Anodic Oxidations of Medium Ring Cycloalkanecarboxylic Acids[1,2]

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Abstract: Product distribution data have been obtained for the oxidation of a series of cycloalkanecarboxylic acids (ring sizes 7–10) at a graphite anode. The composition of the hydrocarbon fraction is considered to provide diagnostic information about the nature of the intermediate cycloalkyl cation. The proportion of the hydrocarbon fraction increases with ring size, and 6–21% of that fraction consists of bicyclo[*x*.1.0]- and -[*y*.3.0]alkanes (products of transannular elimination). The largest amount of bicycloalkanes is obtained from the eight-membered ring; substantial amounts of *trans*-cycloalkene are obtained from the nine- and ten-membered rings. These hydrocarbon product distribution data are compared with those of other medium ring reactions presumed to involve cycloalkyl cations.

The description and differentiation of carbonium ion intermediates derived from various sources continue to promote interest and controversy among organic chemists. Multiple studies have demonstrated that carbonium ions generated from related but different reactants may lead to very different product mixtures.[3] Carbonium ion reactions involving the two processes, solvolysis and deamination, have probably been investigated most extensively among the several sources of the intermediates, and the prevailing attitude is that these processes generally lead to different kinds of carbonium ion intermediates.[3] Because of the types of products formed by the two processes, deamination is usually considered to produce carbonium ions which are more energetic than those produced by solvolysis reactions.[3b,4] In some descriptions, this difference in energy content of the ions has been related to their relative degrees of solvation.

Although other sources of carbonium ions in solutions have been reported, few have been studied extensively. Such studies are of appreciable interest because of the potential significance of the data to our broad understanding of carbonium ion processes.

Some recent papers have demonstrated that anodic oxidations of carboxylic acids may involve carbonium ion intermediates.[5] The most convenient procedure seems to be that reported by Koehl,[5b] who used a graphite anode and low current density. We have electrolyzed solutions of several medium ring cycloalkanecarboxylic acids at a graphite anode and assessed the reactivity of the cycloalkyl cations produced by careful analysis of the hydrocarbon products formed.

Although the total product mixtures contained appreciable amounts of alcohol and ester products (more than the hydrocarbon fraction in nearly all experiments), these oxygenated products are of little diagnostic value in unlabeled systems. The over-all reaction is illustrated for cyclooctanecarboxylic acid.

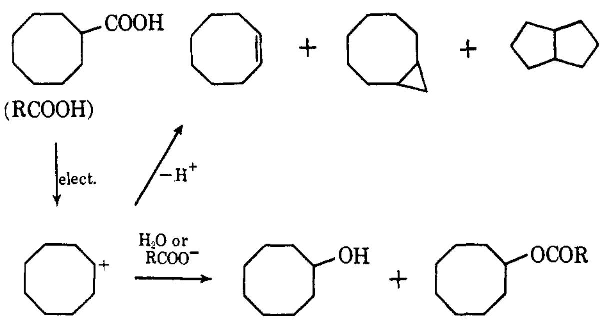

Table I summarizes our data. Along with the "expected" cycloalkenes, the hydrocarbon product mixtures contained appreciable amounts of bicycloalkanes. These bicycloalkanes are products of transannular elimination reactions, comparable to transannular in-

Table I. Composition of Hydrogen Fractions Produced by Anodic Oxidation of Cycloalkanecarboxylic Acids

Acid	Total material bal, %	Hycbn fract[a]	Cyclo-alkene *cis*	Cyclo-alkene *trans*	Bicycloalkane [*x*. 1.0.]	Bicycloalkane [*y*. 3.0.]	Unident
$C_7H_{13}COOH$	82.5[b]	0.05	87	..	12	...	1
$C_8H_{15}COOH$	87.5[b]	0.23	75	..	13	8	4
$C_9H_{17}COOH$	84	0.25	60	28	4	6	2
$C_{10}H_{19}COOH$	100[b]	0.55	34	55	..	6	5[c]
	93[d]	0.31	36	52	..	7	5[c]
	99[e]	0.24	42	51	..	7[g]	
	99.5[f]	0.15	42	51	..	7[g]	

[a] Moles of hydrocarbon/moles of acid consumed. [b] This line of data obtained with a copper rod cathode and a graphite rod anode. [c] This unidentified component is not *cis*- or *trans*-bicyclo[4.4.0]decane, *cis*-bicyclo[8.1.0]decane, or 1-methylcyclononene. [d] This line of data obtained with a circular copper cathode and a graphite rod anode. [e] This line of data obtained with a circular copper cathode and a platinum rod anode. [f] This line of data obtained with a copper rod cathode and a platinum rod anode. [g] Mixture of bicyclo[5.3.0]decane and unidentified component.

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[1] (a) Based upon the Ph.D. Dissertation of J. S. D., Louisiana State University, May 1966. (b) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; Abstracts, p 125S.

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 1817-A).

[3] For examples see (a) J. A. Berson and B. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4094 (1959); (b) M. S. Silver, *ibid.*, **83**, 3482, 3487 (1961); (c) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); (d) J. G. Traynham and J. Schneller, *ibid.*, **87**, 2398 (1965).

[4] (a) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963); (b) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (c) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **86**, 1994 (1964); (d) J. H. Bayles, F. D. Mendocine, and L. Friedman, *ibid.*, **87**, 5790 (1965).

[5] (a) E. J. Corey, N. L. Bould, R. T. La Londi, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2645 (1960); (b) W. J. Koehl, Jr., *ibid.*, **86**, 4686 (1964).

sertion reactions of cycloalkyl methylene intermediates.[6] The bicycloalkane products appear to be formed by 1,3 and 1,5 eliminations; no products of 1,4 or 1,6 eliminations have been identified, and 1,6 elimination has been specifically excluded for the ten-membered ring.

Differences in repulsive interactions (eclipsing strain) in alkyl-substituted, protonated cyclopropanes apparently play an important role in determining the extent to which such intermediates figure in some amine deaminations.[7] Like other strains,[8a] differences in these interactions among a series of cycloalkyl cations (which could give rise to similarly substituted protonated bicycloalkanes) may be a function of ring size and account for the decrease of transannular elimination with increase in ring size from 8 to 10.

Medium ring systems have been used for study of carbonium ion reactions in a number of laboratories.[8] Medium ring solvolytic carbonium ions are particularly subject to transannular rearrangements, but unsubstituted cycloalkyl cations give no transannular elimination products (bicycloalkanes).[8] Deaminations of some medium ring systems have led to transannular rearrangements,[8,9] but others have not.[10] Cycloalkyl cations generated by decomposition of medium ring cycloalkanone tosylhydrazones in protic solvents do give bicycloalkanes by transannular elimination reactions as well as the usual cycloalkenes.[6]

Table II. Comparison of Compositions of Hydrocarbon Fractions Produced from Different Cycloalkyl Cation Sources

Starting material	Hydrocarbons produced, mole % Cycloalkene *cis*	*trans*	Bicycloalkane [*x*.1.0]	[*y*.3.0]	[4.4.0]
$C_7H_{13}COOH$[a]	87	...	12	...	...
$C_7H_{12}{=}N_2HTs$[b]	81	...	18	...	...
$C_8H_{15}COOH$[a]	75	...	13	8	...
$C_8H_{14}{=}N_2HTs$[b]	83	...	10	6	...
$C_8H_{15}Br$[c]	100	...	...	...	...
$C_9H_{17}COOH$[a]	60	28	4	6	...
$C_9H_{16}{=}N_2HTs$[b]	84	12	2	2	...
$C_9H_{17}OTs$[d]	67	33	...	...	...
$C_{10}H_{19}COOH$[a]	34	55	...	6	...
$C_{10}H_{18}{=}N_2HTs$[b]	70	30	...	0.2	0.05
$C_{10}H_{19}OTs$[d]	15	85	...	...	Trace

[a] Anodic oxidation, this work. [b] Decomposition of tosylhydrazone in ethylene glycol; ref 6 and this work. [c] Solvolysis in aqueous tetrahydrofuran, this work; trace amounts of bicyclooctanes formed in HOAc with AgOAc.[6b] [d] Acetolysis; see ref 8.

A comparison of the hydrocarbon products formed in several reactions presumed to proceed through cycloalkyl cation intermediates is made in Table II. Our data for the anodic generation of the cycloalkyl cations from carboxylic acids indicate that these carbonium ions are unlike, so far as product formation is concerned, those produced by decompositions of tosylhydrazones or by solvolysis of halides or tosylates. Each *cis*:*trans* ratio for the cycloalkene products from anodic oxidation is more like that from the corresponding solvolysis, but the extent of bicycloalkane formation exceeds even that from the corresponding tosylhydrazone decomposition with the medium ring compounds.

In the course of our investigation, we used several different electrolytic cell designs. Although the current efficiency of the cell was highest with a carbon anode, the nature of the products formed was little different from that with a platinum anode. Apparently α-branching favors the generation of cation rather than radical intermediates at both carbon and platinum anodes.[11]

We are extending our investigation of anodic oxidations to other cyclic acids and to deuterium-labeled compounds, which will permit the oxygenated as well as the hydrocarbon products to yield data of diagnostic value.

Experimental Section

Gas chromatographic analyses were carried out with a Barber Colman Model 20 instrument equipped with a hydrogen-flame detector and a 100-ft capillary column coated with SE-96 silicone. An Aerograph Autoprep Model A-700 instrument equipped with a $^3/_8$ in. × 10 ft Carbowax 20M column or a $^3/_8$ in. × 20 ft SE-30 silicone column was used for preparative gas chromatography. Infrared spectra were obtained with a Beckman IR-5 and a Perkin-Elmer Model 137 spectrophotometer. Microanalyses were performed by Mr. R. Seab in these laboratories and by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance (nmr) data were obtained with a Varian Associates HA-60 instrument with the assistance of Mr. W. Wegner; all chemical shifts are relative to internal tetramethylsilane reference.

Preparation of Carboxylic Acids. Cycloheptanecarboxylic acid and cyclononanecarboxylic acid were prepared by way of Favorskii rearrangements[12] from cyclooctanone and cyclodecanone, respectively. Each ketone was brominated directly by the addition of a bromine solution (0.166 mole of bromine in 30 ml of carbon tetrachloride) to a mixture of ketone (0.166 mole), carbon tetrachloride (60 ml), and water (90 ml) initially heated to reflux. The mixture was irradiated with a 150-w light bulb during addition of bromine, which was at the rate necessary to maintain reflux temperature. The carbon tetrachloride solution was washed with water until it was neutral, dried, and concentrated on a rotary evaporator to leave a quantitative yield of 2-bromocycloalkanone, which was used directly without further purification in the rearrangement reaction. A solution of the α-bromo ketone (0.166 mole) in methanol (25 ml) was added in 1 hr to a solution of sodium methoxide in methanol (12 g of Na in 200 ml of methanol) at −20°. The mixture was stirred for 0.5 hr longer, allowed to warm to room temperature in 2 hr, refluxed for 1 hr, and then diluted with aqueous potassium hydroxide (30 g of KOH in 75 ml of water). The mixture was refluxed for 3 hr, washed with petroleum ether, acidified with hydrochloric acid, and extracted thoroughly with petroleum ether. Distillation of the extract gave the carboxylic acids cycloheptanecarboxylic acid[13] (40%), bp 88° (0.25 mm), and cyclononanecarboxylic acid[14] (69%), bp 118° (0.15 mm).

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(6) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961); (b) A. C. Cope, M. Brown, and G. L. Woo, *ibid.*, **87**, 3107 (1965). (c) Electrolysis of 6-heptenoic acid (but not 7-octenoic acid) at a platinum anode gives an appreciable amount of cyclization (cyclopentane) product, presumably by a radical mechanism: R. F. Carwood, C. J. Scott, and B. C. L. Weedon, *Chem. Commun.*, 14 (1965).

(7) (a) G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 5649 (1966); (b) G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *ibid.*, **88**, 5651 (1966).

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

(9) In private correspondence during the summer of 1966, Professor L. Friedman, Case Institute of Technology, informed us of his studies of "aprotic" deaminations[4d] of medium ring cycloalkylamines; these reactions lead to the formation of hydrocarbon product mixtures quite similar to those we have obtained from cycloalkanecarboxylic acids. We are grateful to Professor Friedman for giving us the results of his experiments before publication.

(10) J. G. Traynham and M. T. Yang, *J. Am. Chem. Soc.*, **87**, 2394 (1965).

(11) During private discussions about our early results, Professor S. Swann, University of Illinois, suggested that such a conclusion would be supported by experimental data.

(12) A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(13) L. Ruzicka, P. Barman, and V. Prelog, *Helv. Chim. Acta*, **34**, 401 (1951).

(14) K. Schenker and V. Prelog, *ibid.*, **36**, 896 (1953).

Cyclooctanecarboxylic acid and cyclodecanecarboxylic acid were prepared by carbonation of the cycloalkylmagnesium chlorides with crushed Dry Ice: cyclooctanecarboxylic acid[15] (44%), bp 108° (0.12 mm), and cyclodecanecarboxylic acid[13] (67%), bp 122–123° (0.11 mm), mp 53°.

Electrolysis of Carboxylic Acids. The apparatus consisted of a 250-ml electrolytic beaker fitted with a large rubber stopper carrying a thermometer, a Dry Ice finger condenser, and two electrodes. The electrodes were rods 0.55 in. in diameter; the anode was graphite, the cathode, copper. During electrolysis, the mixture was stirred by a magnetic stirrer. The current source was a pair of 85-amp, 12-v batteries in series. A current density of 0.045 amp/cm^2 was maintained for all electrolyses; this current density amounted to 0.8 amp with these electrodes and 100 ml of solution. The current efficiency was approximated by dividing the moles of acid consumed by the faradays of electricity passed as estimated from the volume of gas evolved. Three other cell designs were investigated. A platinum anode was used in place of the graphite one, and a circular copper cathode, perforated to facilitate stirring, was used to allow a uniform field and current density around each anode.

An aqueous mixture consisting of 0.2 mole of cycloalkanecarboxylic acid, 0.075 mole of sodium hydroxide, and enough water to bring the volume to 100 ml was electrolyzed in the cell for 6–8 hr. The mixture was made strongly alkaline with sodium hydroxide, filtered to remove graphite which had crumbled from the anode, and extracted three times with petroleum ether. Cycloalkanecarboxylic acid was recovered from the aqueous layer. The organic extract was dried and distilled. The lower boiling hydrocarbon fraction was easily separated from the higher boiling alcohol and ester products. The hydrocarbon fraction was analyzed by gas chromatography; components in the mixture were identified by comparison of retention times with those of authentic samples and standard mixtures. The data are summarized in Table I. The volume of the gas evolved was measured by its displacement of water and used to compute the current efficiency of the electrolysis.

Preparation of Authentic Hydrocarbon Samples for Analysis. *cis*-Bicyclo[*x*.1.0]alkanes were prepared by methyleneation of the corresponding *cis*-cycloalkenes with methylene iodide and zinc–copper couple.[16] The properties were as follows. *cis*-Bicyclo[4.1.0]heptane[16] had bp 115°, $n^{25}D$ 1.4549; *cis*-bicyclo[6.1.0]nonane[6a] had bp 71–71.5° (26 mm), $n^{25}D$ 1.4682. *cis*-Bicyclo[7.1.0]decane had bp 83–84° (16 mm), $n^{24}D$ 1.4740. *Anal.* Calcd for $C_{10}H_{18}$: C, 86.9; H, 13.1. Found: C, 87.05; H, 13.0. The nmr spectrum included multiplet signals centered at 0.4 (1 H), −0.6 (4.4 H), −1.6 (12.6 H), and −1.8 to −2.2 ppm (2 H). *cis*-Bicyclo[8.1.0]undecane had bp 76–77° (5 mm), $n^{25}D$ 1.4786. *Anal.* Calcd for $C_{11}H_{20}$: C, 86.8; H, 13.2. Found: C, 86.8; H, 13.2. The nmr spectrum included multiplet signals centered at 0.5 (1 H), −0.6 (3.4 H), −1.3 to −1.7 (12.6 H), and −1.9 ppm (3 H).

Bicyclo[4.2.0]octane was prepared by catalytic hydrogenation of bicyclo[4.2.0]oct-7-ene,[17] prepared by photoisomerization of 1,3-cyclooctadiene.[17] The saturated hydrocarbon was obtained with platinum on carbon as catalyst but not with palladium on carbon as catalyst, which apparently isomerized either the bicyclooctene or the bicyclooctane or both. The nmr spectrum of bicyclo[4.2.0]octane includes signals centered at −1.47 (unresolved multiplet, 8 H), −1.82 (quartet with small side bands, 4 H), and −2.32 ppm (unresolved multiplet, 2 H).

cis-Cycloheptene and *cis*-cyclooctene were available commercially. A mixture of *cis*- and *trans*-cyclodecene was obtained from Columbian Carbon Co., Lake Charles, La., and another was prepared from cyclodecanol by treatment with *p*-toluenesulfonyl chloride in pyridine solution. A commercial sample of decalin was resolved into *cis* and *trans* isomers by preparative gas chromatography. Mixtures of other hydrocarbons were prepared by decomposition of the appropriate cycloalkanone tosylhydrazones;[6] peak identities in the gas chromatograms were established by reference to literature descriptions of the mixtures.[6]

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(15) M. Godchot and M. Caquil, *Chim. Ind.* (Paris), **29**, 1019 (1933).

(16) H. E. Simmons and R. D. Smith, in *Org. Syn.*, **41**, 72 (1961).

(17) S. F. Chappell, III, and R. F. Clark, *Chem. Ind.* (London), 1198 (1962). A sample of 1,3-cyclooctadiene was generously provided by Columbian Carbon Co., Lake Charles, La.

Factors Governing the Reaction of the Benzyl Grignard Reagent. II. Evidence for Triene Intermediates in the Reaction with Chloromethyl Methyl Ether

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Abstract: The reaction of the benzyl Grignard reagent with chloromethyl methyl ether has been studied in detail. There are at least five major products of this reaction: 2-phenylethyl methyl ether (I), *o*- (II) and *p*-methylbenzyl methyl ether (III), and *o*- (IV) and *p*-(2-methoxyethyl)benzyl methyl ether (V). When tetrahydrofuran is substituted for diethyl ether as a solvent for the reaction, the yield of I is increased and the diethers IV and V are eliminated. The substitution of benzylmagnesium bromide for benzylmagnesium chloride causes an increased yield of II. Benzyllithium forms only compound I in good yield. The major portion of compounds II and III is formed during the hydrolysis step with strong acid (*e.g.*, aqueous HCl). When hydrolysis was effected with ammonium chloride, compounds II and III were virtually eliminated. The intermediate responsible for the formation of II was characterized in part by causing it to react with maleic anhydride and diethyl maleate. Trimethylchlorosilane failed to trap Grignard intermediates which could conceivably function as precursors of the diethers IV and V. Conclusions based on these results were vitiated by the observations that the benzyl Grignard reacts more rapidly with chloromethyl methyl ether than with trimethylchlorosilane. The intermediate responsible for the formation of II could be made to react with gaseous formaldehyde in the presence of anhydrous magnesium chloride in a Prins-type reaction. The same intermediate failed to react with chloromethyl methyl ether under the same conditions.

The benzyl Grignard reagent possesses the intriguing capability of reacting at the α position, to produce so-called "normal" products, as well as at the *ortho* and *para* positions to form "abnormal" products.[1]

In the first paper in this series,[2] it was shown that

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(1) See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p 1133, for pertinent literature references.