1.64	1.78(m)	17	+0.10	-0.04
	e,f,g	4	~1.68				~0
COOH	γ (b)	3	1.83				+0.15
	β	2	1.84				+0.16
	a	2	~1.90				+0.22
	c	2	2.30	2.15(br)	2	+0.47	+0.62
	COO<u>H</u>	1		10.41	1		

TABLE VIII

CHEMICAL SHIFTS IN 1-SUBSTITUTED DIAMANTANES[a] (δ) (cont.)

Substituent X	Proton Type	Area	δ (calcd)	δ (observed)	Area	Shift from[b] Diamantane	Increments used for calculation[c]
	C<u>H</u>$_3$	3	1.05[g]	0.93 (s)	3		
	β	2	1.38	1.42(d,J≅2.5)	6	-0.26	-0.30
	a	2	1.40				-0.28
	f	2	1.52				-0.16
CH$_3$[f]	d	2	~1.40-1.50	1.68(d,J≅2.5)	9	~0	-0.10
	δ	4	1.58				+0.04
	γ (b)[e]	3	1.72				+0.12
	e, g	2	1.80	2.0 (d)	2	+0.32	
	c	2	1.95	2.2 (AB-J≅12)	2	+0.52	+0.27

[a] In $CDCl_3$ solution with TMS internal standard. [b] A positive value indicates a downfield shift and a negative value an upfield shift from the diamantane resonance of δ 1.68. [c] Substituent shifts for corresponding 1- and 2-adamantane derivatives, cf. refs 24 and 25. [d] CCl_4 solution. [e] If assumed to be a γ position as in 1-adamantane; but if calculated as a δ position in 2-adamantane, the calculated value is δ 1.84. [f] Calculated values from 1-methyladamantane for β, γ, δ protons; other values derived from 60 nmr spectrum of 2-methyladamantane and the 220 MHz nmr spectrum of 2,2-dimethyladamantane. [g] Value for 2-methyladamantane.

3-Substituted Diamantanes. The spectra of the 3-substituted diamantanes listed in Table VII are less complex than expected, with maxima falling between δ 1.30-2.5. The most intense resonance appears as a singlet between δ 1.68-1.88. The calculated shifts in Table VII are based on 2-adamantyl substituent additivity increments.[25] Electronegative substituents facilitate identification since larger variations in chemical shifts are observed. β-Bridgehead protons are deshielded for Br and Cl, but are shielded for OH and methyl. AB quartets resulting from the 1,3-diaxial relationship between the substituent and the methylene proton, d, are observed for Br, Cl, and OH, but are not very intense. This could be due to an interference by proton c which is also axially oriented and is deshielded to about the same extent.

Musher and Segre[26] have determined that an axial methyl is deshielded with respect to an equatorial methyl by 0.14 ppm. Thus, the axial methyl resonance in 3-methyldiamantane at δ 1.0 is deshielded relative to that of 4-methyl diamantane (δ 0.80).

3-Diamantanone and 3-methylenediamantane display essentially two-line spectra; the downfield absorptions are due to the vicinal bridgehead protons. Yurchenko and Isaev[27] found that the deshielding in 2-adamantanone, in the presence of europium shift reagent, decreases with distance from the substituent. This suggests that deshielding of protons in a 1,3 diaxial arrangement for Br, Cl, OH and CH_3 may be a result of a through space[28] and not a through bond inductive interaction.[29]

1-Substituted Diamantanes. The spectra of 1-substituted diamantanes are most complex and display characteristics of both the bridgehead and secondary adamantane derivatives. For the substituents studied (Table VIII), absorptions were observed in the δ 1.32 to 2.3 region, the lowest absorptions being due to 1,3 diaxial substituent-proton interactions, irrespective of the electronegativity of the substituent (e.g., Br and CH_3). A strong resonance in the diamantane absorption region (δ 1.60-1.78), was usually observed; theother resonances were either deshielded (Br, OH, COOH) or shielded (CH_3). In general, 1,3 diaxial interactions are enhanced in 1-diamantanes compared to 3-diamantanes and 2-adamantanes, as seen in greater deshielding of the γ protons. This may reflect the closer proximity to the axial substituent in the 1-position. Surprisingly, the axial methyl resonance in 1-methyldiamantane occurs at δ 0.93 and is therefore deshielded with respect to 4-methyldiamantane (δ 0.80, CH_3 equatorial), but shielded relative to 3-methyldiamantane (δ 1.0 CH_3 axial).

Experimental Section

General. Microanalyses were performed by Robertson Laboratories, Florham Park, N.J., and by Hoffmann-La Roche, Inc., Nutley, N.J. Infrared spectra were determined on a Perkin-Elmer 237-B spectrophotometer. Nmr spectra were taken on a Varian Model A-60A Spectrometer using tetramethyl silane as internal standard. Gas chromatographic analyses were performed on either a Varian Aerograph 90-P instrument or a Perkin-Elmer 810 flame ionization gas chromatograph, with columns as reported in individual preparations.

1-Bromodiamantane (III). The preparation from diamantane by treatment with bromine at room temperature for two hours has been published in preliminary form.[12] A detailed account will be given in the following paper.[1b]

1-Methyldiamantane (VII) The preparation from 1-bromodiamantane by a Grignard coupling reaction has been described by Osawa, Majerski and Schleyer.[30]

4-Bromodiamantane (XVIII). The preparation from diamantane by reaction with bromine-aluminum bromide has been published in preliminary form.[12] The preparation from diamantane with t-butyl bromide-aluminum bromide will be described in a following paper.[1b]

1-Diamantane Carboxylic Acid (V) [Koch-Haaf Reaction[22,31]]. A flask equipped with stirrer, thermometer, dropping funnel, and gas outlet tube was charged with 130 ml of 97.2% sulfuric acid, 50 ml of carbon tetrachloride, and 9.4 g (0.050 mole) of diamantane. The mixture was cooled to 17-19° and 0.5 ml of 98-100% formic acid was added. Then a solution of 19 ml of t-butyl alcohol in 28 g of 98-100% formic acid was added dropwise (about 2 hrs). The reaction mixture was stirred for an additional 30 minutes and then poured onto 330 g of crushed ice. The layers were separated, and the upper acid layer was extracted with three 100 ml portions of CCl_4. The combined CCl_4 layers were shaken with 55 ml of 15 N ammonium hydroxide, and the precipitated ammonium diamantane carboxylate was collected and washed with 20 ml of cold acetone and suspended in about 100 ml of water. The suspension was made strongly acid with concentrated HCl and extracted with chloroform. The organic layer was separated, dried over $MgSO_4$, and evaporated. The residue (3.70 g, 0.0123 mole) of crude 1-diamantane carboxylic acid (V) (25% yield) was crystallized from methanol-water. From the carbon tetrachloride solution (mother liquor) of ammonium salt, 4.0 g of unreacted diamantane was isolated. The acid was purified for analysis by recrystallization from benzene; while fluffy crystals, mp 201.5-202.2°, were obtained; ir (nujol) 1695, 1410, 1275, 1250, 1230 (w), 1100, 1075, 1055 (d), 1040 (w), 935 (b) and 710 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}O_2$: c, 77.55; H, 8.68. Found: C, 77.28; H, 8.97.

1- and 4-Diamantane Carboxylic Acids (V and XXI) [Koch-Haaf Reaction-Mixed Acid Method[22f-i]]. A flask was charged with 140 ml of 1:1 mixture of 97.2% and fuming sulfuric acids, 50 ml of CCl_4 and 10.0 g (0.05- mole) of diamantane. After cooling to 15°, 0.5 ml 98% formic acid was added. Then a solution of 19 ml t-butanol containing 28 g (98%) formic acid was added dropwise within 1/2 hour. Stirring was continued at 15° for 30 minutes and then at room temperature for four hours. Upon workup, as for 1-diamantane carboxylic acid (V), 1.09 g (8.8%) of an acid mixture consisting of 1-diamantane carboxylic acid (V) and 4-diamantane carboxylic acid (XXI) was obtained. The acid composition was determined by conversion of 200 mg of acid to their corresponding methyl esters via reaction with diazomethane in ether. Gas chromatographic analysis on a 1m x 3 mm FFAP column at 190° indicated the ratio of esters with retention times of 6 and 7.5 min to be 76% 1-diamantane methyl carboxylate, and 24% 4-diamantane methyl carboxylate. Retention times were verified by coinjection with authentic esters prepared by diazomethane reaction of pure 1- and 4-diamantane carboxylic acids.

The Koch-Haaf reaction was repeated as above on 5.0 g (0.027 mole) diamantane and stirred at room temperature for 24 hours. Upon the usual workup, 0.175 g (1.4%) of acid mixture consisting of 89% 1-diamantane-carboxylic acid and 11% 4-diamantane carboxylic was obtained. The composition was determined in the same manner as above.

1-Diamantane Carboxylic Acid (V) from 3-Diamantanol (XI) [Koch-Haaf Reaction].[31,32] A Koch-Haaf reaction carried out on 0.4 g (1.9 mmoles) 3-diamantanol with 20 ml carbon tetrachloride, 10 ml 98% sulfuric acid and 5 ml formic acid in the cold, gave after workup what appeared to be 1-diamantane carboxylic acid by nmr analysis. However, the melting point of the acid was not sharp, ca 160°.

1-Diamantanol (VI). 1-Bromodiamantane (III) (1.0 g, 3.8 mmoles) was refluxed overnight with 100 ml of 10% K_2CO_3 solution, 50 ml of acetone, and 0.5 g of $AgNO_3$. The reaction mixture was extracted with 3 x 100 ml of ether. The collected extracts were washed with water until neutral and dried over Na_2SO_4. The solvent was evaporated and the residue crystallized from acetone to give white crystals, 0.63 g (3.01 mmoles, 81% yield), mp 285-288° (sealed capillary). Recrystallization gave an analytical sample, mp 291-292° (lit. mp 292.5-294°); ir (nujol) 3240 (OH), 1115, 1032, and 940 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.00; H, 9.94.

1-Acetamidodiamantane (VIII) [Ritter Reaction][33,34] 1-Bromodiamantane (III) (2.67 g, 10 mmoles) was dissolved in a mixture of 9 ml of cyclohexane and 12 ml of acetonitrile. Then 5.3 ml of concentrated H_2SO_4 was added. The temperature of the reaction mixture rose slightly (ca 10°) and stirring was continued overnight. After 16 hrs the mixture had become a thick orange suspension. Water and ice were added, stirring was continued for 15 minutes, and the white precipitate filtered, washed with 10% aqueous Na_2CO_3 solution and subsequently with water. After drying, 2.2g of white powder was obtained and recrystallized from acetone. White crystals, 1.9 g (78% yield), mp 167-168°, of 1-acetamidodiamantane (VIII) was obtained; ir (KBr) 3283 (NH), 1646 (amide band I), 1572 and 1549 cm^{-1} (amide bands II).

Anal. Calcd for $C_{16}H_{23}NO$: C, 78.31; H, 9.45; N, 5.71. Found: C, 78.18; H, 9.73; N, 5.40.

1-Aminodiamantane Hydrochloride (IX).[34] 1-Acetamidodiamantane (VIII) (1.3 g, 5.3 mmoles) was refluxed in a solution of 2.2 g NaOH in 30 ml diethyleneglycol for 5 hours. The reaction mixture changed color to yellow and then orange-brown. After the reaction was completed, the mixture was poured onto crushed ice, and extracted three times with diethyl ether, dried over KOH pellets and the solvent evaporated. An oily product (1.79 g) was left, which was taken up in 50 ml of anhydrous diethyl ether. Gaseous HCl was introduced and the precipitated solid was filtered and washed twice with ether; 0.90 g (71%) of 1-aminodiamantane hydrochloride (IX) was obtained. A sample for analysis, mp ca 360°, was recrystallized from ethanol/ether.

Anal. Calcd for $C_{14}H_{22}NCl$: C, 70.12; H, 9.25; N, 5.84; Cl, 14.78. Found: C, 69.49; H, 9.30; N, 6.19; Cl, 14.72.

3-Diamantanone (X). To 2.0 g of diamantane was added 100 ml of 96.6% sulfuric acid; the reaction mixture was then heated for four hours at 75° with vigorous stirring. Stirring was continued at room temperature for one additional hour. The black reaction mixture was poured over ice and steam distilled. The steam distillate was extracted with ether, and the combined ether extracts were washed with water and dried over $MgSO_4$. Evaporation of solvent left 1.4 g (70% yield) of crude diamantanone (X). The product may be further purified by chromatography on alumina. The second fraction, eluted with benzene ether (1:1) contained pure diamantanone, 0.8 g (37%). Recrystallization from petroleum ether gave white crystals, mp 249-250° (lit.[13b] 248-249°); ir (nujol) 1745, 1720, 1295, 1245, 1045 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.50; H, 9.43.

3-Diamantanol (XI). A solution containing 0.55 g (2.7 mmoles) of diamantane in 15 ml of anhydrous ethyl ether was added within 1/2 hour to 20 ml of anhydrous diethyl ether containing 0.093 g (2.4 mmole) lithium aluminum hydride. After refluxing for 1 1/2 hours, and stirring at room temperature for an additional 1/2 hour, the reaction mixture was cooled in an ice bath, and 7 ml of 10% sulfuric acid was added slowly. The reaction mixture was worked up in the usual way[35] and evaporation of solvent left 0.4 g (73% yield) of white solid. Recrystallization from petroleum ether gave white fluffy crystals, mp 256-257°; ir (CCl_4) 3150 (OH), 2950, 1065, cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.14; H, 9.78.

3-Diamantyl Tosylate (XII). Diamantanol (XI) (0.180 g) was stirred with tosyl chloride (0.415 g) in pyridine[36] (4.8 g) for 3 days. After the usual workup procedure,[36] 0.301 g (95.6% yield) of white crystalline product was obtained. Recrystallization from petroleum ether gave white crystals, mp 124.2-124.6°; ir (CS_2) 2895, 2855, 2825, 2775, 2275, 2150, 1185, 1175, 945 cm^{-1}.

Anal. Calcd for $C_{21}H_{26}SO_3$: C, 70.35; H, 7.31; S, 8.94. Found: C, 70.55; H, 7.57; S, 8.66.

3-Bromodiamantane (XIII).[37] A mixture of 0.310 g (1.5 mmoles) 3-diamantanol (XI), and 1.15 g (2.7 mmoles) phosphorus pentabromide in 10 ml of anhydrous ether was heated at 45° with stirring for two hours. The reaction mixture was treated with water; the resulting layers were separated, and the ether layer was dried over $MgSO_4$ and evaporated. The white crystalline residue, 0.405 g (99.5% yield) was recrystallized from petroleum-ether to give pure 3-bromodiamantane, mp 93-94°.

Anal. Calcd for $C_{14}H_{19}Br$: C, 62.92; H, 7.17; Br, 29.91. Found: C, 63.20; H, 7.38; Br, 29.69.

3-Chlorodiamantane (XIV).[38] Thionyl chloride (0.58 g, 4.9 mmoles, 0.35 ml) in 5 ml of chloroform was added rather rapidly to 200 mg (0.98 mmoles) of 3-diamantanol in 2 ml of chloroform. After refluxing for 4 hours, the reaction mixture was cooled, and the solvent evaporated. The residue was sublimed at 70°/20 mm pressure. White crystals, 105.2 mg (49% yield), mp 153-156°, of crude 3-chlorodiamantane were obtained. The compound was recrystallized from MeOH-H_2O, and upon cooling, white fluffy crystals, mp 157-158° (sealed capillary), were collected.

Anal. Calcd for $C_{14}H_{19}Cl$: C, 75.44; H, 8.62: Found: C, 75.44; H, 8.68.

3-Methyl-3-diamantanol (XV). A solution of 3-diamantanone (X), 0.5 g (2.5 mmoles) in 25 ml of ethyl ether, was added to 30 ml of an anhydrous ethereal solution containing the Grignard reagent prepared from 2.13 g (15 mmoles) methyl iodide and 0.36 g magnesium. After approximately 1 hour, the excess Grignard reagent was decomposed with saturated ammonium chloride solution and the ether layer separated. The aqueous solution was washed three more times with ether and the combined ether solution dried over $MgSO_4$ and evaporated. A white solid remained, 0.45 g, 82% yield. Recrystallization from petroleum-ether gave white crystals, mp 149-150°; ir (CCl_4) 3600, 2890 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16 Found: C, 82.70; H, 10.21.

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(30) See Table I, ref b.

(31) Cf. H. Koch and W. Haaf, Org. Syn., 44, 1 (1964).

(32) This reaction was carried out by Dr. L. Lam.

(33) Cf. L.I. Krimen and D.J. Cota, "Organic Reactions," Vol. 17, John Wiley and Sons, Inc., New York, New York, 1969, p. 213.

(34) This reaction was carried out by C. Hoogzand.

(35) Cf. L.F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Vol. 1, John Wiley and Sons, Inc., New York, N.Y. 1967, p. 581.

(36) Reference 35, p. 1179.

(37) Reference 35, p. 865.

(38) Reference 35, p. 1160.

3-Methylenediamantane (XVI). 3-Methyl-3-diamantanol (XV) (0.33 g) was heated with 5 g of 85% H_3PO_4 at 135° for 20 min. The mixture was diluted with water and extracted with petroleum-ether. The combined petroleum ether extracts were washed with H_2O, and dried over $MgSO_4$. Removal of solvent left 0.26 g (86% yield) of waxy white solid which was sublimed at 120°/1 atm and recrystallized from petroleum-ether to give product, mp 125-126°; ir (CCl_4) 3090, 1650, 880 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.83; H, 10.03.

3-Methyldiamantane (XVII). 3-Methylenediamantane (XVI), 0.21 g (1.0 mmoles) was dissolved in 30 ml of anhydrous ether containing 0.2 g PtO_2 catalyst, and hydrogenated with a Parr apparatus at room temperature under 3 atm hydrogen pressure. After workup, 0.180 g (0.9 mmoles) (85% yield) of white crystalline 3-methyldiamantane was obtained. Recrystallization from ethanol yielded white crystals, mp 117-118°.

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.82; H, 10.82.

4-Diamantanol (XX). A mixture of 1-(III) and 4-bromodiamantanes (XVIII) (1.0 g, 3.8 mmoles) prepared from bromination of diamantane with t-butyl-bromide/aluminum bromide and equilibrated overnight at 0°,[1b] was hydrolyzed as described for 1-diamantanol above. After workup, 0.60 g (78% yield) of white crystalline material remained; glc on a 5% DC710, 1.5 m x 3 mm column, 195° indicated two peaks of retention time 4.0 and 4.5 min corresponding to VI (41%) and 4-diamantanol (XX) (59%). Separation of the two alcohols was achieved by chromatography on alumina; 1-diamantanol (VI) elutes first with benzene-ether 1:1 and 4-diamantanol (XX) next. 4-Diamantanol (XX) was recrystallized from acetone to give white crystals, mp 204-206° (lit.[13] 206-208°); ir (nujol) 3300 (OH), 1105, 1040 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.02; H, 10.07.

4-Diamantane carboxylic acid (XXI). [Koch-Haaf reaction - High Dilution Method][23] A 2000 ml flask was charged with 450 ml of 97% sulfuric acid which was cooled in an ice-salt bath to -5°. Then, 15 ml 90% formic acid was added slowly. The temperature rose to +5°, and the mixture was stirred at this temperature for an additional 15 minutes until foamy. Then 1.0 g (3.7 mmoles) 4-bromodiamantane (XVIII) dissolved in 300 ml of carbon tetrachloride was added rapidly. At the same time, 15 ml of 90% formic acid was added slowly. The temperature rose to +10°, the ice bath was removed after 1 hour and the reaction mixture allowed to come to room temperature and stirred for additional four hours. The yellow mixture was poured onto 900 g of ice slowly, and the CCl_4 layer separated. The aqueous layer was washed several times with carbon tetrachloride. The combined carbon tetrachloride layers (about 800 ml) were treated with 30 ml ammonium hydroxide and the solids which formed were filtered and suspended in about 30 ml of water and acidified with 30 ml of 3N HCl. The solution was then extracted with chloroform, and the chloroform extract washed with saturated sodium chloride and dried over $MgSO_4$. Removal of solvent left a white solid which was recrystallized from benzene to give 450 mg (52% yield) of crystalline 4-diamantane carboxylic acid (XXI), mp 273.5-274.1°. Further recrystallization from benzene gave white crystals, mp 278.5-279.9°; ir (nujol) 3100, 1700, 1300, 1250, 1200, 1050, 950 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.83; H, 8.90.

Tetrahydro-tricyclopentadiene (XXII). Exo-tricyclopentadiene (50 g, 2.25 mole, gift from Union Carbide) dissolved in 140 ml glacial acetic acid with 0.15 g PtO_2 catalyst (or Pd/C), was shaken in a Parr apparatus at 3 atm hydrogen pressure for 24 hrs at room temperature. Workup gave a quantitative

yield of desired product, which was recrystallized from acetone to give white crystals, mp 92°, (lit.[38] mp 100°). Further purification of the material may be achieved by distillation to give 30.5 g (60.7% yield) of tetrahydro-tricyclopentadiene, mp 93.0-95.1°, bp 144-48°/8 mm (lit.[39] bp 287°/766 mm).

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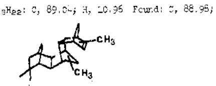
(39) K. Alder and G. Stein, Ber., 67, 613 (1934).

Methylcyclopentadiene-6,6-Dimethylnorbornene Adduct (XXIV).[1a] Methylcyclopentadiene (83 g, 1.04 moles; prepared by dropping dimethylcyclopentadiene (Aldrich) on mineral oil at 240-270°),[40] and 141 g (1.16 moles) of 5,5-dimethylnorbornene[41] (gift from Union Carbide, bp 51-8° at 50 mm Hg, n_D^{20} 1.4556-63, solid at 25°) were heated with a trace amount of hydroquinone at 180-205° for 17.5 hrs in a glass pressure bottle. The reaction mixture was distilled and 75.6 g (53.6%) of unreacted 5,5-dimethylnorbornene was recovered. The main fraction, 115 g, bp 55-82°/0.5-1 mm, was a mixture with XXIV the major component. The lightly colored pot residue contained 29.0 g of 1:2 adduct XXXII. Redistillation of the main fraction gave about 20 ml of forerun, bp 50-67°/1 mm, and 86 g (41% yield), bp 67-81°/1 mm, of a mixture of three main components of which over 70% was the desired XXIV; ir 3044, 2946, 2862, 1471, 1443, and 803 cm^{-1}; mass spectrum m/e 202, 160, 91, 80, and 66, nmr δ 0.99 (methyl at C_4), 1.71 (methyl at C_9 or C_{10}), 5.37 (s) and 6.0-5.55 (complex-olefinic which disappears on irradiation).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96 Found: C, 88.96; H, 10.69.



XXXII

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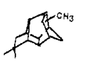
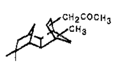
(40) M. Korach, D.R. Nielsen, and W.H. Rideout, Org. Syn., 42, 50 (1962); cf. A. Wilkinson, Org. Syn. Coll., 4, 238, (1963).

(41) M.A. Belikova, L.I. Kovalenko, M.A. Moskaleva, M. Ordubadi, A.F. Plate, E. Kh. Sterin, and R. Jagminas, Zh. Org. Khim., 4, 1363 (1968); Chem. Abstr., 69, 86462m (1968).

Irradiation Product of XXIV (XXV).[1a] A solution of 80.7 g of XXIV from the preceeding experiment in 5 liters of acetone (ACS grade) was irradiated with a 450 W Hanovia medium pressure mercury lamp with pyrex filter under agitation by bubbling nitrogen and with magnetic stirring for 1 week. The reaction mixture was distilled directly and two fractions were collected: (1) 57.7 g (bp 56-69°/1 mm); and (2) 112 g (bp 95-126°/1 mm). Fraction I was a mixture containing XXV as the major component (56-69%); ir 2950, 2858, 1448, and 1359 cm^{-1}; mass spectrum m/e 202, 187 (-CH_3), 131, 107, 105, 95, 94, 93, 91, 80; nmr (CCl_4) δ 2.5-0.5 (complex), 0.95 and 0.89 (methyl). Fraction II is thought to be the acetone adduct[42] XXXIII; ir 1718 cm^{-1} (C=O); mass spectrum m/e 260, 202. Nmr (CCl_4) δ 2.01 (acetyl methyl), 3.0-0.6, 0.99 and 0.94 (other methyls).



XXV



XXXIII

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(42) Cf. H.D. Scharf, Tetrahedron, 23, 3057 (1967).

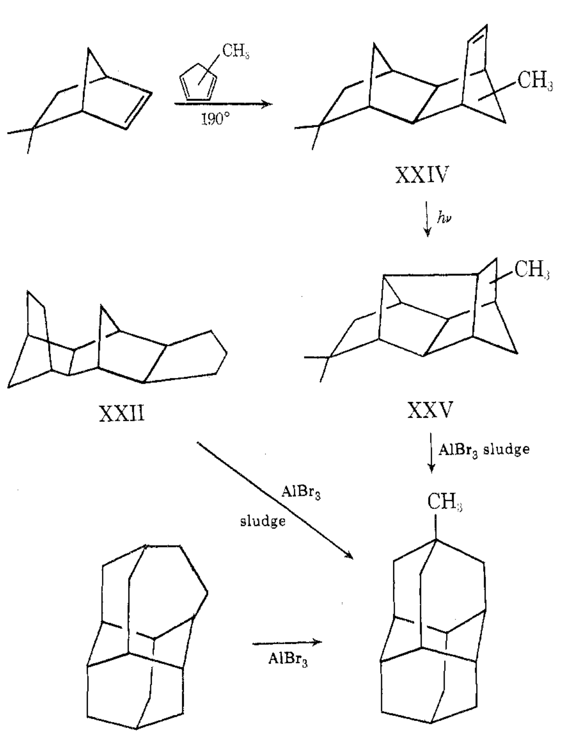
4-Methyldiamantane (XXIII). A. From tetrahydro-tricyclopentadiene (XXII). Sludge catalyst [prepared from t-butyl bromide-aluminum bromide],[1a] 15 ml, was added to 15 g (0.08 mole) of XXII dissolved in 25 ml of carbon disulfide while under a stream of hydrogen bromide gas, and stirred at room temperature for 48 hrs. In cases where starting material was still present, the reaction mixture was treated with more catalyst and heated at 100° without solvent. Following the same workup as described for rearrangement of XXV, an oily material which was a mixture of at least six components was obtained. The volatile materials (mostly alkyl adamantanes) were removed by distillation at 78-108°/10 mm; the residue which crystallized upon standing was recrystallized twice from acetone and gave 0.5 g (3.3% yield) of 4-methyldiamantane (XXIII), mp 91.6-94.4° (sealed tube), identical by nmr and ir to material obtained from XXV.[11]

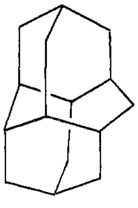
B. From XXV. Freshly prepared aluminum bromide sludge catalyst,[1a] 30 ml, was added in small portions (5-10 ml) over a period of 1 hour to 27 g of C_{15} pentacyclic precursor mixture (XXV) under a stream of hydrogen bromide gas and with vigorous stirring. Vigorous gas evolution, an exothermic process (warming to 50°), and formation of tarry material was observed. After the initial exothermic process subsided, the reaction mixture was

heated at 88-93° for 21 hours and then extracted eight times with 15 ml portions of carbon disulfide. The combined extract was washed with water three times, dried over $CaCl_2$ and evaporated to give 8.41 g (31% yield) of an oil; glc, SE 30 capillary column, 45 m x 0.25 mm, 138°, indicated seven peaks with retention times of 2.6, 3.0, 4.0, 5.5, 5.9, 6.6 and 7.1 minutes corresponding to 1,3,5-trimethyl-7-ethyladamantane, (4%), 1-methyl-3,5-diethyladamantane (14%), unreacted XXV (6%), diamantane (5%), 4-methyldiamantane (55%), 1-methyldiamantane (10%) and 3-methyldiamantane (6%), respectively. 4-Methyldiamantane (XXIII) was separated by preparative gas chromatography on a Carbowax 20M 7.5 m x 9 mm column at 195° and further purified by recrystallization from acetone. Large plate-like crystals, mp 99-100.5°, were obtained; ir (KBr) 2950-2830, 1446, 1375, 1317, and 1047 cm^{-1}; mass spectrum m/e (rel intensity) 202 (M+) (45.7), 187 (loss of CH_3, 100), 91 (1.06).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.00; H, 11.06.

Chart II

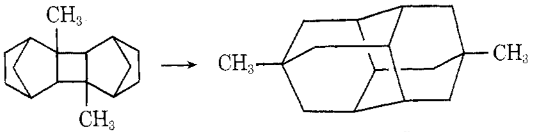




XXVIb

Isomerization of pentacyclic precursor XXV with $AlBr_3$ sludge catalyst at ∼90° gave a complex mixture; final equilibrium composition was not achieved. The glc spectrum indicated the components to be diamantane (5%), 4-methyldiamantane (XXIII, 55%), 1-methyldiamantane (VII, 10%), 3-methyldiamantane (XV, 6%), various alkyl adamantanes (18%), and recovered XXV (6%). No evidence for homodiamantane (XXVIa) was found upon glc comparison with an authentic sample. The rearrangement results are summarized in Chart II.

Similar Lewis acid catalyzed rearrangement of 2-methylnorbornene dimer (XXXI) gave 4,9-dimethyldiamantane (XXVII) as the major product isolable only in small quantity.[10]



XXXI XXVII

Table IV
Axial–Equatorial Energy Differences, Liquid

Substituent	ΔH axial → equatorial cyclohexane derivatives, kcal/mol	ΔH medial → apical diamantane derivatives, kcal/mol
Br	0.476[a,b]	0.60[e]
Cl	0.528[a,b]	0.68[e,f]
OH	1.09–1.18[c]	1.1[g]
CH_3	1.73[c]	2.14,[h] 3.0[i]
COOH	1.6–1.7[a,b,d]	*j*
CO^+	*k*	*k*

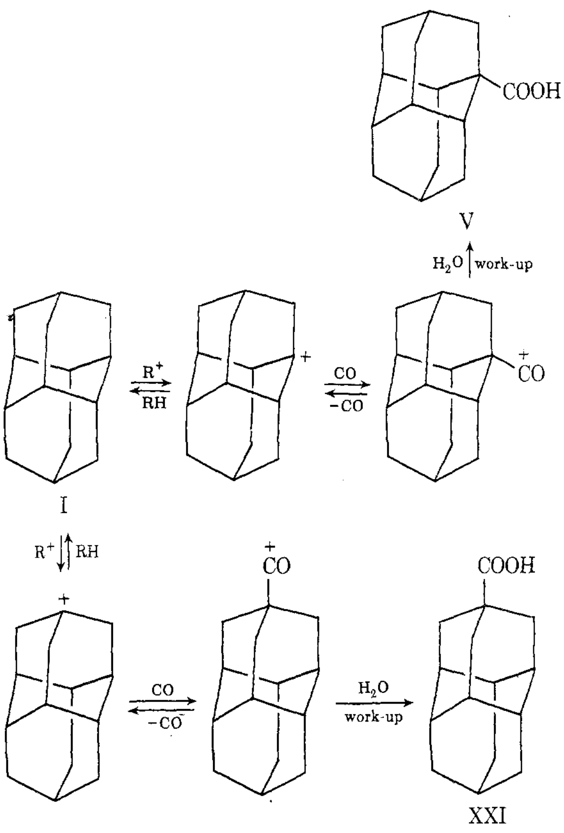
[a] ΔG; ΔS assumed to be zero. [b] F. R. Jensen, C. H. Bushweller, and B. H. Berk, *J. Amer. Chem. Soc.*, **91,** 344 (1969). [c] E. L. Eliel and E. C. Gilbert, *ibid.*, **91,** 5487 (1969). [d] Reference 20. [e] Reference 13 . [f] Reference 14a. [g] Reference 14c. [h] Reference 14b. [i] Calculated by empirical force field calculations, ref 18. [j] *Cf.* data for the adamantanecarboxylic acids: W. V. Steele, A. S. Carson, P. G. Laye, and C. A. Rosser, *J. Chem. Thermodyn.*, **5,** 1257 (1973). [k] A low value is expected; *cf.* ref *b* (ΔG for –CN and –NC = 0.24 and 0.21 kcal/mol, respectively).

Functional substituents can similarly be introduced into the 4 position by rearrangement. We observed that the bromination of diamantane in the presence of traces of $AlBr_3$ at reflux gave a bromide mixture containing 4-bromodiamantane and 4,9-dibromodiamantane; these products were not observed in the absence of the catalyst.[1b] While 4-bromodiamantane could be obtained by separation from the mixture or by selective reduction of 4,9-dibromodiamantane with tri-*n*-butyltin hydride, neither route was very convenient preparatively.[1b]

McKervey demonstrated that not only 1-diamantyl bromide, but also the 1-alcohol and 1-chloride could be equilibrated with acid catalysts to provide mixtures containing roughly comparable amounts of 1 and 4 isomers (owing to a fortuitous balancing of entropy and enthalpy factors; see Table IV).[13b,14] The individual apical and medial halides can be isolated by column chromatography, or else their mixture can be hydrolyzed to the corresponding alcohols VI and XX, which are easier to separate.

Direct bromination of diamantane with *tert*-butyl bromide–aluminum bromide at 0° affords the currently most convenient method of derivatizing the 4 position, since substitution and equilibration are achieved in the same process.[1b] Still, the monobromide product contains ~40% of 1-bromodiamantane (III), which must be separated from the 4-bromide (XVIII).

Since the axial–equatorial ΔG value for the carboxyl group[20] in cyclohexane is about as large as that of a methyl[20,21] (Table IV), we examined the equilibration of the bridgehead diamantanecarboxylic acids (Table V). The use of fuming sulfuric acid, while decreasing the overall yield, did allow equilibration to occur. However, the highest percentage of 4-carboxylic acid in the acid product was only ~25%. It seems likely that the acylium ions, rather than the carboxylic acids, are actually the species undergoing equilibration under those conditions.[22] The low steric demand of the $-CO^+$ group (Table IV) evidently is responsible for the observed result.[22e–j]



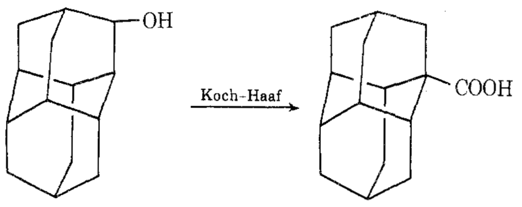
When 3-diamantanol was subjected to ordinary Koch–Haaf conditions, the main product was the 1-carboxylic acid.[9] The 4-carbocylic acid can be prepared from the 4-bromide by the Koch–Haaf procedure, providing that high dilution conditions which preclude intramolecular hydride shifts are employed.[23]

The direct and high-yield conversion of diamantane to 4-diamantyl derivatives relatively free from isomeric contaminants has recently been achieved by reagents with high steric sensitivity.[16]

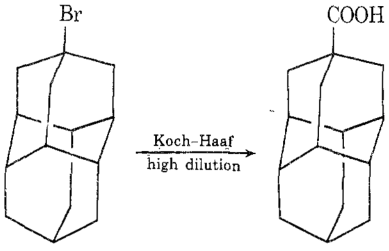
Table V
Koch–Haaf Reaction on Diamantane[a]

Starting material	Conditions concn	Solvent	Time	% 1-diamantanecarboxylic acid	% 4-diamantanecarboxylic acid	Total yield acid, %[b]
Diamantane	97% H_2SO_4	CCl_4 *t*-BuOH	30 min	Only product by nmr		28
Diamantane	1:1 mixture of 97% H_2SO_4 and fuming H_2SO_4	CCl_4 *t*-BuOH	4 hr	76	24	8.8
Diamantane	1:1 mixture of 97% H_2SO_4 and fuming H_2SO_4	CCl_4 *t*-BuOH	24 hr	88	12	1.4
3-Diamantanol	97% H_2SO_4	CCl_4	30 min	Only product by nmr		
4-Bromodiamantane	97% H_2SO_4 High dilution	CCl_4	3 hr	Small amount	Major	52

[a] *Cf.* ref 9, 22, and 23. [b] Diamantane was recovered in varying amounts in all cases.



XI V



XVIII XXI

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Registry No.—I, 2292-79-7; XXII, 51965-76-5; XXIV, 51966-02-0; XXV, 51966-03-1; XXXII, 51966-04-2; XXXIII, 51966-05-3.

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References and Notes

(1) (a) Part I: T. M. Gund, E. Osawa, V. Z. Williams, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **38**, 2979 (1974). (b) Part III: T. M. Gund, P. v. R. Schleyer, G. D. Unruh, and G. J. Gleicher, *ibid.*, **38**, 2995 (1974). For preliminary comunications describing aspects of this work, see ref 5, 6c,e,g, 9, 12, and 15 and T. M. Gund and P. v. R. Schleyer, *Tetrahedron Lett.*, 1959 (1973).

(2) (a) Ph.D. Thesis, Princeton University, 1973; (b) on leave from Kyoto Technical University, 1967.

(3) V. Z. Williams, Jr., A.B. Thesis, Princeton University, 1965.

(4) R. C. Fort, Jr., unpublished observations, 1965.

(5) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(6) Reviews: (a) H. Stetter, *Angew. Chem.*, **66**, 217 (1954); (b) H. Stetter, *ibid.*, **74**, 361 (1962); (c) R. Fort and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (d) V. V. Sevost'yanova, M. M. Krayushkin, and A. G. Yorchenko, *Russ. Chem. Rev.*, **39**, 817 (1970); (e) R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.* **18**, 1 (1971); (f) Z. Weidenhoffer and S. Hála, *Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv*, **22**, 5 (1971); (g) E. M. Engler and P. v. R. Schleyer, *MTP* (*Med. Tech. Publ. Co.*) *Int. Rev. Sci.: Org. Chem., Ser. One. 1973*, 239 (1973).

(7) For nomenclature, see ref 1a, footnote 36.

(8) H. W. Geluk and J. L. M. A. Schlatmann, *Chem. Commun.*, 426 (1967); *Tetrahedron*, **24**, 5361 (1968).

(9) T. M. Gund, M. Nomura, V. Z. Williams, Jr., P. v. R. Schleyer, and C. Hoogzand, *Tetrahedron Lett.*, 4875 (1970).

(10) S. A. Goscin, A.B. Thesis, Princeton University, 1966.

(11) Statistical substitution by methylene insertion gave a ≈6:12:2 statistical mixture of 1-, 3-, and 4-methyldiamantane characterized by gas chromatographic retention indices: S. Hála, J. Novak, and S. Landa, *Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv*, **19**, 19 (1969). The rearrangement of XXII to 4-methyldiamantane (XXIII) was investigated independently at Prague: S. Landa, private communication.

(12) T. M. Gund, P. v. R. Schleyer, and C. Hoogzand, *Tetrahedron Lett.*, 1583 (1971).

(13) (a) D. Faulkner, R. A. Glendinning, D. E. Johnston, and M. A. McKervey, *Tetrahedron Lett.*, 1671 (1971); (b) T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Perkin Trans. 1*, 2691 (1972).

(14) (a) M. A. McKervey, D. E. Johnston, and J. J. Rooney, *Tetrahedron Lett.*, 1547 (1972); (b) R. Hamilton, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1209 (1972); (c) D. E. Johnston, M. A. McKervey, and J. J. Rooney, *ibid.*, 29 (1972).

(15) I. Tabushi, Y. Aoyama, N. Takahashi, T. M. Gund, and P. v. R. Schleyer, *Tetrahedron Lett.*, 107 (1973).

(16) I. Tabushi, S. Kojo, P. v. R. Schleyer, and T. M. Gund, *Chem. Commun.*, 591 (1974).

(17) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

(18) The force field used is described by E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer, Chem. Soc.*, **95**, 8005 (1973). (Data for 3-methyl and 4-methyldiamantane in this paper should be transposed.)

(19) E. M. Engler, K. R. Blanchard, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1210 (1972).

(20) R. D. Stolow, *J. Amer. Chem. Soc.*, **81**, 5806 (1959).

(21) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1967.

(22) (a) H. Koch and W. Haaf, *Angew, Chem.*, **70**, 311 (1958); (b) *Justus Liebigs Ann. Chem.*, **618**, 251 (1958); W. Haaf and H. Koch, *ibid.*, **638**, 122 (1960); (c) H. Christol and G. Solladié, *Bull. Soc. Chim., Fr.*, 1307 (1966); (d) W. Haaf, *Angew, Chem.*, **73**, 144 (1961); (e) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959); (g) A. Lundeen, *ibid.*, **82**, 3228 (1960); (h) W. Haaf, *Chem. Ber.*, **96**, 3359 (1963); (i) H. Hogeveen and C. F. Roobeck, *Tetrahedron Lett.*, 4941 (1969); (j) H. Hogeveen, *Advan. Phys. Org. Chem.*, **10**, 29 (1973).

(23) D. J. Raber, R. C. Fort, E. Wiskott, C. W. Woodworth, and P. v. R. Schleyer, *Tetrahedron*, **27**, 3 (1971).

(24) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965); (b) R. C. Fort, Jr., and T. R. Lindstrom, *Tetrahedron*, **23**, 3227 (1967).

(25) (a) F. W. V. Deursen and P. K. Korver, *Tetrahedron Lett.*, 3923 (1967); (b) F. W. V. Deursen and A. C. Udding, *Recl. Trav. Chim. Pays-Bas*, **87**, 1243 (1968); (c) F. W. V. Deursen and J. Bakker, *Tetrahedron*, **27**, 4593 (1971).

(26) A. Segre and J. I. Musher, *J. Amer. Chem. Soc.*, **89**, 706 (1967).

(27) A. G. Yurchenko and S. D. Isaev, *Zh. Org. Khim.*, **7**, 2628 (1971).

(28) C. L. Liotta, F. W. Fisher, G. H. Greene, Jr., and B. L. Joyner, *J. Amer. Chem. Soc.*, **94**, 4891 (1972); L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972), and references cited therein.

(29) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).