B. At Room Temperature. Lactone 10 (97.5 mg, 3.88 mmol) was suspended in 40 ml of 20% aqueous potassium hydroxide and stirred. The solid gradually dissolved, and after 5 days the clear, colorless solution was acidified, worked up as in A, and esterified to yield 80 mg of methyl esters. VPC examination (XF-1150 column, 200°) showed ester 7 and an unidentified by-product in a ratio of 5:1.

Acid 6 from Acid 8. A 66-mg (2.29 mmol) sample of acid 8 was stirred in 25 ml of 20% aqueous potassium hydroxide under nitrogen for several days. An aliquot worked up as described below yielded only unreacted starting material. The mixture was then refluxed for 5 hr and allowed to cool. The solution was poured into crushed ice and acidified with concentrated hydrochloric acid, and the resulting precipitate was extracted with three portions of ether. The ether extracts were washed with saturated salt solution, dried (MgSO$_4$), and rotary evaporated to yield 50 mg (88%) of acid 6. The formation of acid 6 was confirmed by esterification of the acid with ethereal diazomethane, which gave methyl ester 7 identical with an authentic sample.

Registry No.—2, 20792-01-2; **3**, 54119-85-6; **4**, 54119-86-7; **5**, 54119-87-8; **6**, 54119-88-9; **7**, 54119-89-0; **8**, 54119-90-3; **9**, 54119-91-4; **10**, 54119-92-5.

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(2) National Science Foundation Predoctoral Fellow, 1970–1973.
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Synthesis of Some 4-Substituted Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane Derivatives and Their Reactions. Cyclopropane Ring Expansion and Cleavage

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The direct photolysis of 8-cyanodeltacyclene (1) gave 4-cyanopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (2) in a high yield. 2 was converted to the corresponding carboxylic acid 4, carbinol 6, and amine 10. Buffered hydrolysis of 6 p-nitrobenzoate (7) and 3,5-dinitrobenzoate (8) afforded exclusively pentacyclo[5.3.0.0^{3,6}.0^{2,10}.0^{5,9}]decan-3-ol (9), a cyclopropylcarbinyl–cyclobutyl rearrangement product. Deamination of 10 in C$_6$H$_6$-AcOH gave unrearranged acetate 12 and rearranged acetate 13 in 7:13 ratio. Acid 4 was converted to isocyanate 18, which gave the corresponding urea and urethane derivatives 19–22 on treatment with water, aniline, ethanol, and phenol, respectively. On refluxing with KOH in ethylene glycol, 19–22 afforded a ~1:9 mixture of *exo*-and *endo*-tetracyclo[4.3.0.0^{2,9}.0^{4,8}]nonan-3-ol (23x and 23e) accompanied with a trace amount of ketone 24. The formation of the alcohols was explained by base-catalyzed cyclopropylamine rearrangement, followed by the Meerwein–Ponndorf–Verley reduction.

The chemistry of small-ring compounds combined with cage structure has in recent years received a great deal of attention.[1] We were intrigued by the possibility of obtaining novel ring system by skeletal rearrangement of these systems. In this paper we wish to describe cyclopropylcarbinyl cation and cyclopropylamine anion rearrangements by using appropriately 4-substituted pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane derivatives.

Results and Discussion

Photolysis of 8-cyanodeltacyclene (1)[2] in ether afforded a photoisomer 2 in 88% yield and a trace amount of dimer 3[3] (Scheme I). 2 was identified as 4-cyanopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane, an intramolecular $_2\pi_s + {}_2\sigma_s$ adduct, by spectral characteristics and the photochemical analogy.[4] Mass spectral molecular ion peak at m/e 143 and analysis indicated a formula C$_{10}$H$_9$N for 2. In the NMR (CDCl$_3$, 60 MHz) spectrum, 2 had characteristic signals as summarized in Table I. The lowest 4 H multiplet at δ 2.72 was assigned to H$_1$, H$_8$, H$_2$, and H$_3$ by comparison of the chemical shifts reported for 4,5-bismethoxycarbonyl[4a,d] and 4,5-dicarboxylic acid analogs[4a,b] as well as the parent

pentacyclic compound.[4b] The broad triplet at δ 2.36 was assigned to H$_5$ because of its 1 H peak area and its signal pattern.[5] The complex multiplet at δ 2.17 and broad singlet at δ 1.88 were assigned to H$_6$ and H$_7$, and H$_9$ and H$_9$', respectively. 3 had a molecular ion peak at m/e 286 (C$_{20}$H$_{18}$N$_2$) and ir (KBr) absorptions at 2250 (CN) and 814 and 790 cm^{-1} (nortricylene),[6] and hence 3 was characterized as an intermolecular $_2\pi + {}_2\pi$ photodimer.

On alkaline hydrolysis 2 afforded the corresponding carboxylic acid 4 in 90% yield. Esterification of 4 with diazomethane gave 5 quantitatively, which was reduced to carbinol 6 with lithium aluminum hydride (89%). The p-nitrobenzoate 7 and 3,5-dinitrobenzoate 8 were obtained in high yields by the usual method.[7] Lithium aluminum hydride reduction of 2 afforded the corresponding amine 10 (82%), which was characterized as its phenylurea derivative 11 (Scheme I). The structures of these derivatives were confirmed by the spectral and analytical data (Table I).[8]

On hydrolysis in 70% (v/v) aqueous dioxane in the presence of an excess amount of 2,6-lutidine at 170° for 24 hr, 7 afforded an alcoholic product 9 (40%, 77% based on 7 consumed), 6 (trace), and unreacted 7 (48%) after work-up on a

Scheme I
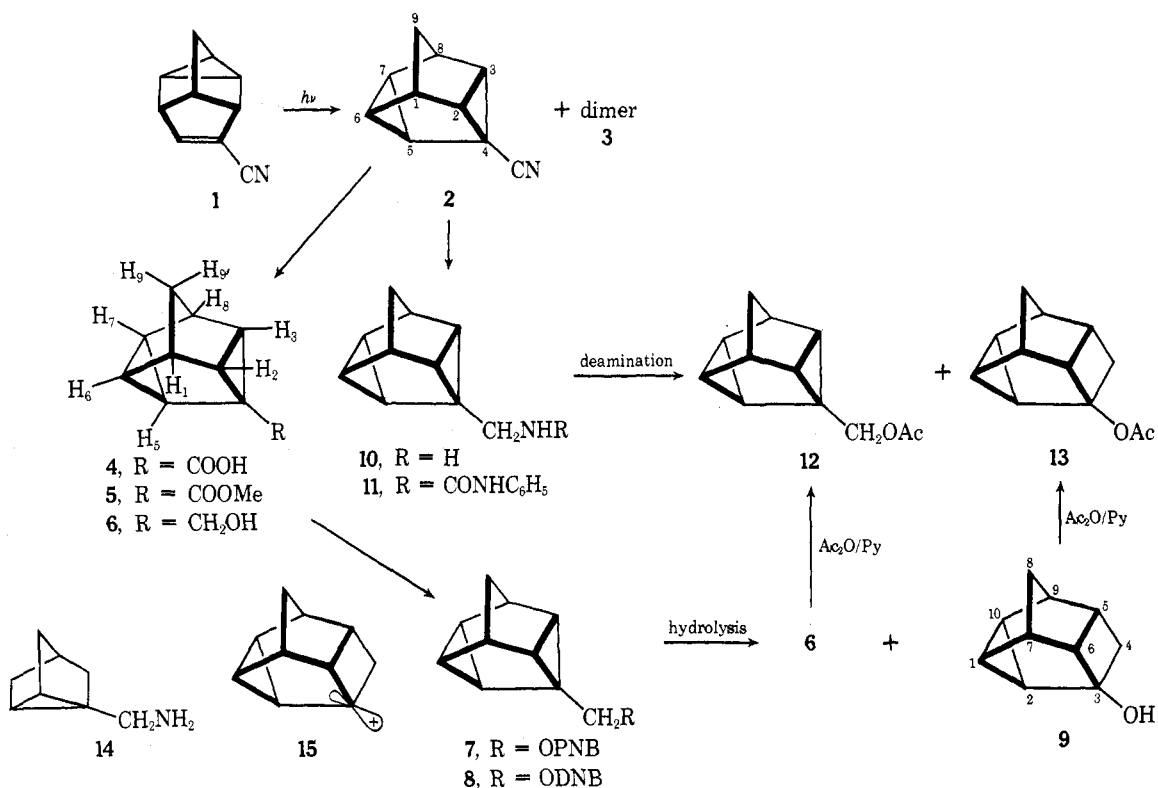
silica gel column. Similar hydrolysis of 8 at 140° for 40 hr gave 65% of 9 (83% based on 8 consumed), a trace amount of 6, and 28% of unreacted 8. Compound 9, mp 122–124°, had a formula $C_{10}H_{12}O$ on the basis of analysis and a mass spectral molecular ion peak at m/e 148. In the NMR spectrum, all protons appeared as a complex multiplet at δ 2.8–1.3, in which the signal at δ 2.30 (ca. 1 H) was assignable to OH by its disappearance on shaking with D_2O, and the absence of the signal due to $-CH_2O-$ suggested a ring-expanded structure for 9. The spectrum was well dissolved on addition of a shift reagent, tris(dipivalomethanato)europium(III) [Eu(dpm)3]. The shift gradient G^9 was calculated by the spectral change with various amounts of Eu(dpm)3 and each signal was assigned with the aid of spin–spin decoupling experiments as shown in Figure 1. The two-proton multiplet at δ 8.82–8.2 was assigned to H_2 and H_6 because of their largest G values (17.3 and 15.0). The double doublet at δ 7.98 was assigned to H_{4x} because it had a large G value (15.7) and was decoupled to a doublet

(J = 7.4 Hz), and to a doublet (J = 9.3 Hz) on irradiations of the doublet at δ 6.28 and of the signal at δ 3.6, respectively. On irradiation of the signal at δ 7.98, the doublet at δ 6.28 due to H_{4n} collapsed to a singlet, indicating that $J_{4n,4x}$ is 9.3 Hz.[10] The signal at δ 3.6 assigned to H_5 was overlapped on the AB quartet due to H_{8a} and H_{8s}, but the decoupling experiments indicated $J_{4x,5}$ to be 7.4 Hz. The dihedral angle for $H_{4n,5}$ on a Dreiding stereomodel is nearly 90°, which is in accord with $J_{4n,5}$ = 0 as observed. The other signals were also assigned as in Figure 1 by considering G values and signal pattern. Hence, 9 was identified as pentacyclo[5.3.0.0^{3,6}.0^{2,11}.0^{5,9}]decan-3-ol [or (trivial) 2,5,7,9-tetradehydroprotoadamantan-3-ol], a cyclopropylcarbinyl–cyclobutyl rearrangement product. The G values were correlated with the measured distance r between the oxygen and the hydrogen on a Dreiding stereomodel by the so-called $1/r^2$ method.[9,11] A good correlation was obtained as shown in Figure 2, supporting the above assignment.
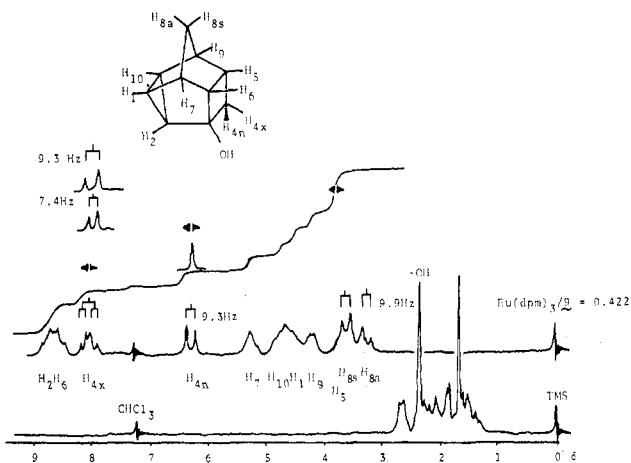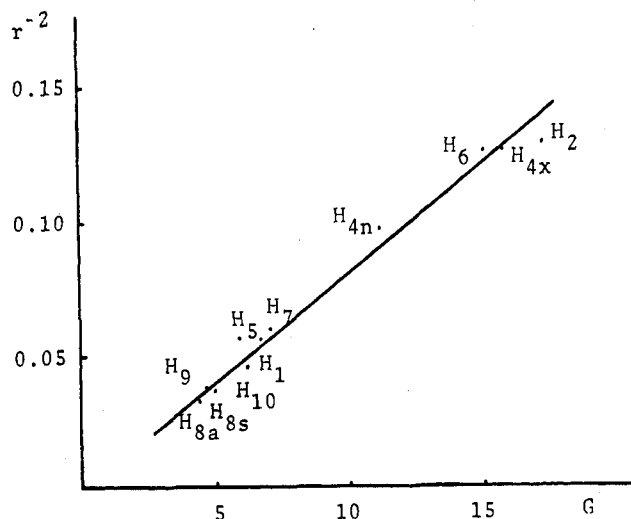

Figure 1. NMR spectra of 9 in CDCl₃ (60 MHz).

Figure 2. Graph of r^{-2} against G.

Table I
Spectral and Analytical Data of 4-Substituted
Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane Derivatives

Compd[h]	Ir, cm^{-1} (KBr)	NMR chemical shift, δ (CDCl$_3$, 60 MHz)[b]	Formula[c]
2	2250, 1300, 775, 740[a]	2.72 (m, 4 H, H$_{1,8,2,3}$), 2.36 (bt, $J = 6.0$ Hz, 1 H, H$_5$), 2.17 (cm, 2 H, H$_{6,7}$), 1.88 (bs, 2 H, H$_{9,9'}$)	C$_{10}$H$_9$N
4	2660–2400, 1670, 1300, 790, 770, 755	10.48 (s, 1 H, COOH),[d] 2.75 (m, 4 H, H$_{1,8,2,3}$), 2.50 (bt, $J = 6.0$ Hz, 1 H, H$_5$), 2.10 (cm, 2 H, H$_{6,7}$), 1.86 (bs, 2 H, H$_{9,9'}$)	C$_{10}$H$_{10}$O$_2$
5	1720, 1300, 1275, 1210, 786, 760	3.58 (s, 3 H, OMe), 2.53 (m, 4 H, H$_{1,8,2,3}$), 2.50 (bt, $J = 6.0$ Hz, 1 H, H$_5$), 2.08 (cm, 2 H, H$_{6,7}$), 1.86 (bs, 2 H, H$_{9,9'}$)	C$_{11}$H$_{12}$O$_2$
6	3360, 1300, 765, 745[a]	3.58 (d, $J = 3.6$ Hz, 2 H, CH$_2$O),[f] 3.12 (t, $J = 3.6$ Hz, 1 H, OH),[d] 2.55 (bs, 2 H, H$_{1,8}$), 2.25–1.60 (cm, 5 H, H$_{2,3,5,6,7}$), 1.82 (m, ~2 H, H$_{9,9'}$)[e]	C$_{10}$H$_{12}$O
7	1705, 1520, 1345, 1300, 1275, 1103, 780, 755	8.25 (s, 4 H, C$_6$H$_4$), 4.50 (s, 2 H, CH$_2$O), 2.65 (bs, 2 H, H$_{1,8}$), 2.11 (cm, 5 H, H$_{2,3,5,6,7}$), 1.86 (bs, 2 H, H$_{9,9'}$)	C$_{17}$H$_{15}$NO$_4$
8	1715, 1615, 1530, 1340, 1279, 1158, 717	8.87 (s, 3 H, C$_6$H$_3$), 4.45 (s, 2 H, CH$_2$O), 2.57 (bs, 2 H, H$_{1,8}$), 2.3–1.45 (cm, 7 H, H$_{2,3,5,6,7,9,9'}$)	C$_{17}$H$_{14}$N$_2$O$_6$
10	3360, 3280, 1620, 1300, 765, 745	2.85 (s, 2 H, CH$_2$N), 2.60 (bs, 2 H, H$_{1,8}$), 2.02 (bs, 2 H, H$_{2,3}$), 1.90 (cm, 5 H, H$_{5,6,7,9,9'}$), 1.84 (2, 2 H, NH$_2$)[d]	C$_{10}$H$_{13}$N
11	3360, 3280, 1640, 1600, 1300, 765	7.28 (m, 5 H, C$_6$H$_5$), 7.03 (t, $J = 4.5$ Hz, 1 H, CH$_2$NHCO),[d] 5.32 (bs, 1 H, CONHC$_6$H$_5$),[d] 3.45 (d, $J = 4.5$ Hz, 2 H, CH$_2$NH),[f] 2.59 (m, 2 H, H$_{1,8}$), 1.99 (cm, 5 H, H$_{2,3,5,6,7}$), 1.82 (bs, 2 H, H$_{9,9'}$)	C$_{17}$H$_{18}$N$_2$O
12	1735, 1372, 1300, 1240, 1025, 770[a]	4.13 (s, 2 H, CH$_2$O), 2.58 (bs, 2 H, H$_{1,8}$), 2.05 (bs, 8 H, O=CMe, H$_{2,3,5,6,7}$), 1.82 (bs, 2 H, H$_{9,9'}$)	C$_{12}$H$_{14}$O$_2$
17	2140, 1690, 1370, 1248, 1190, 734[a]	2.75 (bs, 4 H, H$_{1,8,2,3}$), 2.50 (m, 1 H, H$_5$), 2.13 (cm, 2 H, H$_{6,7}$), 1.87 (bs, 2 H, H$_{9,9'}$)	C$_{10}$H$_9$N$_3$O
18	2250, 1342, 1290, 759[a]	2.67 (bs, 2 H, H$_{1,8}$), 2.25 (m, 2 H, H$_{2,3}$), 2.06 (cm, 3 H, H$_{5,6,7}$), 1.71 (bs, 2 H, H$_{9,9'}$)	C$_{10}$H$_9$NO
19	3320, 3038, 1635, 1562, 1295, 1260, 759, 704	5.37 (bs, 2 H, 2 NH),[d] 2.68 (bs, 4 H, 2 H$_{1,8}$), 2.23 (bs, 4 H, 2 H$_{2,3}$), 2.10 (m, 6 H, 2 H$_{5,6,7}$), 1.75 (s, 4 H, 2 H$_{9,9'}$)	C$_{19}$H$_{20}$N$_2$O
20	3310, 1646, 1593, 1550, 760, 690	7.34 (m, 5 H, C$_6$H$_5$), 5.80 (m, 2 H, 2 NH),[d] 2.60 (bs, 2 H, H$_{1,8}$), 2.23 (m, 2 H, H$_{2,3}$), 2.05 (cm, 3 H, H$_{5,6,7}$), 1.70 (bs, 2 H, H$_{9,9'}$)[g]	C$_{16}$H$_{16}$N$_2$O
21	3390, 1690, 1520, 1264, 1258, 1072, 784, 772	5.21 (bs, 1 H, NH),[d] 4.41 (q, $J = 7.5$ Hz, 2 H, OCH$_2$), 2.65 (bs, 2 H, H$_{1,8}$), 2.21 (m, 2 H, H$_{2,3}$), 2.05 (m, 3 H, H$_{5,6,7}$), 1.71 (s, 2 H, H$_{9,9'}$), 1.25 (t, $J = 7.5$ Hz, 3 H, Me)	C$_{12}$H$_{15}$NO$_2$
22	3340, 3050, 1705, 1590, 1293, 1243, 764, 682	7.20 (bs, 5 H, C$_6$H$_5$), 5.55 (bs, 1 H, NH),[d] 2.66 (bs, 2 H, H$_{1,8}$), 2.30 (m, 2 H, H$_{2,3}$), 2.07 (m, 3 H, H$_{5,6,7}$), 1.71 (bs, 2 H, H$_{9,9'}$)	C$_{16}$H$_{15}$NO$_2$

a As neat film. *b* For hydrogen numbering, see Scheme I; bs = broad s, bt = broad t, cm = complex m. *c* Satisfactory analytical data for C, H, N (±0.3%) were provided for these compounds. Ed. *d* Disappeared on shaking with D$_2$O. *e* In CCl$_4$. *f* The signal became a singlet on shaking with D$_2$O. *g* In 30% (v/v) pyridine–CDCl$_3$. *h* Registry no. are, respectively, 53940-92-4, 42132-22-9, 42132-21-8, 53940-93-5, 53940-94-6, 53940-95-7, 53940-96-8, 53940-97-9, 53940-98-0, 53940-99-1, 53941-00-7, 53941-05-2, 53941-01-8, 53941-02-9, 53957-19-0.

On deamination with isoamyl nitrite in acetic acid–benzene **10** afforded acetates **12** and **13** in 7:13 ratio (58% yield). The structures of **12** and **13** were determined as the acetates of **6** and **9** respectively, on the basis of analysis, spectral data, and the same GLC retention times with samples prepared by acetylation of **6** and **9** (Scheme I).

In the above solvolysis and deamination of **7, 8,** and **10,** the formation of the ring-expansion product in higher ratio but no formation of cyclopropylcarbinyl-homoallylic rearrangement products or of secondary rearrangement products might be useful for synthesis of such strained cyclobutane derivatives combined with cage structure. However,

Scheme II

16, R = Cl
17, R = N₃

18

19, R = NH

20, R = NHC₆H₅
21, R = OEt
22, R = OC₆H₅

23x　　　23e　　　24

Scheme III

19–22 →

→ 24 → 23x + 23e
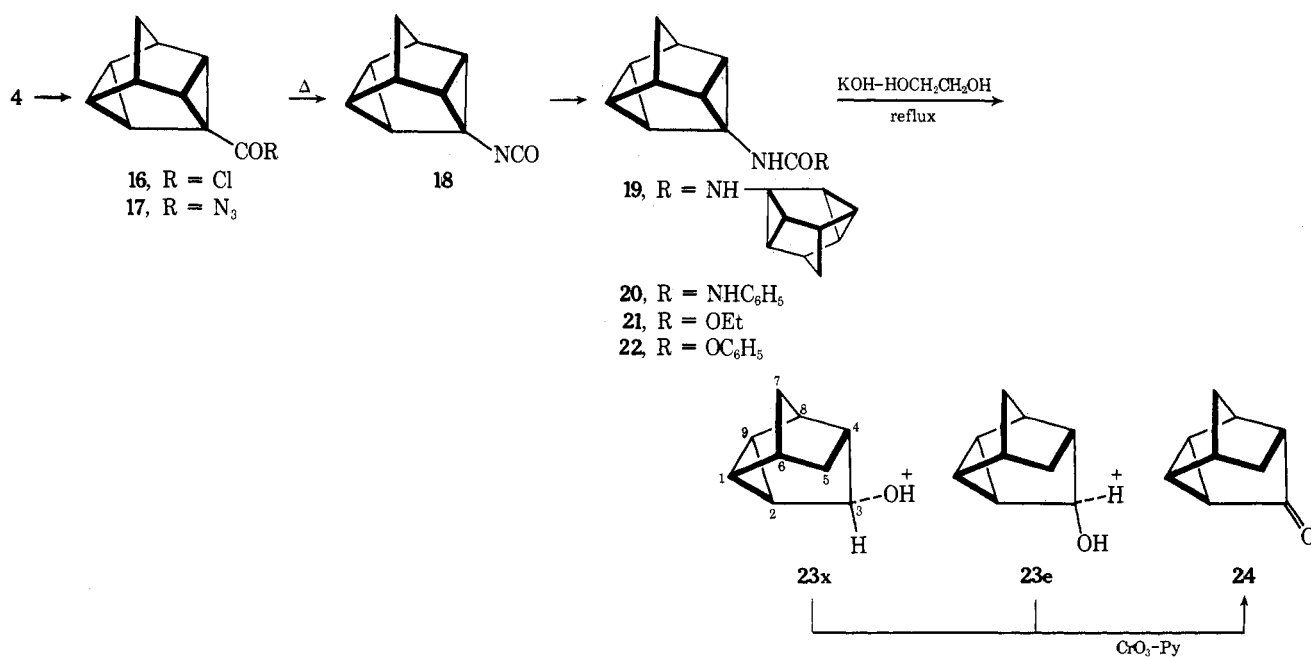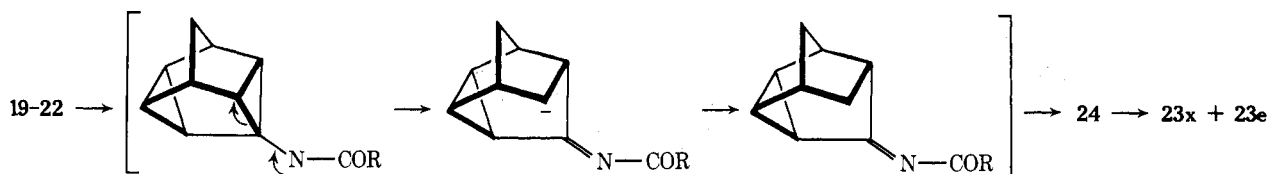
2-nortricyclylcarbinylamine (14) as one of some related systems is known to afford only unrearranged acetate as the major product on deamination.[12] For the present system the prohibition of further rearrangement of an intermediate cation 15 could be rationalized in terms of a nonbisected geometry of the cyclopropylcarbinyl cation moiety.[13,14]

Primary cyclopropylamine has recently been shown to rearrange with base, similar to the well-known cyclopropanol rearrangement.[15] For example, 1-methyl-2,2-diphenylcyclopropylamine gives 4,4-diphenyl-2-butanone on treatment with aqueous sodium bicarbonate at room temperature.[15] The present pentacyclic system was converted to appropriate cyclopropylamine derivatives 19–22 and their base-catalyzed rearrangement was examined (Scheme II).

Carboxylic acid 4 was converted to the corresponding carbonyl azide 17 via acid chloride 16, which on heating in refluxing benzene afforded isocyanate 18 as an oil in 89% overall yield from 4. 18 gave the corresponding urea and urethane derivatives 19–22 on treatment with water, aniline, ethanol, and phenol, respectively. The structures of these derivatives were confirmed by analytical and spectral data (Table I). In the nmr spectra, 19–22 revealed characteristic signals due to the pentacyclo[4.3.0.0²,⁴.0³,⁸.0⁵,⁷]nonane moiety in 2:2:3:2 ratio at δ 2.68–1.70.

Treatment of bisurea 19 with sodium bicarbonate in 20% aqueous ethanol at 80° for 3 days resulted only in recovery of 19. However, on refluxing with potassium hydroxide in ethylene glycol 19 afforded crystalline products in 73% yield, which on GLC analysis revealed three peaks (23x, 23e, and 24) in 10:89:1 ratio. The major product 23e was isolated after repeated sublimations, mp 141–143°, and had a formula C₉H₁₂O on the basis of analysis and mass spectral molecular ion peak at m/e 136. Ir (KBr) absorption at

3400 cm⁻¹ indicated 23e to be an alcohol, and the NMR (CDCl₃, 100 MHz) spectrum after addition of Eu(dpm)₃ [Eu(dpm)₃/23e = 0.12] had signals at δ 12.9 (broad s, 1 H, OH), 7.60 (d, J = 6.0 Hz, 1 H, H₃), 4.05 (d, J = 12.0 Hz, 1 H, H₅), 3.44 (m, 1 H, H₄), 3.05 (m, 3 H, H₂, H₆, H₈), and 2.25–1.70 (m, 5 H, other protons). From these spectral data 23e was characterized as *endo*-tetracyclo[4.3.0.0²,⁹.0⁴,⁸]-nonan-3-ol. Conclusive evidence for the structure assigned was obtained by oxidation (Sarett) of 23e to the known tetracyclo[4.3.0.0²,⁹.0⁴,⁸]nonan-3-one (24), mp 89.5–9.5° (lit.[16] mp 90.5–92°), which was identified with an authentic sample by ir and NMR spectal comparison.[17] The minor product 24 in the above base-catalyzed reaction was identified as this ketone also by the same GLC retention times. The second major product 23x, was identified as an exo isomer of 23e because comparison of the NMR spectrum of the mixture with that of 23e indicated that 23x had a characteristic H₃ signal at δ 4.15 as unsymmetrical triplet (J ≃ 1.5 Hz),[17,18] and oxidation (Sarett) gave the ketone 24 on GLC analysis. Under the same conditions 20–22 afforded also 23x and 23e in ~1:9 ratio accompanied with a trace amount of 24 (Scheme III).

The formation of 23x and 23e can be rationalized by considering an initial cyclopropylamine rearrangement to give 24, followed by its Meerwein–Ponndorf–Verley reduction.[19]

These results are of interest in view of the applicability of base-catalyzed cyclopropylamine rearrangement to urea and urethane derivatives also.

Experimental Section[20]

Photolysis of 8-Cyanodeltacyclene (1). A solution of 1[2] (4.0 g, 28 mmol) in ether (1.0 l.) was irradiated through a quartz jacket with a 300-W high-pressure mercury lamp under nitrogen at ~5° for 49 hr. After removal of the solvent, an oily residue (4.8 g) was

purified on a silic gel column eluting with n-hexane-CH_2Cl_2 to afford 4-cyanopentacyclo[4.3.0.0^{2,4}.0^{3,8}0^{5,7}]nonane (2) as the first fraction (3.53 g, 88%), mp 48–49°.

The second fraction gave 3 (20 mg, 1%): mp 187–190°; NMR (CDCl$_3$, 60 MHz) δ 2.50 (m, 4 H), 2.12 (m, 4 H), 1.72 (broad s, 4 H), 1.35 (m, 4 H), and 1.05 (m, 2 H).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.82; H, 6.43; N, 9.76.

Similar irradiation of 1 in n-hexane gave 2 and 3 in yields of 13 and 35%, respectively. Irradiation of 1 in acetone gave 2 (39%) and an acetone adduct as an oil (20%), n^{19}D 1.5296.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.45; H, 7.57; N, 7.26.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic Acid (4). A mixture of 2 (3.31 g, 23.2 mmol), potassium hydroxide (25.5 g), water (85 ml), and ethanol (7 ml) was refluxed under nitrogen for 18 hr. Neutralization of the cooled mixture with 10% hydrochloric acid afforded 4 as colorless crystals (3.39 g, 90%): mp 169–170°; mass spectrum m/e 162 (M^+) and 117 (M – CO_2H).

Methyl Ester 5 from 4. Treatment of 4 with a ca. threefold excess amount of diazomethane in ether gave the corresponding methyl ester 5 quantitatively after removal of the solvent and excess diazomethane as an oil which on standing crystallized, mp 55–56°.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-methyl Alcohol (6). A mixture of 5 (360 mg, 2.04 mmol) and lithium aluminum hydride (400 mg, 10.5 mmol) in dry ether (30 ml) was stirred for 15 hr. After decomposition of the excess reagent by addition of water, the mixture was extracted with ether (5 × 30 ml) and dried (Na$_2$SO$_4$). Removal of the solvent gave carbinol 6 as an oil (270 mg, 89%), n^{22}D 1.5223.

p-Nitrobenzoate (7) of 6. To an ice-cooled and stirred mixture of p-nitrobenzoyl chloride (560 mg, 3.26 mmol) in pyridine (3.5 ml) was added a solution of 6 (400 mg, 2.70 mmol) in pyridine (3.5 ml). After stirring was continued for 2 hr at room temperature, the mixture was poured onto ice–water (50 ml) to afford faintly yellowish crystals which were filtered and recrystallized from aqueous ethanol to give analytically pure 7 (565 mg, 70%), mp 69–70°.

3,5-Dinitrobenzoate (8) of 6. To an ice-cooled and stirred mixture of 3,5-dinitrobenzoyl chloride (1.169 g, 5.07 mmol) in pyridine (5 ml) was added a solution of 6 (0.750 g, 5.07 mmol) in pyridine (3 ml). After stirring was continued for 3 hr at room temperature, the mixture was poured onto ice–water (50 ml). Resulting precipitates were collected and recrystallized from ethanol to give 8 as needles (1.38 g, 79%), mp 97–98°.

Hydrolysis of 7 and 8. A mixture of 7 (250 mg, 0.875 mmol) and 2,6-lutidine (360 mg, 3.36 mmol) in 70% dioxane–water (v/v) (20 ml) was heated in a sealed tube under nitrogen for 24 hr at 170°. The cooled mixture was diluted with water (50 ml) and extracted with ether (4 × 50 ml). The combined extracts were washed with 10% hydrochloric acid (3 × 50 ml), saturated aqueous sodium bicarbonate (3 × 50 ml), and water (50 ml) successively and dried (Na$_2$SO$_4$). After removal of the solvent, the residue was purified on a silica gel column eluting with chloroform. The first fraction gave unreacted 7 (120 mg, 48% recovery) and the second fraction afforded **pentacyclo[5.3.0.0^{3,6}.0^{2,10}.0^{5,9}]decan-3-ol (9)** as crystals which were sublimed to afford an analytical sample (52 mg, 40%), mp 122–124°.

GLC analysis of the crude product indicated that a trace amount of unrearranged alcohol 6 was also produced.

A similar hydrolysis of 8 at 140° for 40 hr and work-up as above afforded 9 (65%), 6 (trace), and unreacted 8 (28%).

Lithium Aluminum Hydride Reduction of 2. A mixture of 2 (0.80 g, 5.6 mmol) and lithium aluminum hydride (0.42 g, 11 mmol) in dry ether (30 ml) was stirred at room temperature for 1 day. After decomposition of the excess reagent by addition of water, the mixture was extracted with ether (6 × 30 ml). The combined extracts were dried (Na$_2$SO$_4$) and the solvent was removed to give crude product which was purified by sublimation (100°, 23 mm) to afford **pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-methylamine (10)** as colorless crystals (0.67 g, 82%), mp 86–88°.

Stirring of a mixture of 10 (40 mg, 0.27 mmol) and phenyl isocyanate (40 mg, 0.33 mmol) in benzene (5 ml) for 0.5 hr at room temperature afforded colorless precipitates which were collected and recrystallized from ethanol to give phenylurea derivative 11 (60 mg, 67%), mp 181–183°.

Acetylation of 6. A mixture of 6 (50 mg, 0.34 mmol) and acetic anhydride (48 mg, 0.47 mmol) in dry pyridine (0.25 ml) was stirred at room temperature for 15 hr. After addition of water (10 ml) the mixture was extracted with chloroform (2 × 10 ml) and the com-

bined extracts were washed with water (5 ml) and dried (Na$_2$SO$_4$). Removal of the solvent gave an oily residue which was purified on a silica gel column (CHCl$_3$) to give 4-pentacyclo[4.3.0.0^{2,4}.-0^{3,8}.0^{5,7}]nonylcarbinyl acetate (12) as a viscous oil (50 mg, 78%), n^{20}D 1.5022.

Deamination of 10. A mixture of 10 (1.0 g, 6.8 mmol), acetic acid (0.40 g, mmol), and isoamyl nitrite (0.81 g, 6.1 mmol) in benzene (13 ml) was refluxed for 4 hr. After removal of the solvent the residue was chromatographed on a silica gel column eluting with benzene to give an acetate mixture (0.73 g, 58%) which on GLC analysis revealed two peaks in 13:7 ratio. The mixture was purified by preparative GLC (30% silicone SE-30 on 45/60 mesh Chromosorb W at 165°). The minor product, however, decomposed under the GLC conditions employed but it was characterized as the unrearranged acetate 12 based upon the same retention times as an authentic sample. The major product was isolated as a viscous oil which was identified as the rearranged acetate 13: ir (neat) 1735, 1250, and 1016 cm^{-1}; nmr (CDCl$_3$, 60 MHz) δ 2.93 (m, 1 H), 2.67 (m, 1 H), 2.38 (m, 1 H), 2.24 (m, 1 H), 2.01 (s, 3 H), 2.13–1.9 (m, 5 H), 1.75 (d, J = 9.0 Hz, 1 H), and 1.59 (d, J = 9.0 Hz, 1 H).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.92; H, 7.26.

Acetylation of 9. A mixture of 9 (11.0 mg, 0.0743 mmol) and acetic anhydride (20.4 mg, 0.200 mmol) in pyridine (0.3 ml) was heated at 75° for 5 hr. The cooled mixture was diluted with chloroform (10 ml), washed with water (2 × 10 ml), and dried (Na$_2$SO$_4$). Removal of the solvent gave crude acetate, which was purified on a silica gel column (CHCl$_3$) to give acetate 13 as a viscous oil (13.0 mg, 93%), n^{20}D 1.5028, which was identical with the sample from deamination by ir and GLC comparisons.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carbonyl Azide (17). A mixture of 4 (973 mg, 6.00 mmol) and thionyl chloride (5.0 ml, 8.35 g, 70.0 mmol) in n-pentane (50 ml) was stirred for 87 hr at room temperature. Removal of the solvent and excess reagent under reduced pressure gave crude acid chloride, to which dry benzene (5 ml) was added and the solvent was removed under reduced pressure repeatedly to give acid chloride 16 as an oil (1.08 g, 100%), ir (neat) 1770 cm^{-1}.

To an ice-cooled and stirred solution of 16 (0.54 g, 3.0 mmol) in dry acetone (10 ml) was added sodium azide (0.60 g, 9.2 mmol) in water (3 ml) and the mixture was stirred for 4 hr at room temperature. Diluted mixture with water (80 ml) was extracted with ether (3 × 50 ml). The combined extracts were washed with saturated sodium bicarbonate solution (3 × 30 ml) and dried (Na$_2$SO$_4$), and removal of the solvent under reduced pressure afforded 17 as an oil (0.50 g, 89%).

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-4-isocyanate (18). A solution of 17 (1.00 g, 5.35 mmol) in dry benzene (25 ml) was added dropwise to refluxing dry benzene (65 ml) in 40 min and the refluxing was continued for 3 hr. The solvent was removed under reduced pressure (25 mm) to afford 18 as an oil (0.850 g, 100%) which was practically pure. An analytical sample was obtained after dry distillation (80°, 0.2 mm), n^{19}D 1.5240.

N,N'-Bis-4-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonylurea (19). A mixture of 18 (971 mg, 6.10 mmol) in 50% aqueous tetrahydrofuran (35 ml) was stirred for 1 day at room temperature. Concentration of the mixture to ∼20 ml afforded colorless precipitates (645 mg) which were collected and recrystallized from methylene chloride to give 19 (530 mg, 59%), mp 259–260° dec.

N-Phenyl-N'-4-pentacyclo[4.3.0.0^{2,4}0^{3,8}.0^{5,7}]nonylurea (20). A mixture of 18 (40 mg, 0.25 mmol) and aniline (24 mg, 0.26 mmol) in dry benzene (3 ml) was stirred for 0.5 hr at room temperature. The resulting precipitates were filtered and washed with benzene to give 20 as colorless crystals which were analytically pure (60 mg, 95%), mp 261–262°.

Ethyl N-4-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonylcarbamate (21). A mixture of 18 (330 mg, 2.08 mmol) and pyridine (0.1 ml) in ethanol (10 ml) was refluxed for 17 hr. Concentration of the mixture gave crude product which was recrystallized from ethanol to give 21 as colorless crystals (285 mg, 67%), mp 79–81°.

Phenyl N-4-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonylcarbamate (22). A mixture of 18 (460 mg, 2.89 mmol), phenol (315 mg, 3.35 mmol), and potassium hydroxide (10 mg) in benzene (9 ml) was stirred for 15 hr at room temperature. Removal of the solvent gave crude product which was recrystallized from n-hexane to give 22 as colorless crystals (270 mg, 37%), mp 132–134°.

Base-Catalyzed Rearrangement of 19. A mixture of 19 (274 mg, 0.971 mmol) and potassium hydroxide (21 g) in ethylene glycol (50 ml) was refluxed for 15 hr under nitrogen. A colorless solid was sublimed at the refluxing condenser, which was taken up in ether.

The reaction mixture was diluted with ice–water (200 ml) and extracted with ether (5 × 50 ml). The combined extracts and sublimed portion were washed with water (30 ml) and dried (Na_2SO_4). Removal of the solvent afforded a colorless solid (185 mg, 73%) of a 10:89:1 mixture of 23x, 23e, and 24 (GLC analysis). Three sublimations of the mixture (100°, 25 mm) gave pure *endo*-tetracyclo[4.3.0.0^{2,9}.0^{4,8}]nonan-3-ol (23e) as a colorless solid (79 mg, 30%): mp 141–143° (lit.[21] mp 143.5–145.5°); mass spectrum m/e 136 (M$^+$); NMR (CDCl$_3$, 100 MHz) δ 4.55 (d, J = 6.0 Hz, 1 H, H$_3$), 1.95 (s, ~1 H, OH, disappeared on shaking with D$_2$O), and 2.7–0.8 (m, 10 H, other protons).

Anal. Calcd for C$_9$H$_{12}$O: C, 79.37; H, 8.88. Found: C, 79.27; H, 8.98.

In the nmr spectrum of the mixture, an unsymmetrical triplet signal was observed at δ 4.15 (H$_3$ of 23x) in addition to others overlapped with the signals due to 23e. The integral ratio of the signals at δ 4.55 (H$_3$ of 23e) and 4.15 (H$_3$ of 23x) was 9:1.

Oxidation of 23e to Tetracyclo[4.3.0.0^{2,9}.0^{4,8}]nonan-3-one (24). To an ice-cooled and stirred mixture of chromic anhydride (200 mg, 2.00 mmol) in pyridine (4 ml) was added 23e (136 mg, 1.00 mmol) and the mixture was stirred for 2 days at room temperature. The diluted mixture with water (60 ml) was extracted with ether (3 × 20 ml) and the combined extracts were washed with water (10 ml) and dried (Na_2SO_4). Removal of the solvent gave crude product (80 mg) which was purified by preparative TLC (silica gel, CHCl$_3$) to afford 24 as colorless crystals (45 mg, 34%), mp 89.5–90.5° (lit.[16] mp 90.5–92°). 24 gave a 2,4-dinitrophenylhydrazone, mp 196–198° (lit.[16] mp 210–211°).

Oxidation of the mixture of 23x and 23e gave also 24 (GLC analysis).

Base-Catalyzed Rearrangement of 20–22. A mixture of 20 (or 21, or 22) (5 mg) and potassium hydroxide (0.5 g) in ethylene glycol (3 ml) was refluxed for 15 hr under nitrogen. The mixture was diluted with water (10 ml) and extracted with ether (3 × 10 ml). The combined extracts were dried (Na$_2$SO$_4$), concentrated to ~2 ml, and analyzed on GLC.

References and Notes

(1) For some examples related to adamantane and noradamantane, see (a) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968); (b) H. W. Geluk and T. J. De Boer, *Tetrahedron*, **28**, 3351 (1972); (c) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968); (d) R. M. Coates and J. L. Kirpatrick, ibid., **92**, 4883 (1970); P. v. R. Schleyer and R. E. Leone, ibid., **90**, 4164 (1968); (e) B. R. Ree and J. C. Martin, ibid., **92**, 1660 (1970); V. Buss, R. Gleiter, and P. v. R. Schleyer, ibid., **93**, 3927 (1971); (f) K. J. Shea and P. S. Skell,

ibid., **95**, 6728 (1973); (g) J. E. Baldwin and M. W. Grayston, ibid., **96**, 1629 (1974).
(2) T. Sasaki, S. Eguchi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, **37**, 2317 (1972). The yield of 1 in the homo-Diels–Alder reaction of norbornadiene with cyanoacetylene was improved up to 52% from 31% by using a catalytic amount of polymerization inhibitor such as hydroquinone.
(3) Photolysis of 1 in *n*-hexane afforded 2 and 3 in yields of 13 and 35%, while photolysis in acetone gave 2 and an acetone adduct in yields of 39 and 20%, respectively.
(4) (a) C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donely, *Chem. Commun.*, 419 (1966); (b) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967); (c) E. Wiskot and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **6**, 694 (1967); (d) H. Prinzbach and D. Hunkler, ibid., **6**, 247 (1967); see also ref 1d.
(5) For the characteristic long-range coupling between H$_5$ and H$_9'$, see ref 1d.
(6) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Am. Chem. Soc.*, **92**, 2051 (1970).
(7) For example, cf. R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed, Wiley, New York, N.Y., 1965; see also ref 1c.
(8) Compounds 5, 6, and 12 have been synthesized recently by heavy metal ion (e.g., Ag$^+$) catalyzed rearrangement of 4-substituted homocubane derivatives but detailed characterization seems not to be reported: L. A. Paquette and J. S. Ward, *Tetrahedron Lett.*, 4909 (1972); L. A. Paquette, *Acc. Chem. Res.*, **4**, 280 (1971).
(9) For a recent review on the lanthanide shift reagent, see A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
(10) For geminal coupling constants of methylene group in cyclobutane derivatives, see R. Cahill, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, **25**, 4724 (1969).
(11) This is an approximate method but many successful applications have been reported, especially for rigid system such as adamantanol; A. F. Cockerill and D. M. RacKham, *Tetrahedron Lett.*, 5153 (1970).
(12) H. Hart and R. A. Martin, *J. Am. Chem. Soc.*, **82**, 6362 (1960).
(13) For recent extensive reviews on cyclopropylcarbinyl cation, see (a) H. G. Richey, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1972, pp 1201–1294; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in ref 13a, pp 1295–1345.
(14) For a cyclopropylcarbinyl cation system having an unfavorable perpendicular conformation, see ref 13b, pp 1300–1305, and ref 1e.
(15) H. M. Walborsky and P. E. Ronman, *J. Org. Chem.*, **38**, 4213 (1973), and references cited therein.
(16) A. Nickon, H. Kwasnick, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965).
(17) Professor A. Nickon has kindly sent us the spectral data of 24 as well as the epimeric alcohols 23x and 23e.
(18) The dihedral angles between H$_3$ and H$_4$, and H$_3$ and H$_2$ were ca. 80 and 70°, respectively, on a Dreiding stereomodel, suggesting that the coupling constants between these protons are very small.
(19) Cf. H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 154.
(20) Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Melting points were determined with a Yanagimoto micromelting point apparatus (hot-stage type) and are uncorrected. Ir spectra were obtained with a Jasco IRA-1 spectrophotometer. Nmr spectra were taken with a Jeol-C-6OHL or a Jeol-JNM-MH-100 spectrometer using Me$_4$Si as internal standard, and mass spectra with a Jeol-O1SG spectrometers at 75 eV. Glc analyses were performed with a Neva gas chromatograph, Model 1400, and preparative glc with a Varian Aerograph Model 700 (silicone SE-30 column).
(21) Private communication from Professor A. Nickon; see ref 17.