chloride was allowed to stand for 20 min and the excess reagent was removed under reduced pressure. The residue was chromatographed over 20 g of Florisil, gradient elution with Skellysolve B–acetone, to give 80 mg of product **7**. Recrystallization from ether–Skellysolve B gave the analytical sample: mp 152–154°; nmr (benzene-d_6) δ 3.87 (t, 1, J = 6 Hz, $\mathrm{CH}\!\!>\!\!\mathrm{CHOS}$),

3.38 (m, 1, $\mathrm{O}\!\!=\!\!\mathrm{S}\!<\!\!{\mathrm{OCH} \atop \mathrm{OC}}\!\!>\!\!\mathrm{CHCH_2}$), 1.87 (s, 3, NCH₃), 1.13 (s, 3, OCCH₃) (see Discussion for spectrum at 100 Mc).

Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.13; H, 6.41; S, 8.87. Found: C, 63.28; H, 6.41; S, 8.89.

(1*R*)*N*-Benzoyl-*N*,4β-dimethyl-1-adamantanamin-4-ol-6-one (**8**).—Compound **6** (140 mg) in acetone was oxidized by the Jones method and the crude was recrystallized from aqueous acetone to give **8**: mp 179–182°; ir (Nujol) 3500 (OH), 1725 (C=O), 1620 cm⁻¹ (amide); nmr (CDCl₃) δ 2.84 (s, 3, NCH₃), 1.55 (s, 3, COHCH₃).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.81; H, 7.40. Found: C, 72.88; H, 7.40.

(1*R*)-*N*-Benzoyl-*N*-methyl-6-methylene-1-adamantanamin-4-one (**9**).—Compound **8** (0.900 g) and 10.0 ml of thionyl chloride was warmed on a steam bath for 5 min and the excess reagent was removed under reduced pressure. The residue was triturated with water to give 0.72 g of solid. The nmr spectrum of this material indicated a mixture of about ²/₃ methylene-C-6 and about ¹/₃ chloro compound; so it was taken up in 12 ml of methanol and 5.0 ml of 10% aqueous potassium hydroxide solution and

heated at reflux for 3 hr. Dilution with water and concentrating gave a crude solid product which was recrystallized from acetone–water: yield of **9**, 0.26 g; mp 162–163°; ir (Nujol) 1730 (C=O), 1625 cm⁻¹ (amide); nmr (CDCl₃) δ 4.75 (m, 2, C=CH₂), 2.84 (s, 3, NCH₃).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 76.78; H, 7.62; N, 4.76.

(1*R*)-*N*-Benzoyl-6α,*N*-dimethyl-1-adamantanamine-4-one (**12**) and the 6β-Methyl Isomer (**10**).—A mixture of 155 mg of **9**, 25 ml of methanol, and 40 mg of 10% palladium on carbon was shaken with hydrogen (35 psig) for 110 min. The catalyst was removed by filtration and the residue from the filtrate was examined by nmr. The spectrum indicated a mixture of two parts of **10** to three parts of **12**. We were unable to separate the two isomers by chromatography, but pure **12** (90 mg) was obtained by direct crystallization from methanol–water: mp 138–139°; ir (Nujol) identical with **12** prepared by oxidation as described above and the mixture melting point was not depressed; nmr (CDCl₃) δ 2.85 (s, 3, NCH₃), 0.97 (d, 3, J = 7 Hz, CHCH₃). The filtrate residue from **12** was rich in **10** and melted at 83–112°, but we were unable to obtain this compound pure.

Reactive Intermediates in the Anodic Oxidation of Cycloalkanecarboxylic Acids[1,2]

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Anodic oxidations of a series of α-deuteriocycloalkanecarboxylic acids (I-*n*-*d*) in aqueous solution and at carbon anodes produce mixtures containing bicycloalkanes, cycloalkene, cycloalkanol, cycloalkyl cycloalkanecarboxylate, and bicycloalkyl. The extents of internal hydrogen rearrangement accompanying the formation of alkene and alcohol products have been measured by nmr techniques. The alcohols are formed from intermediates that have undergone more hydrogen shifts than are the alkenes, with the maximum difference being found for the cyclooctane derivatives. Thermal decompositions of *tert*-butyl cyclooctaneperoxycarboxylate (II and II-*d*) and of dicyclooctylmercury in aqueous solvents produced, presumably from cyclooctyl radical intermediates, cyclooctane, cyclooctene, and cyclooctanol. The α-D peroxy ester (II-*d*) gave cyclooctene without detectable rearrangement of the deuterium label. The interpretation of these data has focused on the nature of the intermediates from which most products are formed in the electrolyses. We conclude that alcohol formation is not a dependable indication of a cationic process in aqueous solution, but still cationic rather than radical pathways account for most (if not all) of the cycloalkene, cycloalkanol, and bicycloalkane products obtained from these anodic oxidations.

Part A

The Kolbe electrolysis of salts of carboxylic acids has been known for over 100 years, and the process has been usefully employed for the synthesis of radical coupling products.[3] Renewed interest in these electrolyses has been spurred recently, however, by observations of products presumed to be formed from

cationic rather than radical intermediates.[4] Although these reactions appear quite unpromising for general synthetic applications, they do appear to be reasonably convenient sources of high energy, probably poorly solvated, cationic intermediates of theoretical interest. We have investigated the anodic oxidation of a series

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(1) (a) Based in part upon the Ph.D. Dissertation of E. E. Green, Louisiana State University, May 1969; (b) presented in part at Southwest Regional Meetings of the American Chemical Society, Little Rock, Arkansas, Dec 1967, Abstracts, No. 171, and Austin, Texas, Dec 1968, Abstracts, No. 175.

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(3) For reviews, see (a) B. C. L. Weedon in "Advances in Organic Chemistry," Vol. I, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience, New York, N. Y., 1960, pp 1–34; (b) G. W. Thiessen, *Rec. Chem. Progr.*, **21**, 243 (1960); (c) A. K. Vijh and B. E. Conway, *Chem. Rev.*, **67**, 623 (1967).

(4) (a) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960); (b) W. J. Koehl, Jr., *ibid.*, **86**, 4686 (1964); (c) L. Rand and A. F. Mohar, *J. Org. Chem.*, **30**, 3885 (1965); (d) P. H. Reichenbacher, M. Y. C. Liu, and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 1816 (1968); (e) P. S. Skell and P. H. Reichenbacher, *ibid.*, **90**, 2309 (1968); (f) P. H. Reichenbacher, M. D. Morris, and P. S. Skell, *ibid.*, **90**, 3432 (1968); (g) P. S. Skell and P. H. Reichenbacher, *ibid.*, **90**, 3436 (1968); (h) J. T. Keating and P. S. Skell, *ibid.*, **91**, 695 (1969); (i) L. Eberson, *ibid.*, **91**, 2402 (1969); (j) J. T. Keating and P. S. Skell, *J. Org. Chem.*, **34**, 1479 (1969); (k) W. B. Smith and Y. H. Yuh, *Tetrahedron*, **24**, 1163 (1968); (l) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 497 (1968); (m) G. Atherton, M. Fleischmann, and F. Goodridge, *Trans. Faraday Soc.*, **63**, 1468 (1967); (n) A. A. Humffray and L. F. G. Williams, *Chem. Commun.*, 616 (1965); (o) L. Eberson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963); (p) N. A. Bonner and R. D. Mango, *J. Org. Chem.*, **29**, 430 (1964); (q) J. G. Traynham and J. S. Dehn, *J. Amer. Chem. Soc.*, **89**, 2139 (1967); (r) K. Sasaki, K. Uneyama, and S. Nagaura, *Electrochim. Acta*, **11**, 891 (1966).

of α-deuteriocycloalkanecarboxylic acids[5] (I-*n*-d) (at carbon anodes) to ascertain the extent of intramolecular hydrogen rearrangements[6] occurring in the high-energy intermediates. We have also investigated, for comparison, two nonelectrolytic radical reactions (thermolyses of *tert*-butyl cyclooctaneperoxycarboxylate, II, and of dicyclooctylmercury) in aqueous solutions,

I-*n* (I-*n*-d)   II (II-*d*)
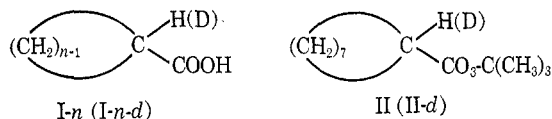
since information on product formation from alkyl radical intermediates in aqueous solutions, apart from polymerization, is meager.[7] Although bicycloalkanes (formed by the anodic oxidation but not by the nonelectrolytic processes) appear to be formed from cycloalkyl cations[4a] but not from cycloalkyl radicals under the reaction conditions, both anodic oxidation and nonelectrolytic radical reactions of cyclooctane derivatives in aqueous solutions produce cyclooctene and cyclooctanol. Nonetheless, hydrogen rearrangements (revealed by deuterium-label scrambling) in the anodic oxidation products make it unlikely that cycloalkene and cycloalkanol are formed to significant extents from radical intermediates during electrolysis.

The product distribution data for the electrolyses are summarized in Table I. Analysis of deuterium

TABLE I

RELATIVE PRODUCT PROPORTIONS FROM AQUEOUS
ELECTROLYSES OF α-DEUTERIOCYCLOALKANECARBOXYLIC
ACIDS (CYCLOALKANOL = 1)

Acid ring size	Gc[a] column, temp, °C	Bicyclo-alkane	Cyclo-alkane	Cyclo-alkene	Cyclo-al-kanol	Ester[b] + bi-cyclo-alkyl
6	A, 86	0.0	0.05	0.5	1	~1
	B, >100					
8	A, 120	0.5[c]	Trace	2.0	1	~1
9	C, 100	0.2	Trace	2.0[d]	1	~1
10	D	0.1	0	5.0[d]	1	

[a] Gc specifications; see ref 12. [b] Cycloalkyl cycloalkanecarboxylate. [c] Bicyclo[3.3.0]- and -[5.1.0]octanes. [d] cis + trans.

content of starting acids and content and rearrangement in alkene and alcohol products were accomplished by nmr spectroscopy. These rearrangement data are summarized in Table II.

Thermolyses of compounds containing the cyclooctyl ring system were carried out to obtain comparable radical product distribution and rearrangement data. Thermal decomposition of II-*d*[8] in aqueous solution yielded cyclooctene with no rearrangement of the deuterium label detectable by nmr analysis. The product distribution data for thermal decomposition of the unlabeled peroxy ester and dicyclooctylmercury[9] in aqueous solution are shown in Tables III and IV.

(5) See ref 4q for a report on unlabeled acids, I-*n*.

(6) For reviews see (a) V. Prelog and J. G. Traynham, in "Molecular Rearrangements," P. de Mayo, Ed., Vol. 1, Wiley-Interscience, New York, N. Y., 1963, Chapter 9; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev. (London)*, 20, 119 (1966).

(7) See, for example, W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(8) Thermal decomposition of *tert*-butyl alkaneperoxycarboxylates leads to *tert*-butoxy and alkyl radicals: ref 7, p 105.

TABLE II

EXTENTS OF DEUTERIUM REARRANGEMENT IN
ELECTROLYSIS PRODUCTS

Ring size	% rearrangement	
	Cycloalkene	Cycloalkanol
6	0	0[a]
8	5	40
9	16	25
10	0	

[a] Hydrolysis of the ester product gave unrearranged cyclohexanol.

TABLE III

THERMAL DECOMPOSITIONS OF II IN AQUEOUS SOLVENTS

Conditions			
Temp, °C	105	80	80
Concn of solute (*M*)	0.06	0.5	2.5
Atmosphere	N₂	Air	Air
H₂O:*tert*-BuOH, mol %	85:15	60:40	60:40
Products[a,b]			
Cyclooctane	0.4	0.5	1
Cyclooctene	1	1	1
tert-Butyl cyclooctyl ether		2	4.5
Cyclooctanone	0.1	0.5	3.0
Cyclooctanol	0.2	1.9	3.5

[a] Mole ratios within one reaction mixture, relative to cyclooctene = 1. A secondary deuterium isotope effect was not detected in comparisons between labeled and unlabeled peroxy ester decompositions. [b] Acetone, 2-methylpropene, and uncharacterized high-molecular-weight materials were also products of the decompositions. Control experiments with cyclooctene and cyclooctanol under conditions similar to the thermal decompositions produced no hydration or dehydration, respectively. *tert*-Butyl alcohol heated in water and under pressure did yield 2-methylpropene.

TABLE IV

THERMAL DECOMPOSITIONS OF DICYCLOOCTYLMERCURY IN
AQUEOUS SOLVENT[a,b]

	Atmosphere	
Product	N₂	Air
Cyclooctane	0.5	0.3
Cyclooctene	1.0	1.0
Cyclooctanol	0.6	0.6
Cyclooctanone	0.4	0.5

[a] Water:*tert*-butyl alcohol, 85:15 mol %; 80°. [b] Mole ratios of products, relative to cyclooctene = 1.

Of special interest is the large proportion of oxygenated products formed in these reactions. Particular care was taken to exclude oxygen from some of these thermolyses,[10] and it seems improbable that enough oxygen was present to account for the yields of cyclooctanol and cyclooctanone.[11] Even though it is

(9) Photolysis and pyrolysis of dicyclooctylmercury in pentane solvent have been reported: A. C. Cope and J. Englehart, *J. Amer. Chem. Soc.*, 90, 7092 (1968).

(10) (a) Reactions of organomercury compounds with oxygen are reviewed by T. G. Brilkina and V. A. Shushunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides," A. G. Davies, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, pp 58–63. (b) Because of the decomposition of solvent water during the electrolyses, the anode was probably a continuing source of oxygen in those reactions. We, nonetheless, took care to exclude oxygen from the thermolyses in order to obtain information about the behavior of alkyl radicals in aqueous systems.

(11) Oxidations of cyclooctanol or *tert*-butyl cyclooctyl ether to cyclooctanone by radical reactions are examples of reactions which are well documented: (a) ref 7, p 12; (b) E. Staude and F. Patat, in "The Chemistry of the Ether Linkage," S. Patai, Ed., Wiley-Interscience, London, 1967, p 74; (c) G. A. Rasunajew, in "Vistas in Free Radical Chemistry," W. A. Waters, Ed., Pergamon Press, New York, N. Y., 1959, pp 225 ff.

difficult to rationalize an apparent reaction between cyclooctyl radical and water to give cyclooctanol with previously summarized data on the behavior of radical intermediates, it does seem that the formation of alcohol product is not a sure indicator of a cationic intermediate in the anodic oxidation of carboxylic acids.[4a,b] In the case of medium ring systems, bicycloalkane products appear to be the more dependable indicator of cationic intermediates.

Part B

Experimental Section

The compounds used in all syntheses were reagent grade commercial chemicals or materials on hand from previous work in these laboratories[4q] and, unless indicated otherwise, required no further purification. The infrared (ir) spectra were obtained with a Perkin-Elmer Infracord Model 137 spectrometer and with thin films on sodium chloride plates. The nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates Model A-60A nmr spectrometer, usually with chloroform-*d* solutions containing tetramethylsilane (TMS) as internal reference (negative chemical shift indicates downfield). Mass spectra (ms) were obtained from a Varian Associates M-66 mass spectrometer by Cheryl White, and element microanalyses were performed by R. Seab, both members of the technical staff of these laboratories. Several different instruments were used for gas chromatographic (gc) analyses.[12]

Deuterium Labeling of Cycloalkanecarboxylic Acids.[13]—A mixture of cycloalkanecarboxylic acid, sulfuric acid-d_2, and water-d_2 (1:2:1 mol ratio) was stirred at 90–100° for 5–7 days in a sealed vessel. The dark reaction mixture was extracted with pentane, and the pentane solution was washed with 1 M sodium hydroxide solution. The deuterated carboxylic acid was obtained by acidifying the basic wash with dilute hydrochloric acid, extracting into pentane, and removing the solvent at reduced pressure. The extent of deuterium incorporation was always less than that calculated for complete equilibration and was determined by nmr and ms techniques. The acids prepared, mole fraction of α-deuterium incorporated by one exchange, and yield were I-6-*d*, 0.20, 90%; I-8-*d*, 0.60, 91%; I-9-*d*, 0.78, 85%; I-10-*d*, 0.90, 60%.

Electrolyses[4q] of α-Deuteriocycloalkanecarboxylic Acids. General.—A Kontes, K-25005, 125-ml Universal Electrode Vessel was fitted with the appropriate graphite (+) and copper (−) electrodes, nitrogen inlet and exit, and magnetic stirring bar. The graphite anode had a surface area of about 3 cm², smaller than the copper cathode.

For each electrolysis, the current was initially adjusted to give an anode current density of about 0.05 A/cm² of exposed surface. This current was supplied either with a bank of lead–acid storage batteries (22 V) through a variable resistor, or with a direct current power supply that allowed variation of the voltage applied across the electrolysis cell. Normally the current through the cell varied during the course of the electrolysis as the resistance of the solution changed and substrate was consumed. The electrolysis was always initiated with slightly acidic solution. As the reaction proceeded, the solution became more basic (sometimes reaching a pH of 9). Product distributions did not vary significantly with differences in the duration of the electrolysis, (always greater than 20 V across the cell), or concentration of substrate.

To help remove evolved carbon dioxide and volatile hydrocarbons, nitrogen was introduced in a gently bubbling stream. After leaving the apparatus, the gas flowed through a drying tube (calcium chloride or Drierite), then through a small cold

finger condenser immersed in an acetone–solid carbon dioxide bath (−78°), and finally through a preweighed U tube filled with number 8 mesh Ascarite.

After the electrolysis had continued for 9 hr, dilute hydrochloric acid was very quickly added to the basic reaction mixture (to displace dissolved carbon dioxide), and the system was resealed to force the gases to flow on through the system of traps. After bubbling had ceased and the mixture had been purged for a few minutes by the nitrogen stream, the U tube was weighed to determine the amount of carbon dioxide evolved. Based on the number of coulombs passed through the respective electrolysis solutions, the following yields of carbon dioxide were obtained: from I-6, 25%; I-8, 20%; I-10, 200%.[14]

The acidic reaction mixture was made basic with 1 M sodium hydroxide solution and removed to a separatory funnel. The reaction vessel was washed with distilled water and ethyl ether (100 ml of each), and these washings were also added to the separatory funnel. The basic aqueous layer was removed and set aside for recovery of unreacted acid. The ether layer was extracted twice with 50-ml portions of distilled water, and these washings plus the first aqueous basic layer were mixed, acidified with dilute hydrochloric acid, and extracted with ether. This second ether solution was dried over Drierite and concentrated under reduced pressure to give the following yields of recovered α-deuteriocycloalkanecarboxylic acids: I-6-*d*, 37%; I-8-*d*, 36%; I-9-*d*, 24%; and I-10-*d*, 86%.

The first ether layer containing the neutral products of the electrolysis was dried and concentrated by rotary evaporation. The residual liquid was analyzed by gas chromatographic (gc) and distillation techniques. Cycloalkane, cycloalkenes, bicycloalkanes, and cycloalkanol[15] were determined in the total mixture by gc; the amounts of the less volatile cycloalkyl cyclo-alkanoate and bicycloalkyl were estimated by distillation of the reaction mixture. These individual products were identified by comparisons of their ir, nmr, and gc data with those of authentic samples. The product distribution data are summarized in Table I.

Samples of cycloalkene and cycloalkanol, obtained by distillation of the reaction mixture, were examined by nmr techniques. The extents of hydride shifts accompanying formation of these products were established by comparing the relative intensity of the HC=C or HCOH absorptions with those of the rest of the alkene or alcohol molecule, respectively.[16] These data are summarized in Table II.

Electrolysis of Cyclooctanecarboxylic Acid in Binary Solvent.—Cyclooctanecarboxylic acid (6.2 g, 0.04 mol), sodium hydroxide (1.3 g, 0.035 mol), and 28 g of mixed solvent (60 mol % water, 40 mol % *tert*-butyl alcohol) were mixed in the electrolysis cell previously described. The electrolysis was run at about 0.06 A (total current) and 80 V. The current density at the anode, 0.02 A/cm², was lower than in the previously described electrolyses because of greater resistance of the cell when the binary solvent was employed. The electrolysis was run as described. After 17 hr, about 30% (0.50 g, 0.011 mol) of the theoretical amount of carbon dioxide, based on coulombs passed through the solution, had been collected.

The usual work-up of the reaction was carried out except that more water washings were employed to remove the *tert*-butyl alcohol. The neutral portion was analyzed by gc (D,[12] 180°) and found to contain cyclooctene, *tert*-butyl cyclooctyl ether, cyclooctanone, and cyclooctanol in relative amounts 0.25:7: 0.15:1, respectively.

tert-**Butyl Cyclooctaneperoxycarboxylate (II).**—The peroxy ester was prepared by the reaction of acyl chloride with sodium

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(12) A, Micro Tek Model GC 1600 instrument, flame ionization detector (FID), 1/8 in. × 18 ft column, 10% tricresyl phosphate on 60–80 mesh Chromosorb P. B, Aerograph Autoprep Model A-700 instrument, 3/8 in. × 12 ft column, 17% ethylene glycol adipate on 80–100 mesh Chromoport XX. C, Barber–Colman IDS Model 20 instrument, FID, 100-ft capillary column, GE-96 silicone. D, Beckman CC-5 instrument, FID, 1/8 in. × 10 ft column, 10% Carbowax 20M on 60–80 mesh Chromosorb P. E, Hewlett–Packard 700 instrument, FID, 1/8 in. × 9.5 ft column, 10% Carbowax 20M on 80–100 mesh Chromosorb P.

(13) A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience, New York, N. Y., 1958, p 1311.

(14) Several other apparently difficult electrolyses in these laboratories have produced unexpectedly high yields of CO_2, probably from oxidation of the graphite anode by oxygen formed from the electrolysis of solvent water.

(15) (a) In a control experiment simulating electrolysis conditions, a mixture of cyclooctanecarboxylic acid (0.01 mol) and cyclooctene (0.001 mol) in 7 g of mixed solvent (60 mol % water, 40 mol % *tert*-butyl alcohol) did not generate any cyclooctanol, even after being refluxed for 3 days. (b) Although actual yields were seldom determined, the combined amount of product was always substantial and roughly equivalent to the amount of carboxylic acid consumed in the electrolysis.

(16) In a control experiment simulating electrolysis conditions, a mixture of cyclohexanecarboxylic acid (0.02 mol), D_2O (5 ml, 0.25 mol), and a few drops of 30% sodium deuterioxide (in D_2O) solution was heated at 50° for 14 hr. The nmr spectrum of the recovered acid gave no evidence for α-hydrogen exchange. It is, therefore, improbable that any loss of D label by exchange in the acid (or anion) occurred during electrolysis.

tert-butyl peroxide.[17] Cyclooctanecarboxylic acid,[4a] both with and without α-D label, was converted to acyl chloride[18] [bp 99–100° (8 mm)] by refluxing with thionyl chloride. The nmr spectrum of the unlabeled acyl chloride included absorptions centered at −2.95 ppm (α-H) and at −1.9 ppm (β-H), but in the spectrum of the labeled chloride the absorption at −2.95 ppm was nearly absent and the one at −1.9 ppm was appreciably sharper. The unlabeled peroxy ester (II) was obtained in 57% yield by removal of ethyl ether solvent on a rotary evaporator and was not distilled: ir (film) 5.63 (ester C=O), 7.25, 8.4, and 9.3 μ; nmr (CDCl₃) −2.4 (m, 1, CHCO₃), −1.75 (m, 4, CH₂-CCO₃R), −1.4 (m, 10, CH₂CH₂CH₂), and −1.2 ppm (s, 9, CH₃). Anal. Calcd for C₁₃H₂₄O₃: C, 68.3; H, 10.6. Found: C, 67.8; H, 10.6.

The α-D labeled peroxy ester (II-d) was obtained in 73% yield from pentane solution; it exhibited little nmr absorption at −2.4 ppm and a sharper one at −1.75 ppm than did the unlabeled ester.

Thermal Decomposition of II.—A solution (0.056 M in solute) of II (5.1 g, 0.022 mol) in 40 ml of mixed solvent (40 mol % tert-butyl alcohol, 60 mol % water) was refluxed for 8 hr without protection from the air. The mixture then gave a negative potassium iodide test for peroxides.[19] The reaction mixture was diluted with pentane (50 ml) and washed with dilute sodium hydroxide solution. The organic layer was washed with five 50-ml portions of water to remove tert-butyl alcohol, the remaining organic solution was dried over Drierite, and the solvent was removed to yield about 1 g of neutral products. The sodium hydroxide wash solution was acidified, extracted with pentane, and concentrated to yield 1.7 g (0.011 mol, 50%) of I-8. Analysis of the neutral products by gc (D,[12] 100–180°), showed cyclooctane, cyclooctene,[20] tert-butyl cyclooctyl ether, cyclooctanone, and cyclooctanol[20] present in the relative amounts 0.5:1:2:0.5:1.9, respectively.

Other decompositions of this peroxy ester at different pressures, under different atmospheres, or for different lengths of reaction time produced no significant variations in product distribution. Decompositions at higher and lower concentration of substrate (see Table III) did suggest an influence on the product distributions.

A solution (about 0.03 M in solute) of II-d (14.4 g, 0.063 mol) in 200 g of solvent (85 mol % water, 15 mol % tert-butyl alcohol) was heated in a Parr medium-pressure autoclave under nitrogen at 118° for 18 hr. The same products as above were obtained in only slightly different ratios. Nmr analysis of the cyclooctene isolated from the decompositions of labeled peroxy ester gave no indication of rearrangement of the deuterium atom label.

Decomposition of Dicyclooctylmercury.—For 3 hr, nitrogen was bubbled through 21 g of refluxing solvent (85 mol % water, 15 mol % tert-butyl alcohol) to remove dissolved oxygen. The solvent was allowed to cool slightly. The flask was covered with aluminum foil, and, while the flask was being flushed with nitrogen, freshly prepared dicyclooctylmercury[9] (1.0 g, 2.4 mmol) was added. While a nitrogen atmosphere in the flask was being maintained, the mixture was stirred and heated at 80° (reflux) for 40 hr. Extraction of the mixture with pentane, washing the pentane extract with water 4 times, drying over Drierite, and removal of solvent by rotary evaporation yielded 0.2 g of products. (Some metallic mercury was observed in the reaction vessel after 40 hr.) The products were analyzed by ir, nmr, and gc (E,[12] 60 and 150°) methods. Cyclooctane, cyclooctene, cyclooctanone, and cyclooctanol were detected in the relative amounts of 0.5:1.0:0.4:0.6, respectively. No bicycloalkanes were detected.

Another experiment, duplicating that above except for the

use of air instead of nitrogen, gave a product mixture almost identical with that above (see Table IV). In some other experiments for which a nitrogen atmosphere was used, the proportions of oxygenated products were even higher (e.g., cyclooctene:cyclooctanol, 1:3 and 1:12).

Discussion

Anodic oxidation of the cycloalkanecarboxylic acids gives more hydrocarbon than oxygenated products, and, like solvolysis reactions which have been studied,[6] product formation from the medium-ring systems, but not the cyclohexane system, is accompanied by internal hydrogen rearrangements. The medium-ring alcohols are formed with more extensive intramolecular rearrangement of deuterium than are the alkenes (Tables I and II). These relative rearrangement data are similar to those obtained in the deamination of ¹⁴C-labeled cyclononyl- and cyclodecylamines.[21] The deuterium label in cyclooctene obtained from radical decomposition of II-d was not rearranged. This result almost certainly ensures that (rearranged) alkene product from the electrolysis reaction was not formed directly from a radical precursor.

These data support the suggestion that the alcohol and alkene electrolysis products are formed from cationic intermediates. There is probably a common intermediate which reacts, by pathways having different energy requirements, to give alkene, alcohol, rearranged intermediate, and, to a substantially lesser degree, bicycloalkane. The fact that alcohol is formed with more extensive rearrangement than is the alkene indicates that the energies of the transition states for reaction of the cycloalkyl cation fall in the order: alkene formation < alcohol formation < rearrangement of cation.

Alternatively, of course, the possibility of different intermediates, possibly different charge types, leading to different products must be considered. Reactions presumably involving cyclooctyl radicals in aqueous solution yielded cyclooctane, cyclooctene, and unexpectedly substantial amounts of oxygenated products (but no bicyclooctane). Since data from II-d reveal no rearrangement in the cyclooctene product, and electrolytic cyclooctanol is more extensively rearranged than electrolytic cyclooctene, both electrolytic products must come from (nonradical) intermediates capable of internal hydrogen rearrangements.

Some product formation directly from cycloalkyl radicals must accompany the cationic processes during anodic oxidations, however. Radical mechanisms for the formation of cyclooctane and bicycloalkyl are quite reasonable. Disproportionation of cycloalkyl radicals, or other hydrogen abstraction reactions, will lead to cyclooctane (a trace product), and dimerization of the radicals will produce bicycloalkyl. Still, the amount of cyclooctane produced during electrolysis is too small for disproportionation alone to be responsible for the difference in extents of apparent rearrangement in the cyclooctene and cyclooctanol products, and most of the cyclooctene must come from cationic intermediates.

In summary, we conclude that cycloalkyl radical and cationic processes in aqueous solution can produce

(17) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965). We modified the published procedure by using ethyl ether rather than tetrahydrofuran as solvent.

(18) Use of cyclooctanecarbonyl chloride as an intermediate has been reported previously: A. C. Cope, M. Burg, and S. W. Fenton, *ibid.*, **74**, 173 (1952); A. O. Hellwig and H. Schubert, *Z. Chem.*, **4**, 227 (1964).

(19) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p 161.

(20) In a control experiment simulating peroxy ester decomposition conditions, a mixture of cyclooctanol (4 g, 0.031 mol), crude II (1 g, 0.045 mol), and 100 g of solvent (85 mol % water, 15 mol % tert-butyl alcohol) was heated for 2 days at 125° (50 psig) in a Paar medium-pressure apparatus. Analysis (nmr and gc) of the reaction mixture provided no evidence for the dehydration of cyclooctanol to cyclooctene.

(21) See ref 6a. The extents of ¹⁴C rearrangement in alkene and alcohol products from solvolysis of cyclononyl toluenesulfonate were essentially equal.

quite similar product mixtures. Anodic oxidation of carboxylic acids at a carbon anode produces products from both radical and cationic intermediates, but the cationic pathway is the major one. With cycloalkyl systems, the cations undergo internal hydrogen re-

arrangements and competitive product formation similar to those from amine deaminations.

Heterocyclic Studies. 33.
5-Methyl-6-phenyl-1,2-diazabicyclo[3.2.0]-2,6-heptadien-4-one.   Thermolysis to 4-Methyl-5-phenylpyridazine[1]

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The preparation and properties of the title dienone 2 are described. The dienone is quite stable to hydrolysis; addition occurs with borohydride and methyllithium to give dienols. Thermolysis of 2 at 475° gives 4-methyl-5-phenylpyridazine; a mechanism involving a diazatropone intermediate is discussed. The thermal stability of 2 and the related diazabicyclo[3.2.0]-6-heptenone 1 and diazabicyclo[3.2.0]heptanone 19, prepared by hydrogenation of 1 (R = Ac), are compared. The dimer of 2-methyl-3-phenylcyclopentadienone is described.

Part A

As previously reported,[2] the 1,2-diazabicyclo[3.2.0]-heptadienone 2 is obtained as a by-product in the photochemical preparation of **1a** and can be prepared by the base-catalyzed elimination of toluenesulfinic acid from **1b**. In this paper are described the details of the preparation and the chemical properties of 2. This strained polyfunctional dienone appeared at the outset to offer possibilities for reactions of several types. Compounds containing the transoid cyclic unit –N=C–C=O are not well known, and the few examples that have been described are quite prone to solvolysis[3] or dimerization,[4] particularly in the absence of a substituent on the central carbon atom. The monomeric structure of 2, which is consistent with the solubility and volatility of the compound, was confirmed by the mass spectrum, which contained no peaks above m/e 200 (P + 2).
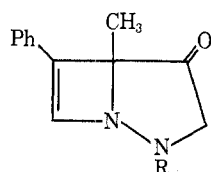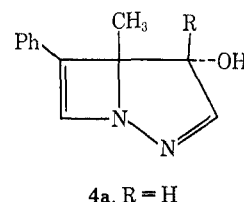

1a, R = H
b, R = p-CH₃C₆H₄SO₂

2
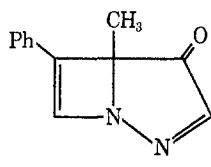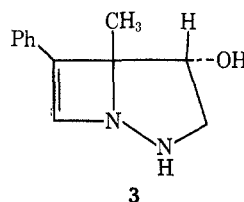
Contrary to expectation, 2 proved to be relatively inert; the dienone was recovered largely unchanged after refluxing for 16 hr with methanolic sodium methoxide or with methanolic hydrochloric acid. Treatment of 2 with sodium borohydride at room temperature leads to the saturated alcohol **3**.[5] At

−40°, reduction with borohydride gave a small amount of 3 and, as the major product, the secondary alcohol **4a**, which was not further reduced to 3 at higher temperature, suggesting that 3 may arise from 2 by 1,4 addition. Methyllithium at −70° also added selectively to the carbonyl group to give **4b**. The *endo*-hydroxyl configuration in **4a,b** is assumed on the basis of exo attack of hydride; this has been established in the reduction of **1a** to 3. Reactions with acetic anhydride, Grignard reagents, a phosphorus ylide, or organolithium compounds at higher temperature gave mixtures of starting material and several products which were not resolved. From this survey of the reactivity of 2, the only clearly defined pathway observed is nucleophilic addition at the C-4 carbonyl group; the azetine and –N=C–C=O systems are surprisingly resistant to solvolytic attack.

3

4a, R = H
b, R = CH₃

One of the main points of interest in the chemistry of 2 was the possibility of thermal conversion to a diazatropone by ring opening analogous to the isomerization of bicyclo[3.2.0]-2,6-heptadienone to tropone.[6] The dienone 2 decomposed slowly in refluxing toluene to give a mixture containing apparently polymeric material. Heating 2 in higher boiling solvents or in sealed ampoules, or sublimation through a glass coil at temperatures up to 320° similarly caused incomplete conversion to material showing broad featureless nmr absorption. However, mixtures from pyrolysis at higher temperature showed evidence of two products, and these were isolated from a preparative scale pyrolysis in which a benzene solution of 2 was vaporized into a helix-packed column heated to 475°. After

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(2) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 1369 (1968).

(3) 3-Oxo-2-phenylindolenine, R. J. Richman and A. Hassner, *J. Org. Chem.*, **33**, 2548 (1968); 1-alkyl-1,2-diazepin-4-one, J. A. Moore and W. J. Theuer, *ibid.*, **30**, 1887 (1965); imidazolinedione, E. Goldstein and D. Ben-Ishai, *Tetrahedron Lett.*, 2631 (1969).

(4) E. D. Hannah, W. C. Peaston, and G. R. Proctor, *J. Chem. Soc. C*, 1280 (1968), and earlier papers.

(5) J.-L. Derocque, W. J. Theuer, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968).

(6) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965).