crystallized from hexane–CCl_4, affording 2.95 g (48%) of stout prisms: mp 89–92.5 °C (lit.[33] mp 94–95 °C); ^1H NMR ($CDCl_3$) δ 1.80 (m, 4, $OCH_2CH_2CH_2CH_2$), 2.30 (s, 3, CH_3), 2.85 (m, 2, Ar CH_2), 4.24 (m, 2, OCH_2), 7.27 (d, J = 2 Hz, 1, Ar H, position 6), 7.85 (d, J = 2 Hz, 1, Ar H, position 8), 11.20[32] (br s, 1, OH); IR ($CHCl_3$) 1730 cm^{-1} (C=O); analytical sample, mp 91.5–93 °C.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.82; H, 6.95.

1-Bromo-5-(2-bromo-4-methylphenoxy)pentane (17). This was prepared in 72% yield from 2-bromo-4-methylphenol and 1,5-dibromopentane by the method[6] used for the lower homologues: bp 152–155 °C (0.03 torr); ^1H NMR ($CDCl_3$) δ 1.80 (m, 6, $OCH_2CH_2CH_2CH_2CH_2$), 2.23 (s, 3, CH_3), 3.40 (t, J = 7 Hz, 2, CH_2Br), 3.94 (t, J = 6 Hz, 2, OCH_2), 6.60–7.35 (AMX m, 3, Ar H).

Anal. Calcd for $C_{12}H_{16}Br_2O$: C, 42.89; H, 4.80; Br, 47.55. Found: C, 42.88; H, 4.98; Br 47.49.

Results of Bromine–Lithium Exchange of 17. (a) Using Butyllithium. A solution of **17** (10.08 g, 30 mmol) in 200 mL of THF and 50 mL of hexane was cooled to −100 °C and treated in the usual way with 33 mmol of butyllithium. After 30 min[34] at −100 °C the mixture was allowed to warm slowly (~1.5 h) to 25 °C and then stirred an additional 6 h. The mixture was poured into water, and the organic materials were extracted with ether (3 × 150 mL). The dried solution was concentrated to afford 7.4 g of yellow oil which was analyzed by gas chromatography/mass spectroscopy (2% OV-1 column, 3 ft × 0.125 in.) programmed from 150 to 230 °C at 10 °C/min (flow rate 30 mL He/min). The major components, identified only by interpretation of the fragmentation patterns, were as follows. 4-(4-Methylphenoxy)-1-pentene: 34% yield; retention time 3.2 min; mass spectrum, m/e (relative intensity) 176 (M^+, 22), 108 (100), 107 (28), 41 (24). 8-Methyl-3,4,5,6-tetrahydro-2*H*-1-benzoxocin: 21% yield; retention time 4.1 min; mass spectrum, m/e (relative intensity) 176 (M^+, 36), 147 (17), 121 (100), 91 (23). 1-Bromo-5-(4-methylphenoxy)pentane: 10% yield; retention time 8.4 min; mass spectrum, m/e (relative intensity) 256, 258 (M^+ isotopes, 6, 5), 151 (15), 149 (16), 108 (100), 107 (27), 69 (30). 1-Bromo-5-(2-butyl-4-methylphenoxy)pentane: 36% yield; retention time 11.5 min; mass spectrum, m/e (relative intensity) 312, 314 (M^+ isotopes, 7, 8), 165 (44), 151 (23), 149 (25), 121 (100), 69 (64). No further effort was made to separate the mixture.

(b) Using *tert*-Butyllithium. The halogen–metal exchange experiment was repeated except that 10.08 g (30 mmol) of **17** was treated with 66 mmol (2.2 equiv[29]) of *tert*-butyllithium. At the conclusion of the experiment, the product consisted of 6.17 g of yellow oil which was analyzed in the same way by GC/MS. The major components appeared to be 5-(4-methylphenoxy)-1-pentene (33%), 1-(4-methylphenoxy)pentane [35%; retention time 3.4 min; mass spectrum, m/e (relative intensity) 178 (M^+, 16), 108 (100), 107 (18), 91 (5)], and 8-methyl-3,4,5,6-tetrahydro-2*H*-1-benzoxocin (29%).[35]

Registry No. 4a, 18800-28-7; **4b**, 76429-63-5; **4c**, 76429-64-6; **4d**, 76429-65-7; **4e**, 76429-66-8; **4f**, 76429-67-9; **6a**, 496-16-2; **6b**, 76429-68-0; **6c**, 13391-30-5; **6d**, 76429-69-1; **6e**, 66826-78-6; **6f**, 76429-70-4; **7**, 76429-71-5; **8**, 76429-72-6; **10**, 76429-73-7; **11a**, 37136-84-8; **11b**, 66246-12-6; **11c**, 76429-74-8; **11d**, 76429-75-9; **11e**, 76429-76-0; **13a**, 493-08-3; **13b**, 3722-74-5; **13c**, 3722-76-7; **13d**, 3722-71-2; **13e**, 76429-77-1; **14**, 76429-78-2; **15a**, 76429-79-3; **15b**, 76429-80-6; **16a**, 41177-64-4; **16b**, 76429-81-7; **16** (R = COOH), 35700-37-9; **17**, 76429-82-8; ethylene bromide, 106-93-4; 2-bromophenol, 95-56-7; 4-methyl-2-bromophenol, 6627-55-0; 4-methoxy-2-bromophenol, 17332-11-5; 4-chloro-2-bromophenol, 695-96-5; 2,4-dibromophenol, 615-58-7; 4-methyl-2,6-dibromophenol, 2432-14-6; dimethylformamide, 68-12-2; 1,3-dibromopropane, 109-64-8; 1,4-dibromobutane, 110-52-1; 1,5-dibromopentane, 111-24-0; 4-(4-methylphenoxy)-1-pentene, 6793-72-2; 8-methyl-3,4,5,6-tetrahydro-2*H*-1-benzoxocin, 76429-84-0; 1-bromo-5-(4-methylphenoxy)pentane, 53178-42-0; 1-bromo-5-(2-butyl-4-methylphenoxy)pentane, 76446-90-7; 5-(4-methylphenoxy)-1-pentene, 76429-83-9; 1-(4-methylphenoxy)pentane, 33426-70-9.

Supplementary Material Available: Augmented forms of Tables I and II giving ^1H NMR data for both cyclization products and precursors (2 pages). Ordering information is given on any current masthead page.

(33) Christenson, H. *Synth. Commun.* **1974**, *4*, 1.

(34) A preliminary experiment showed that exchange of the aryl bromine was complete after only 15 min at −100 °C (AA'MM' pattern in ^1H NMR of a quenched sample). There was no further change observed after an additional 2 h at −100 °C.

(35) The retention time and mass spectroscopic fragmentation pattern were as described in part a.

Heteroadamantanes. 2. Synthesis of 3-Heterodiamantanes[1a,b]

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Received October 14, 1980

Diamantane (1) has been converted into the unsaturated ketone 8, which is the common precursor in syntheses of 3-azadiamantane (16), 3-oxadiamantane (9), and 3-thiadiamantane (19). An oxaprotodiamantane also has been synthesized and shown to rearrange to 3-oxadiamantane upon treatment with aqueous sulfuric acid.

Numerous heteroadamantanes have been prepared[2] and give evidence of interesting chemistry dependent upon the stereochemically defined interaction of the heteroatom with various reactive sites in the molecule.[2-6] Furthermore, the physical properties of the solid phase of these substances, which are indicative of considerable orientational disorder,[7,8] also contribute to the current interest in heteroadamantanes.

(1) (a) Abstracted from the Ph.D. dissertation of V.V.K., Kent State University, Dec 1980. (b) Presented in part at the Northeast Regional Meeting of the American Chemical Society, Potsdam, NY, June 1980, Abstract 240.

(2) (a) R. C. Fort, Jr. "Adamantane: The Chemistry of Diamond Molecules", Marcel Dekker, New York, 1976, Chapter 6; (b) C. Ganter, *Fortschr. Chem. Forsch.*, **67**, 15 (1976).

(3) R. C. Fort, Jr., and T. A. Flood, Abstracts, Northeast Regional Meeting of the American Chemical Society, Potsdam, NY, June 1980, No. 239.

(4) J. G. Henkel and W. C. Faith, Abstracts, Second Chemical Congress of North American Continent, Las Vegas, NV, Aug 1980, No. 0-326.

(5) W. P. Meyer and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 1231 (1976).

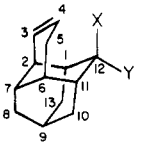
(6) P. M. Starewicz, E. A. Hill, P. Kovacic, and A. R. Gagneux, *J. Org. Chem.* **44**, 3707 (1979).

(7) Reference 2a, Chapter 1.

(8) J. T. S. Andrews, R. E. Carpenter, T. M. Martinko, R. C. Fort, Jr., T. A. Flood, and M. G. Adlington, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 257 (1978).

0022-3263/81/1946-1388$01.25/0

Table I. ^{13}C NMR Spectra of Tetracyclic Alkenes



compd	X	Y	resonances[a]
3	CO_2H	H	180.94 (s, CO_2H), 132.76 (d, C-3 or C-4), 128.70 (d, C-4 or C-3), 48.16 (d, C-12), 26.75 (d, C-9), 40.29 (t), 38.42 (t), 38.20 (d), 38.03 (t), 37.07 (d), 33.63 (d), 32.91 (t), 32.49 (d), 32.32 (d)
4	OAC	H	170.45 (s, OCO), 131.31 (d, C-3 or C-4), 128.44 (d, C-4 or C-3), 78.74 (d, C-12), 26.37 (d, C-9), 21.33 (q, CH_3), 38.84, 38.39, 38.31, 37.81, 37.42, 36.44, 35.12, 33.64, 32.88
5	H	OAC	170.34 (s, OCO), 130.73 (d, C-3 or C-4), 128.88 (C-4 or C-3), 72.45 (d, C-12), 25.94 (C-9), 21.44 (q, CH_3), 40.44, 38.75, 38.28, 37.37, 33.80, 33.34, 32.34, 31.88, 31.65
6	OH	H	136.35 (d, C-3 or C-4), 129.92 (d, C-4 or C-3), 78.10 (d, C-12), 26.12 (d, C-9), 41.36 (d), 38.80 (t), 38.19 (t),[b] 38.19 (t),[b] 37.75 (d),[b] 37.75 (d),[b] 36.37 (d), 33.63 (t), 32.81 (d)
7	H	OH	131.20 (d, C-3 or C-4), 128.65 (d, C-4 or C-3), 68.01 (d, C-12), 26.16 (d, C-9), 41.64 (t), 40.57 (d), 38.66 (d), 37.46 (t), 36.29 (d), 33.69 (t), 31.90 (d), 31.50 (d), 30.97 (t)
8	O	O	218.53 (s, C-12), 130.63 (d, C-3 or C-4), 125.57 (d, C-4 or C-3), 53.77 (d, C-1 or C-11), 50.86 (d, C-11 or C-1), 26.23 (d, C-9), 42.54 (d), 42.07 (d), 40.15 (t), 38.51 (t), 36.99 (t), 32.75 (t), 31.82 (d)
18	S	S	270.39 (C-12), 130.51 (C-3 or C-4), 125.99 (C-4 or C-3), 64.57 (C-1 or C-11), 60.25 (C-11 or C-1), 26.52 (C-9), 44.10, 43.80, 42.77, 41.02, 37.30, 32.94, 31.36

[a] In parts per million downfield from internal Me_4Si in $CDCl_3$ solution. Letters in parentheses are multiplicities observed in off-resonance decoupled spectra: s = singlet, d = doublet, t = triplet, q = quartet. Where no multiplicities are given, either extensive overlap prevented observation (4 and 5) or the off-resonance spectrum was not obtained (18). [b] Resonances resolved with the aid of $Eu(dpm)_3$.

On the other hand, only two heterodiamantanes, 3,10-dioxadiamantane[9] and hexaoxadiamantane,[10] are known, and each was prepared by a method unique to itself. No chemical or physical properties of these systems have been investigated.

We report here the first synthesis of several monoheterodiamantanes, the proofs of their structures, and the first heterodiamantane rearrangement.

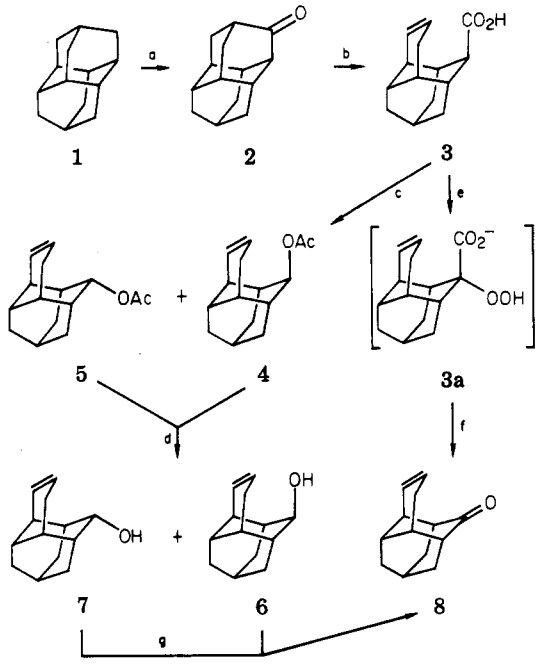
Results and Discussion

The key intermediate in our approach to heterodiamantanes is the ketone 8, which was obtained as shown in Scheme I. Diamantane (1) was prepared and oxidized to diamantanone (2) according to the procedures of McKervey et al.[11] Fragmentation of 2 to the unsaturated acid 3 by an abnormal Schmidt reaction likewise followed McKervey[12] and is analogous to the behavior reported for adamantanone.[13]

We initially attempted to remove the unwanted carboxyl carbon of 3 by oxidation with lead tetraacetate in sodium acetate–acetic acid solution. This reaction gives in poor and variable yield (9–28%) a mixture of the *endo*- and *exo*-acetates 4 and 5, in which the proportion of endo isomer never exceeded 25%. *exo*-Acetate 5 could be obtained free of endo isomer by careful distillation at reduced pressure; pure *endo*-acetate 4 was prepared by acetylating the *endo*-alcohol 6.[14]

The assignment of stereochemistry to these acetates was made in the first instance on the basis of their ^{13}C NMR spectra (Table I), which show the expected deshielding of C_{12} (6.29 ppm) in the axial (endo) epimer. Similar deshielding of C-12 (10.09 ppm) in the derived alcohols and the subsequent chemical behavior of those alcohols confirm the assignment.

Scheme I[a]



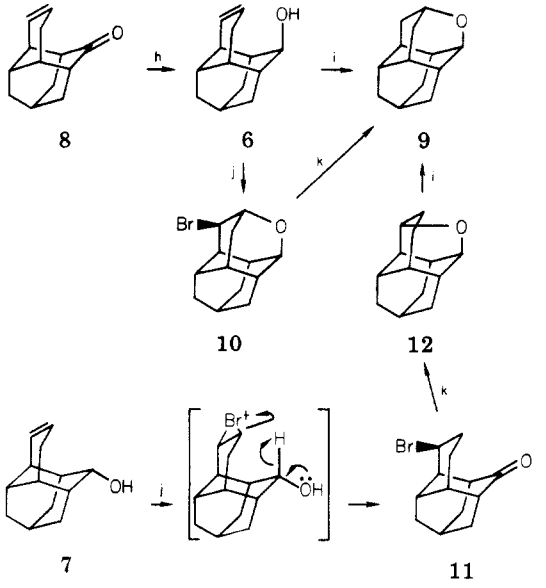
[a] Reagents: a = H_2SO_4, 75 °C; b = NaN_3, $MeSO_3H$; c = $Pb(OAc)_4$, AcOH; d = $LiAlH_4$, ether; e = LDA, O_2, H_2O; f = 25 °C; g = CrO_3, acetone.

Lithium aluminum hydride reduction of the mixture of 4 and 5 gives in 90% yield a mixture of the *endo*- and *exo*-alcohols, from which pure *exo*-7 can be obtained by recrystallization. Jones oxidation of the individual alcohols, or a mixture of the two, yields 85% of ketone 8, the spectral properties of which (Table I; Experimental Section) are in accord with the assigned structure.

The overall yield of 8 achieved by this pathway is only 20% at best, owing to the unreliability of the lead tetraacetate oxidation. Hence, we investigated the second decarboxylation shown in Scheme I. In a variation of

(9) W. Ammann, R. A. Pfund, and C. Ganter, *Chimia*, **31**, 61 (1977).
(10) O. Vogl, B. C. Anderson, and D. M. Simons, *Tetrahedron Lett.*, 415 (1966); *J. Org. Chem.*, **34**, 204 (1969). It was Vogl and his co-workers who suggested the name diamantane for this ring system.
(11) T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Perkin Trans. 1*, 2691 (1972).
(12) F. Blaney, D. Faulkner, and M. A. McKervey, *Synth. Commun.*, **3**, 435 (1973).
(13) T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).
(14) All intermediates gave satisfactory elemental analyses, save thione 18, which was not isolated.

Scheme II[a]



[a] Reagents: h = $LiAlH_4$, ether; i = 50% H_2SO_4; j = NBS, H_3O^+, dioxane; k = $LiAlH_4$, ether.

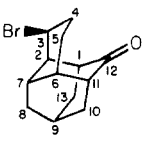
methods developed by Corey[15] and Wasserman,[16] we generated the dianion of **3** by reaction with excess lithium diisopropylamide in tetrahydrofuran (THF); oxygenation of the cold dianion solution, followed by quenching with water, gives the α-hydroperoxycarboxylate anion **3a**. Decarboxylation occurs upon warming the solution to room temperature to produce **8** in 93% yield.

Reduction of **8** with lithium aluminum hydride in refluxing ether gives exclusively the *endo*-alcohol **6** in 87% yield. Comparison of the ^{13}C NMR spectrum of **6** with that of its exo epimer **7** confirms the stereochemical assignment, both in the chemical shift of C-12 as noted above and in the substantial change induced in the chemical shift difference of the olefinic carbons (Table I). In **7**, these differ by 2.55 ppm, whereas in **6**, the difference is 6.43 ppm; the change may be a result either of steric compression or of intramolecular hydrogen bonding[17] in **6**.

The conversion of **6** to 3-oxadiamantane is shown in Scheme II. Stirring **6** with 50% aqueous sulfuric acid[18-20] for 24 h at room temperature gives 3-oxadiamantane (**9**) in 73% yield (61% from acid **3**). The reaction presumably involves protonation of the double bond, and intramolecular capture of the resulting carbocation. The structure of **9** is confirmed by the remarkably high melting point (178–180 °C) typical of adamantanes[7] and by the nine-line ^{13}C NMR spectrum (Table IV), indicative of C_s symmetry.

Interestingly, there is no indication of the formation of the isomeric 3-oxapentacyclo[8.3.1.$0^{2,8}$.$0^{4,13}$.$0^{7,12}$]tetradecane (3-oxaprotodiamantane, **12**) which would be produced by protonation and capture in the opposite sense. This is consistent with the expected higher energy of a transition state leading to the more strained **12**.

Table II. ^{13}C NMR Spectrum of Bromo Ketone 11



resonance[a]	lanthanide shift[b]
219.38 (s, C-12)	--
56.26 (d, C-3)	1.55
52.33 (d, C-1 or C-11)	4.83
52.33 (d,[c] C-11 or C-1)	4.30
50.75 (d, C-2)	2.90
42.14 (d, C-6)	3.00
41.38 (t, C-4)	3.95
37.16 (t, C-8)	1.55
29.37 (t,[c] C-13 or C-10)	2.20
29.37 (d,[c] C-7)	1.98
26.95 (t, C-10 or C-13)	2.55
26.86 (d, C-9)	1.83
26.80 (t, C-5)	1.95

[a] In parts per million downfield from Me_2Si in $CDCl_3$ solution. Letters in parentheses are multiplicities in off-resonance decoupled spectra: s = singlet, d = doublet, and t = triplet. [b] Calculated in parts per million for a 1:1 molar ratio of **11** and Eu(dpm)$_3$. [c] Resolved by Eu(dpm)$_3$.

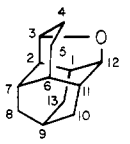
Treatment of **6** with *N*-bromosuccinimide (NBS) in aqueous acidic dioxane leads to 5-bromo-3-oxadiamantane (**10**) in 60% yield by intramolecular interception of the initially formed bromonium ion. The ^{13}C NMR spectrum of **10** consists of only 12 lines; however, introduction of Eu(dpm)$_3$ shift reagent into the NMR sample resolves the signal at 35.83 ppm into two resonances. The stereochemistry of **10** (Br anti to O) is assigned on the basis of the upfield shifts of C-11 (5.50 ppm) and C-14 (5.68 ppm) produced by the γ effect of axial bromine.[21] Further structure proof of **10** is its reduction to **9** by lithium aluminum hydride (LAH) in refluxing tetrahydrofuran. Here too, there is no evidence for formation of a bromooxaprotodiamantane by capture of the bromonium ion in the opposite sense.

Reaction of *exo*-alcohol **7** with aqueous acidic NBS leads, remarkably, to the bromo ketone **11** (57%). We view this transformation as involving an intramolecular hydride shift in the bromonium ion (Scheme II), of a kind that is well documented in bicyclo[3.3.1]nonanes.[22] Such a shift is facilitated by the formation of a protonated carbonyl and accounts nicely for both the regio- and stereoselectivity of the reaction.

The structure of **11** rests upon its subsequent chemistry and its ^{13}C NMR spectrum (Table II). As with **10**, the spectrum of **11** consists of fewer than the anticipated number of lines (11) and, indeed, initially led us to an incorrect assignment of structure. However, use of the Eu(dpm)$_3$ shift reagent resolves the peak at 52.33 ppm into two, and likewise the peak at 29.37 ppm into two, thus accounting for all 13 carbons of **11**. The axial stereochemistry is assigned by analogy to **10**, which is formed in a mechanistically similar fashion, by the result of its subsequent reduction, which requires anti placement of alkoxide ion and bromine, and by the presence in the ^{13}C NMR spectrum of two upfield resonances at 29.37 ppm (a doublet) and 26.80 ppm (a triplet) not present in the

(15) E. J. Corey, R. H. Wollenberg, and D. R. Williams, *Tetrahedron Lett.*, 2243 (1977).
(16) H. H. Wasserman and B. Lipschutz, *Tetrahedron Lett.*, 1731, 4611 (1975).
(17) P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).
(18) H. Stetter, P. Tacke, and J. Gartner, *Ber. Dtsch. Chem. Ges.*, **99**, 1435 (1966).
(19) H. Stetter and V. Tillmanns, *Ber. Dtsch. Chem. Ges.*, **105**, 735 (1972).
(20) C. A. Grob and H. Katayama, *Helv. Chim. Acta*, **60**, 1890 (1977).
(21) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972.
(22) G. Ourisson, L. Stehelin, and L. Kanellias, *J. Org. Chem.*, **38**, 847, 851 (1973).

Table III. ^{13}C NMR Spectrum of Oxaprotodiamantane 12



shift[a]	mult[b]	shift[a]	mult[b]
80.07	d (C-3 or C-12)	35.99	t
78.43	d (C-12 or C-3)	35.12	t
41.61	d	32.03	t
41.55	d	29.91	d
40.99	d	25.71	d
39.58	t	25.11	d
		23.94	t

[a] In parts per million downfield from internal Me_4Si in $CDCl_3$ solution. [b] Multiplicities in off-resonance decoupled spectra: d = doublet, and t = triplet.

spectrum of 8. We attribute these peaks to an upfield shift of C-5 and C-7 by the γ effect of axial bromine.

Upon reduction with lithium aluminum hydride in refluxing ether, 11 gives directly 3-oxaprotodiamantane (12, 85%). The structure of 12 is confirmed by its *low* melting point (89 °C), by its 13-line ^{13}C NMR spectrum (Table III), and by its rearrangement to 3-oxadiamantane (9) when stirred with 50% sulfuric acid. We believe this latter reaction, which can be rationalized by a series of protonation–deprotonation equilibria, to be the first example of a *hetero*adamantane rearrangement.

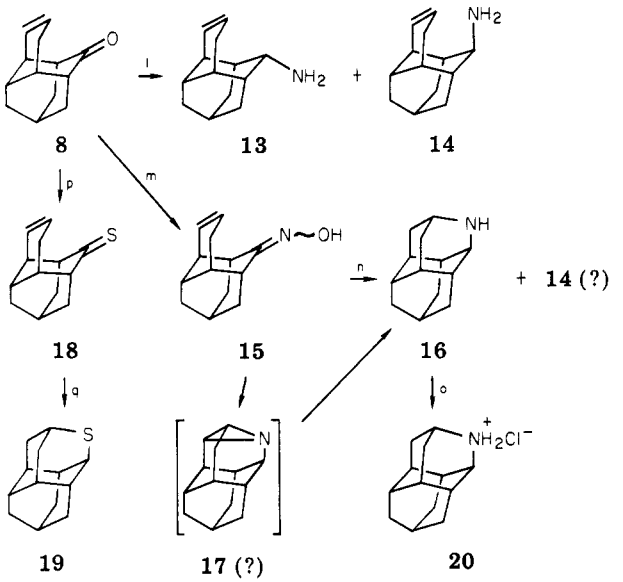
Incidentally, the formation of 9 by rearrangement is much slower (ca. 3 times) than its formation by the ring closure of 6; hence, the formation of 9 exclusively in that reaction is not the result of rearrangement of any 12 that might have been produced.

Our routes to azadiamantane and thiadiamantane are shown in Scheme III. Reductive amination of 8 with ammonium acetate and sodium cyanoborohydride leads to a mixture of the *exo*- and *endo*-amines 13 and 14 (60%, 3:2 endo/exo). Rather than separate these and accept the consequent loss of exo material, we chose to try another reaction, employing a bulkier reducing agent, in hopes of obtaining pure 14.

Thus, 8 was reacted with hydroxylamine in pyridine to yield oxime 15 as a mixture of diastereomers (80%). Lithium aluminum hydride reduction of 15, however, produces no more than a trace of 14. The major product, in 75% yield (58% from 3), is 3-azadiamantane (16) itself. The structure of 16 is established by the ^{13}C NMR spectra of 16 and its hydrochloride 20, which have the nine lines appropriate to C_s symmetry, and by the high melting point (216–218 °C).

We have no solid evidence regarding the mechanism of this striking transformation. However, it can be demonstrated that 14 is *not* an intermediate: the mixture of 13 and 14 received in reductive amination was subjected to the reaction conditions, including the acidic workup, and was recovered unchanged. On the other hand, the lithium aluminum hydride reduction of oximes has been suggested to involve a nitrene intermediate.[23] In our case, the nitrene might cycloadd to the double bond to produce aziridine 17. Although ring opening of aziridines by LAH is uncommon and indeed, aziridines have been isolated from LAH reductions of oximes,[24-26] the considerable strain

Scheme III[a]



[a] Reagents: l = NH_4OAc, $NaCNBH_3$; m = NH_2OH, pyridine; n = $LiAlH_4$, ether; o = HCl (dry); p = HCl (dry), H_2S; q = $LiAlH_4$, ether.

in 17 might make it an exception to the rule. We are at present working on tests of these possibilities.

The preparation of 3-thiadiamantane is straightforward. Passage of HCl and H_2S through an ethanol solution of 8 produces the thioketone 18, which was not isolated. However, the ^{13}C NMR spectrum of the crude product showed the typical[27] thiocarbonyl resonance at 270.39 ppm, as well as the appropriate 13 lines.

Reduction of 18 with lithium aluminum hydride directly yields 19 (49% from 8). It is not clear whether 19 results from mercaptide ion addition to the double bond during reduction or (more likely) from acid-promoted mercaptan addition to the double bond during the acidic workup. The structure of 19 follows from its (again!) extremely high melting point (264–266 °C) and its nine-line ^{13}C NMR spectrum.

The synthesis of these three heterodiamantanes in good yield (45–60%) from a readily available precursor offers the opportunity of studying heteroatom participation in a stereochemically defined system and suggests the possibility of new heteroadamantane and retroheteroadamantane rearrangements. We are exploring these possibilities.

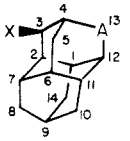
Preliminary thermodynamic investigations[28] have established that 9, 16, and 19 are the first members of a new family of plastic crystalline substances. Detailed analyses of their properties will be published elsewhere.

Experimental Section

All nuclear magnetic resonance spectra were obtained with a Varian FT-80 spectrometer. The solvent was $CDCl_3$ with Me_4Si as internal standard. Proton spectra are at 80 MHz, and carbon spectra are at 20 MHz. Infrared spectra were obtained with Perkin-Elmer 337 and 283 spectrometers; solids were run in Nujol mulls, and liquids were run neat. All elemental analyses were

(23) S. H. Graham and A. J. S. Williams, *Tetrahedron Lett.*, 3263 (1965).
(24) Y. Girault, M. Decouzon, and M. Azzaro, *Tetrahedron Lett.*, 1176 (1976).
(25) J. C. Phillips and C. Perianayagam, *Tetrahedron Lett.*, 3263 (1975).
(26) A. P. Stoll, H. R. Loosli, P. Nicklaus, and T. Zardin-Tartaglia, *Helv. Chim. Acta*, 61, 648 (1978).
(27) Reference 21, p 294.
(28) J. T. S. Andrews, S. E. Read, R. C. Fort, Jr., and V. V. Krishnamurthy, Abstracts, Northeast Regional Meeting of the American Chemical Society, Potsdam, NY, June 1980, No. 241.

Table IV. ^{13}C NMR Spectra of Heterodiamantanes



compd	A	X	resonances[a]
1	CH_2	H	38.40 (d, C-1,2,7,6,11,12), 37.68 (t, C-3,5,14,8,10,13), 25.98 (d, C-4,9)
9	O	H	74.83 (d, C-12), 65.68 (d, C-4), 24.97 (d, C-9), 37.43 (d), 36.84 (d), 36.49 (t), 36.27 (t), 36.09 (t), 36.00 (d)
10	O	Br	73.88 (d, C-12), 68.89 (d, C-4), 56.25 (d, C-3), 30.50 (d, C-7), 30.41 (t, C-5), 25.02 (d, C-9), 43.48 (d), 39.97 (d), 36.52 (t), 36.25 (d), 35.83 (t),[b] 35.83 (t),[b] 35.08 (d)
16	NH	H	55.0 (d, C-12), 44.77 (d, C-4), 25.19 (d, C-9), 38.10, 37.78, 37.57, 37.09, 36.93, 36.73
20	$NH_2^+Cl^-$	H	68.14 (d, C-12), 55.83 (d, C-4), 25.85 (d, C-9), 37.64 (t), 36.61 (t), 36.42 (d), 35.66 (d), 35.14 (d), 34.61 (t)
19	S	H	42.03 (d, C-12), 30.99 (d, C-4), 25.23 (d, C-9), 39.81 (t), 39.77 (t), 38.71 (d), 38.30 (t), 36.93 (d), 36.70 (d)

[a] In parts per million downfield from internal Me_4Si in $CDCl_3$ solution. Letters in parentheses are multiplicities in off-resonance decoupled spectra. [b] Resolved with $Eu(dpm)_3$.

performed by Galbraith Laboratories, Inc. Melting points were obtained in sealed capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected.

12-Acetoxytetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-ene (4 and 5). To 10 g (45.9 mmol) of the carboxylic acid **3** were added 120 mL of glacial acetic acid and 36.7 g (44.8 mmol) of anhydrous sodium acetate. The mixture was stirred and heated to 70 °C. Lead(IV) acetate (30 g, 60 mmol; 90% pure, 4% acetic acid) was added in three portions over 30 min. Stirring was continued for 45 min at 70 °C. The mixture then was cooled to room temperature and diluted with 200 mL of water. The resulting suspension was stirred with 200 mL of ether, and a few drops of hydrazine hydrate were added to dissolve the precipitated lead dioxide. The ether layer then was separated, washed several times with water and once with saturated sodium bicarbonate, and dried over anhydrous sodium sulfate. Removal of the ether gave an oily material from which a mixture of **4** and **5** could be distilled [112–150 °C (0.3 torr)]. Redistillation gave pure **5**, bp 145–147 °C (1.5 torr). The yield varied from 1.0 g (4 mmol, 9%) to 2.8 g (12 mmol, 26%): IR (**5**) 1735 cm^{-1} (CO); ^1H NMR (**5**) δ 5.8 (2 H, m), 1.7–2.3 (18 H, complex).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.58; H, 8.62. Found: C, 77.56; H, 8.68.

***exo*-Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-en-12-ol (7).** To a solution of 2 g (8.62 mmol) of the *exo*-acetate **5** in 50 mL of anhydrous ether was added 1.3 g (34 mmol) of lithium aluminum hydride, and the mixture was refluxed with stirring for 24 h. The excess LAH was destroyed by addition of water dropwise, and the precipitated lithium and aluminum hydroxides were dissolved in excess 10% hydrochloric acid. The ether layer was separated, washed with water, dried over anhydrous sodium sulfate, and evaporated to give nearly pure **7**. The **7** was further purified by recrystallization from methanol–water: yield 1.5 g (7.9 mmol, 91%); mp 172–174 °C; IR 3340 (OH) 1655 (C=C) cm^{-1}; ^1H NMR δ 5.8 (2 H, m), 4.2 (1 H, br s), 1.6–2.4 (15 H, complex).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 81.92; H, 9.24.

Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-en-12-one (8). Method A. A solution of 2 g (10.5 mmol) of the alcohol **7** or a mixture of **6** and **7** in 50 mL of acetone was stirred in an Erlenmeyer flask at 25 °C. To this solution was added dropwise 8 N chromic acid until the orange color persisted, the temperature being kept at 25 °C. The orange solution was then stirred at 25 °C for an additional 3 h. Most of the acetone was removed by distillation at water pump pressure, and 50 mL of water was added to the residue. The aqueous mixture was extracted twice with ether, and the combined extracts were washed with saturated sodium bicarbonate, dried over anhydrous sodium sulfate, and evaporated to give crude **8**. Sublimation on a steam bath gave pure **8**, yield 1.7 g (9.04 mmol, 86%).

Method B. A solution of 1 g (4.59 mmol) of acid **3** in 15 mL of dry tetrahydrofuran (distilled from LAH) was stirred under dry argon and cooled to 0 °C. A solution of 1.5 g (13.76 mmol) of lithium diisopropylamide in 25 mL of dry tetrahydrofuran under argon was added through a syringe to the solution of **3** at such a rate that the temperature did not rise above 10 °C. The resulting solution of the dianion of **3** was stirred at 0 °C for 3 h. It was then cooled to −78 °C with a dry ice–acetone bath, and dry oxygen was bubbled slowly through the solution for 3 h more. A mixture of 10 mL of tetrahydrofuran and 1 mL of water was added to the reaction mixture, which was then allowed to warm to room temperature and was stirred overnight. The solution was concentrated to 10 mL at water pump pressure, poured into excess 10% HCl, and extracted with ether. The ether layer was washed with 5% NaOH to remove unreacted **3**, which was recovered by acidification of the basic wash (700 mg). The ether layer was dried over anhydrous sodium sulfate and stripped to yield crude **8**. Sublimation on a steam bath at 3–5 torr gave pure **8**: 250 mg (93%, based on recovered **3**); mp 122–124 °C; IR ν_{CO} 1700, 1650 (C=C) cm^{-1}; ^1H NMR δ 5.65 (2 H, m), 1.8–2.5 (14 H, complex).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.98; H, 8.51. Found: C, 82.79; H, 8.43.

***endo*-Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-en-12-ol (6).** To a solution of 1.7 g (9.04 mmol) of ketone **8** in 50 mL of anhydrous ether was added 1.3 g (34 mmol) of lithium aluminum hydride, and the mixture was stirred and refluxed for 24 h. The excess LAH was destroyed by dropwise addition of water, and the precipitated lithium and aluminum hydroxides were dissolved in excess 10% HCl. The ether layer was separated and dried over anhydrous sodium sulfate. Removal of the solvent gave the crude but stereochemically pure **6**, which was purified by sublimation on a steam bath at water pump pressure: yield 1.5 g (7.89 mmol, 87%); mp 158–160 °C; IR 3450 (OH), 1620 (C=C) cm^{-1}; ^1H NMR δ 5.9 (2 H, m), 3.74 (1 H, s), 1.74–2.4 (15 H, complex).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 81.98; H, 9.42.

3-Oxapentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane (3-Oxadiamantane, 9). Method A. To 300 mg (1.58 mmol) of **6** was added 25 mL of 50% sulfuric acid, and the solution was stirred vigorously at room temperature for 24 h. The reaction mixture was then poured onto 100 g of ice and the mixture extracted twice with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. The crude **9** was purified by sublimation on a steam bath at water pump pressure; yield 220 mg (1.16 mmol, 73%).

Method B. To a solution of 200 mg (0.74 mmol) of **10** (vide infra) in 50 mL of dry tetrahydrofuran was added 1 g (26.3 mmol) of lithium aluminum hydride, and the mixture was refluxed with stirring for 5 days. Excess LAH was destroyed by dropwise addition of water, and the precipitated lithium and aluminum hydroxides were separated and dissolved in excess 10% HCl. A single ether extract of the acidic material was combined with the tetrahydrofuran, and the mixture was dried over anhydrous sodium sulfate. The solvents were stripped, and the residue was purified by sublimation on a steam bath at water pump pressure; yield 70 mg (0.37 mmol, 50%).

Method C. A mixture of 100 mg (0.53 mmol) of **12** and 25 mL of 50% sulfuric acid was stirred at room temperature for 3 days. The mixture was then poured into ice–water and the mixture extracted with ether. The extracts were dried over anhydrous sodium sulfate and stripped. Sublimation of the residue on a steam bath at water pump pressure gave pure **9**: yield 95 mg (0.51 mmol, 96%); mp 178–180 °C; ^{1}H NMR δ 3.93 (1 H, complex), 3.77 (1 H, complex), 1.80 (16 H, complex).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 82.35; H, 9.56.

5-Bromo-3-oxapentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane (5-Bromo-3-oxadiamantane, 10). To a suspension of 300 mg (1.58 mmol) of **6** in 20 mL of water was added enough dioxane to dissolve the solid. To this solution was added, with constant stirring, 600 mg (3.37 mmol) of freshly recrystallized *N*-bromosuccinimide. The pH of the solution was brought to about 3 by addition of drops of concentrated sulfuric acid and was maintained there for 3 h by addition of drops of acid. The mixture was then stirred overnight at room temperature and extracted with ether. The extracts were washed with 10% sodium bisulfite to remove bromine, dried over anhydrous sodium sulfate, and stripped to give crude **10**, which was purified by recrystallization from benzene–petroleum ether and subsequent sublimation on a steam bath at 0.3 torr: yield 250 mg (0.93 mmol, 59%); mp 68–70 °C; ^{1}H NMR δ 4.54 (1 H, complex), 3.94 (1 H, complex), 3.77 (1 H, complex), 1.7–2.3 (14 H, complex).

Anal. Calcd for $C_{13}H_{17}OBr$: C, 58.01; H, 6.32; Br, 29.71. Found: C, 57.78; H, 6.29; Br, 30.01.

3-Bromotetracyclo[7.3.0^{2,7}.0^{6,11}]tridecan-12-one (11). The procedure for the preparation of **10** was followed by using 500 mg (2.63 mmol) of **7** and 1 g (5.62 mmol) of NBS. Recrystallization from ethanol–water gave pure **11**: yield 400 mg (1.49 mmol, 57%); mp 122 °C; IR ν_{CO} 1710 cm^{-1}; ^{1}H NMR δ 4.5 (1 H, br s), 1.7–2.5 (16 H, complex).

Anal. Calcd for $C_{13}H_{17}OBr$: C, 58.01; H, 6.32; Br, 29.71. Found: C, 58.31; H, 6.46; Br, 30.04.

3-Oxapentacyclo[8.3.1.0^{2,8}.0^{4,13}.0^{7,12}]tetradecane (3-Oxaprotodiamantane, 12). To a solution of 250 mg (0.93 mmol) of **11** in 50 mL of anhydrous ether was added 500 mg (13.1 mmol) of lithium aluminum hydride, and the mixture was stirred and refluxed for 24 h. The excess LAH was destroyed by dropwise addition of water, and the precipitated lithium and aluminum hydroxides were dissolved in excess 10% HCl. The phases were separated, and the aqueous phase was extracted with ether. The combined ether layers were dried over anhydrous sodium sulfate and stripped; sublimation of the residue on a steam bath at water pump pressure gave pure **12**: yield 150 mg (0.79 mmol, 85%); mp 89 °C; ^{1}H NMR δ 4.33 (1 H, complex), 3.96 (1 H, complex), 1.90 (16 H, complex).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.10; H, 9.47. Found: C, 81.91; H, 9.50.

12-Aminotetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-ene (13 and 14). A solution of 500 mg (2.66 mmol) of **8**, 10 g of anhydrous ammonium acetate, and 500 mg (7.94 mmol) of sodium cyanoborohydride in 25 mL of dry methanol was refluxed with stirring for 5 days. An additional 100 mg (1.59 mmol) of borohydride was added every 24 h. The mixture was concentrated to half-volume in a stream of air and brought to pH 2 with concentrated HCl. The remainder of the solvent was evaporated, and the residue was dissolved in water. The acidic aqueous solution was extracted once with ether (which was discarded) and then basified with 10% sodium hydroxide. The precipitated solid was extracted into ether, and the ether solution was dried over anhydrous sodium sulfate and stripped. Sublimation on a steam bath at water pump pressure gave a pure mixture of **13** and **14**, yield 300 mg (1.59 mmol, 60%).

Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-en-12-one Oxime (15). To a solution of 300 mg (1.6 mmol) of **8** in a mixture of pyridine and 95% ethanol (1:1) was added 250 mg (3.6 mmol) of hydroxylamine hydrochloride, and the mixture was stirred at reflux for 3 days. Most of the solvent was evaporated in a stream of air, and the residue was taken up in 25 mL of water. An ether extract of the aqueous solution was washed with 10% HCl to extract the oxime. Neutralization of the acid wash with 10% sodium hydroxide precipitated the oxime, which was filtered off and recrystallized from ethanol–water: yield 250 mg (1.23 mmol, 77%); mp 162–165 °C dec.

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.85; H, 8.37; N, 6.90. Found: C, 76.72; H, 8.36; N, 6.72.

3-Azapentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane (3-Azadiamantane, 16). A solution of 200 mg (0.98 mmol) of **15** in 25 mL of anhydrous ether was added dropwise to a stirred suspension of 250 mg (6.58 mmol) of lithium aluminum hydride in 25 mL of anhydrous ether. The mixture was stirred at reflux for 2 days. Excess LAH was destroyed with water, and the precipitated lithium and aluminum hydroxides were dissolved in excess 25% sodium hydroxide. The resulting basic solution was extracted twice with ether, and the combined extracts were then washed with 10% HCl. Neutralization of the acidic wash with 10% sodium hydroxide precipitated **16**, which was extracted back into fresh ether. The ether solution was dried over anhydrous sodium sulfate and stripped. The crude **16** was purified by repeated sublimation on a steam bath at water pump pressure: yield 150 mg (0.74 mmol, 75%); mp 216–218 °C; ^{1}H NMR δ 2.95 (2 H, m), 1.51–1.81 (17 H complex).

Anal. Calcd for $C_{13}H_{19}N$: C, 82.54; H, 10.05; N, 7.41. Found: C, 82.30; H, 10.14; N, 7.13.

Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridec-3-ene-12-thione (18). Hydrogen sulfide was passed continuously for 2 days through a solution of 200 mg (1.06 mmol) of **8** in 15 mL of absolute ethanol. The solution was kept acidic by passing hydrogen chloride during every other 12-h period. The reaction mixture was kept at 0 °C during the passage of the gases. The resulting orange solution was extracted with 50 mL of ether in portions. The ether extracts were washed twice with water, dried over anhydrous sodium sulfate, and stripped to yield an orange semisolid. The ^{13}C NMR spectrum of this solid indicated it to be **18**, contaminated with traces of **8**. No attempt at further purification was made, and the material was used directly in the following reaction.

3-Thiapentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane (3-Thiadiamantane, 19). The crude **18** was dissolved in 100 mL of anhydrous ether, and 500 mg (13.16 mmol) of lithium aluminum hydride was added. The mixture was stirred at reflux for 2 days. Excess LAH was destroyed with water, and the precipitated lithium and aluminum hydroxides were dissolved in excess 10% HCl. The layers were separated, and the aqueous phase was extracted with 50 mL of ether. The combined ether extracts were dried over anhydrous sodium sulfate and stripped. Sublimation of the residue on a steam bath at water pump pressure gave **19**, contaminated with a small amount of **6**. This mixture was chromatographed on neutral alumina (40 × 1 cm column). Elution with hexane gave pure **19**; subsequent elution with ether gave **6**. Further purification of **19** was by sublimation on a steam bath at water pump pressure: yield (from **8**) 100 mg (0.49 mmol, 49%); mp 264–266 °C; ^{1}H NMR δ 2.68 (2 H, m), 1.76–2.41 (16 H, complex).

Anal. Calcd for $C_{13}H_{18}S$: C, 75.73; H, 8.74; S, 15.53. Found: C, 75.93; H, 8.74; S, 15.28.

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Registry No. **1**, 2292-79-7; **3**, 58801-28-8; **4**, 76173-14-3; **5**, 76231-33-9; **6**, 76173-15-4; **7**, 76231-34-0; **8**, 76173-16-5; **9**, 76173-17-6; **10**, 76173-18-7; **11**, 76173-19-8; **12**, 76173-20-1; **13**, 76173-21-2; **14**, 76231-35-1; **15**, 76173-22-3; **16**, 76173-23-4; **18**, 76173-24-5; **19**, 76173-25-6; **20**, 76173-26-7.