Proximity Effects. XLVII. The Acid-Catalyzed Rearrangement of 5-Hydroxycyclooctanecarboxylic Acid Lactone[1]

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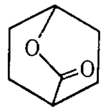
Abstract: The solvolysis of 5-hydroxycyclooctanecarboxylic acid lactone in 33% sulfuric acid gave 4-hydroxycyclooctanecarboxylic acid lactone (33.5%), 3-hydroxycyclooctanecarboxylic acid lactone (43.1%), 4-hydroxy-4-methylcycloheptanecarboxylic acid lactone (4.9%), 3-hydroxy-3-methylcycloheptanecarboxylic acid lactone (8.8%), and unidentified material (9.8%).

A number of reactions of cyclooctyl derivatives of the type commonly formulated as proceeding through carbonium ion intermediates lead to products formed by transannular hydride migration.[4] It is not surprising that transannular reactions are frequently observed under conditions which favor carbonium ion formation, since these are also the conditions under which rearrangements are most often encountered in other systems.

Rearrangements of lactones under acid conditions are known and 1,2-hydride shifts and alkyl migrations have been demonstrated. Treatment of either 4-hydroxycyclohexanecarboxylic acid lactone (**1**) or 3-hydroxycyclohexanecarboxylic acid lactone (**2**) with aqueous acid gives a mixture of the two.[5] Among other examples are the transformations **3** → **4**[6] and **5** → **6**.[7] It was of interest to determine whether an hydroxycyclooctanecarboxylic acid lactone would give rise to products that could be ascribed to proximity effects when treated with acid. Accordingly the solvolysis of 5-hydroxycyclooctanecarboxylic acid lactone was studied. The lactone **7**, prepared from bicyclo[3.3.1]nonan-9-one as previously described,[8] was heated with 33% sulfuric acid at 90° for 4 hr.[9] Extraction of the reaction mixture followed by distillation gave a complex mixture of products (78% yield based on $C_9H_{14}O_2$). Gas chromatographic analysis showed that it consisted of 4-hydroxycyclooctanecarboxylic acid lactone (**8**), 3-hydroxycyclooctanecarboxylic acid lactone (**9**), 4-hydroxy-4-methylcycloheptanecarboxylic acid lactone (**10**), 3-hydroxy-3-methylcycloheptanecarboxylic acid lactone (**11**), and a lactone **12** which remains unidentified. The individual components were isolated by gas chromatography and were identified by comparison of their infrared spectra and gas chromatographic retention times with those of authentic samples. Lactone **8** was indistinguishable from the starting lactone in its retention time on gas chromatography. The nmr spectrum was similar to that of the starting lactone but comparison of the mass spectra and infrared spectra showed minor differences. Comparison of the infrared spectrum of **8** with that of authentic 4-hydroxycyclooctanecarboxylic acid lactone[10] showed that these were identical.[11]



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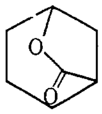

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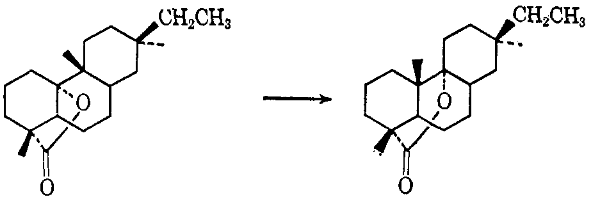
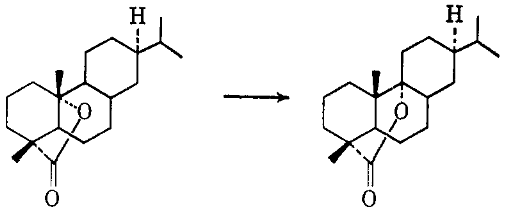


3 **4**



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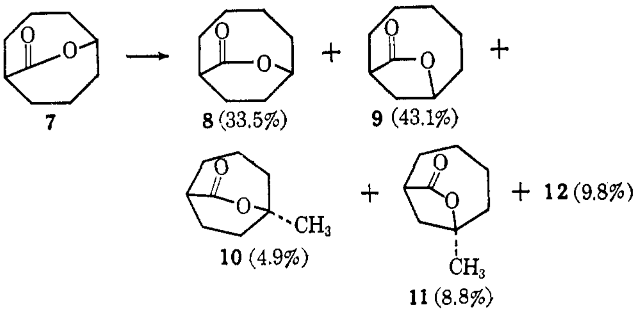

7 **8** (33.5%) **9** (43.1%) **10** (4.9%) **11** (8.8%)

The major product **9**, which showed an infrared absorption band at 1775 cm^{-1} indicating the presence of a γ-lactone group,[12] was synthesized in the following

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(3) Author to whom inquiries may be addressed: Department of Chemistry, Queens University, Belfast, Ireland.

(4) For a general discussion see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

(5) D. S. Noyce, H. I. Weingarten, and L. J. Dolby, *J. Org. Chem.*, **26**, 2101 (1961).

(6) L. J. Gough, T. F. Sanderson, V. I. Steinberg, and E. Wenkert, *ibid.*, **25**, 1269 (1960).

(7) L. A. Subluskey and T. F. Sanderson, *J. Am. Chem. Soc.*, **76**, 3512 (1954).

(8) A. C. Cope and D. M. Gale, *ibid.*, **85**, 3743 (1963).

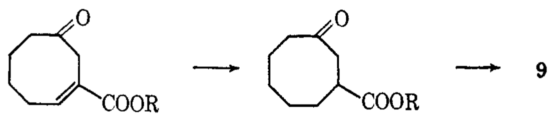
(9) Four hours proved to be the optimum time for solvolysis to produce the maximum amount of reaction without producing large amounts of what appeared to be secondary products.

(10) A. C. Cope and G. L. Woo, *J. Am. Chem. Soc.*, **85**, 3601 (1963).

(11) The comparison did not exclude the presence of a small amount (<5%) of the starting lactone.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 168.

way. 7-Oxo-1-cyclooctenecarboxylic acid[13] (**13a**) could not be hydrogenated to lactone **9** directly nor to the intermediate 3-oxocyclooctanecarboxylic acid (**14a**). The corresponding methyl ester **13b**, however, was smoothly converted to **14b** using Raney nickel. Further reduction of the ketone function was attempted catalytically followed by saponification and lactonization. Although this did provide some of the desired lactone, superior results were obtained by carrying out the reduction using sodium borohydride in sodium hydroxide solution. The lactone thus obtained was identical with the major product of the rearrangement of lactone **7**.

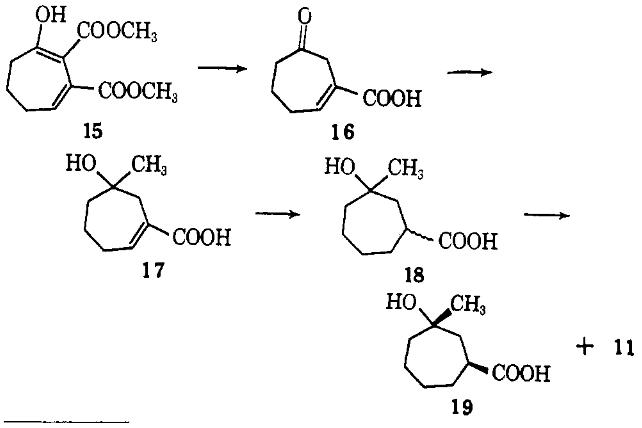


13a, R = H
b, R = CH_3

14a, R = H
b, R = CH_3

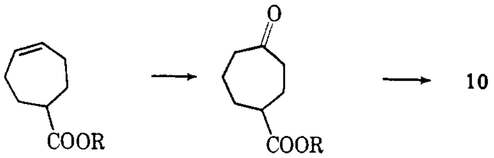
The spectroscopic characteristics of the remaining unknown compounds suggested that they might be products resulting from Wagner–Meerwein-type ring contraction. Thus the infrared spectrum of compound **11** indicated the presence of a γ-lactone and from the intensity of the peak appearing at *m/e* 139 ($M^+ - 15$) in the mass spectrum, it seemed likely that a tertiary methyl group was present on the oxygen-bearing carbon atom. The scheme used for the synthesis of lactone **11** was analogous to that employed for the synthesis of lactone **9**. Dimethyl 7-hydroxy-2,7-cycloheptadiene-1,2-dicarboxylate (**15**)[14] was heated under reflux with 20% aqueous hydrochloric acid to give 6-oxo-1-cycloheptenecarboxylic acid (**16**). The original plan involved catalytic reduction of the double bond followed by treatment with methylmagnesium iodide to give **18**. However, difficulty was again encountered in the hydrogenation step. This difficulty was overcome by simply reversing the steps in the sequence. Dehydration of the hydroxy acid **18** gave a lactone, in 6.7% over-all yield from **15**, which was identical in all respects with lactone **11** obtained from the solvolysis reaction. An hydroxy acid, presumably the *trans* isomer **19**, was also isolated.

The method of synthesis of lactones **9** and **11** was not applicable to lactone **10** due to the 1,4 relationship of the hydroxyl and carboxylate groups. 4-Cycloheptenecarboxylic acid (**20a**)[15] was esterified using methanol and sulfuric acid. Treatment of the ester **20b** with diborane generated *in situ* followed by oxidation of the organoborane with chromic acid gave methyl 4-oxocycloheptanecarboxylate (**21b**) which was hydrolyzed to the keto acid **21a**.[16] Treatment of the keto acid in tetrahydrofuran with an ethereal solution of 2.3 equiv of methylmagnesium iodide gave an oil from which the desired lactone could be isolated by preparative gas chromatography. The infrared and mass spectra of the lactone were identical with those of the lactone isolated in 4.9% yield from the solvolysis reaction.



15 → **16** → **17** → **18** → **19**

The identity of the remaining material **12** is still obscure. However, some observations on its characteristics are pertinent. At normal concentrations the material showed only one carbonyl absorption at 1775 cm^{-1} in the infrared spectrum, although a second absorption at 1749 cm^{-1} could be detected when the concentration was increased. The mass spectrum of this material showed no peak at *m/e* 139 ($M^+ - 15$), but medium-intensity peaks at *m/e* 126 and 125 were present.



20a, R = H
b, R = CH_3

21a, R = H
b, R = CH_3

An nmr spectrum of the distilled solvolysis mixture showed, in addition to the two methyl group singlets due to lactones **10** and **11**, an absorption centered at 1.02 ppm which could be interpreted as either two overlapping doublets or one triplet. At this point a gas chromatographic column became available which was capable of separating the unknown material into two components. An nmr spectrum[17] of the larger of the two compounds showed an absorption at 0.9 ppm which appeared to be a triplet and which integrated for three protons. The proton on the carboxyl-bearing carbon atom was clearly visible as a multiplet centered at 2.5 ppm, as was an absorption centered at 4.5 ppm. The remaining protons were grouped together in a broad multiplet at 1.2–2.2 ppm. The loss of 29 mass units in the mass spectrum and the presence of the triplet at 0.9 ppm in the nmr spectrum suggested the presence of an ethyl group. To test this theory, two ethyl-substituted hydroxycyclohexanecarboxylic acid lactones **22** and **23** were synthesized and an infrared spectrum of lactone **24** was obtained.[18,19] However, none of these compounds was identical with either of the unknown compounds comprising **12**.

In the solvolysis reaction a distinction based on the stereochemistry of the products between a mechanism involving formation and subsequent hydration of olefinic intermediates and one involving direct hydride shifts cannot be made. In view of the absence of isolated olefinic products and of the results of other in-

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[13] A. K. Bose, G. Mina, M. S. Mankas, and E. Rzucidlo, *Tetrahedron Letters*, 1467 (1963).

[14] G. A. Berchtold and G. F. Uhlig, *J. Org. Chem.*, **28**, 1459 (1963).

[15] G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

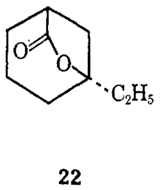
[16] C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 2208 (1963).

[17] This spectrum was obtained by computer addition of many individual spectra.

[18] D. S. Noyce and L. J. Dolby, *J. Org. Chem.*, **26**, 3619 (1961).

[19] We thank Professor D. S. Noyce for kindly supplying the infrared spectrum of lactone **24**.

vestigations[20-22] on the solvolysis of cyclooctyl compounds, a mechanism (summarized in Chart I) involving direct hydride shifts is preferred. Initial protonation and cleavage of the lactone grouping in **7** followed by a sequence of 1,2- or 1,3-hydride shifts and ring contraction could lead to the observed products. No products were identified which could arise *via* a 1,5-hydride shift. A similar result has been observed in the solvolysis of the tosylates of methyl *cis*- or *trans*-hydroxycyclooctanecarboxylate.[23] Thus the 5-carboxyl and the 5-carbomethoxy substituents prevent or retard 1,5-hydride shifts because of their electron-withdrawing properties.



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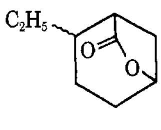

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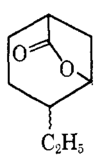

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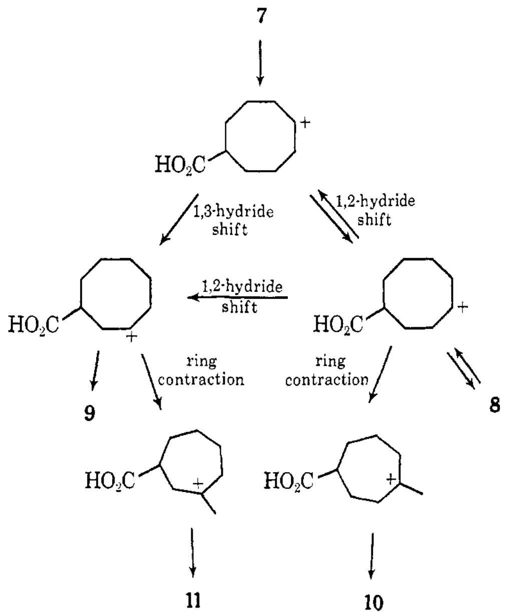
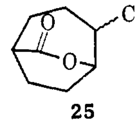
Chart I



It was established by suitable control experiments that lactones **9**, **10**, and **11** were stable to the reaction conditions. Solvolysis of lactone **8** led to a mixture of products that was identical in all respects with that formed on solvolysis of lactone **7**. The former result eliminates the possibility of formation of lactones **25** and **26** by rearrangement of lactone **10**, although it was established that lactone **27** does rearrange to **28** under the reaction conditions.



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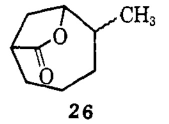

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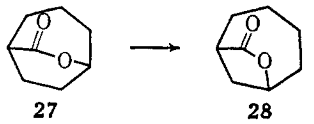

27 **28**

Experimental Section[24]

Solvolysis of Lactone 7. To 60 ml of 33% sulfuric acid was added 2.5 g of lactone **7**. The mixture was heated at 85–90° for 4 hr with stirring. The solution, which contained some black insoluble material, was extracted with four portions of pentane and four portions of ether. The combined organic layers were washed once with saturated sodium chloride solution and dried. Removal of solvent gave a yellow oil (2.2 g). Distillation in a short-path still gave 1.9 g (76%) of a clear oil, bp 77–81° (0.25 mm). The infrared spectrum of the distilled products showed carbonyl absorptions at 1775 and 1749 cm^{-1}. Gas chromatographic analysis on a 10-ft 5% XF 1150 column[25] at 180° showed the presence of five components. The individual products were collected and identified by comparison of their gas chromatographic retention times and infrared spectra with those of authentic samples.

7-Oxo-1-cyclooctenecarboxylic Acid (13a). Dimethyl 3-(N-morpholino)-2,8-cyclooctadiene-1,2-dicarboxylate (20 g) was dissolved in 30% methanolic potassium hydroxide (115 ml), and the resulting solution was heated under reflux for 1 hr. The solution was evaporated to dryness and the solid residue neutralized with concentrated hydrochloric acid with cooling. An additional 100 ml of 20% hydrochloric acid was added, and the white precipitate which formed was isolated by filtration. Recrystallization from benzene–pentane gave 2-carbomethoxy-3-hydroxy-2,8-cyclooctadienecarboxylic acid as white crystals, mp 174–175.5°; infrared (KBr): 1690, 1650, 1624, and 1605 cm^{-1}; λ_{max}^{EtOH} 210 mμ (ε 11,750) and 256 mμ (ε 10,700).

Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.63; H, 6.24. Found: C, 58.40; H, 6.24.

In subsequent preparations this acid was not isolated. The hydrochloric acid slurry was heated under reflux with efficient stirring until an aliquot showed no color with ferric chloride solution. This required from 4 to 24 hr on different preparations. The cooled solution was extracted with five 100-ml portions of methylene chloride. The combined extracts were washed once with water and dried. Removal of the solvent gave a brown solid which was recrystallized three times from benzene–hexane to give 7-oxo-1-cyclooctenecarboxylic acid, 6.6 g (61%), mp 108–109°; infrared ($CHCl_3$): 3500–2400, 1700, and 1640 cm^{-1}; nmr 11.7 (1 H, singlet), 7.31 (1 H, triplet), 3.50 (2 H, singlet), 2.68–1.50 (8 H, multiplet); λ_{max}^{EtOH} 214 mμ (ε 9040).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.29; H, 6.98.

Methyl 7-Oxo-1-cyclooctenecarboxylate (13b). The ester was prepared in 95% yield on a small scale by treatment of the acid with diazomethane. Larger amounts were more conveniently prepared using the normal Fisher procedure (54%). The product had bp 95–99° (0.75 mm); $n^{25}D$ 1.4997; infrared ($CHCl_3$): 1720–1705 and 1625 cm^{-1}; *nmr:* 7.01 (1 H, triplet), 3.75 (3 H, singlet), 3.39 (2 H, singlet), and 2.6–1.5 (8 H, multiplet); λ_{max}^{EtOH} 214 mμ (ε 8930).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.90; H, 7.82.

Methyl 3-Oxocyclooctanecarboxylate (14b). A solution of the keto ester **13b** (0.78 g) in methanol (15 ml) containing *ca.* 0.1 g of Raney nickel W2 catalyst was hydrogenated at room temperature and atmospheric pressure. After 1 hr, 96% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration through Celite, and the solvent was evaporated to give 0.69 g (88%) of a colorless oil, $n^{25}D$ 1.4754; infrared ($CHCl_3$): 1737 and 1700 cm^{-1}; nmr: 3.77 (3 H, singlet), 2.92–2.18 (5 H, multiplet), 2.18–1.18 (8 H, multiplet).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.54; H, 8.98.

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(20) A. C. Cope, A. Fournier, and H. E. Simmons, *J. Am. Chem. Soc.*, **79**, 3905 (1957).

(21) A. C. Cope and B. C. Anderson, *ibid.*, **79**, 3892 (1957).

(22) A. C. Cope, S. W. Fenton, and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

(23) A. C. Cope and D. L. Nealy, *ibid.*, **87**, 3122 (1965).

(24) Melting points were taken on a Kofler hot stage and are corrected; boiling points are uncorrected. Gas chromatographic analyses were carried out using a F & M Model 720 gas chromatograph. Nmr spectra were recorded on a Varian Associates A-60 instrument and are reported in parts per million downfield from TMS. The solvent employed was deuteriochloroform unless otherwise specified. Microanalyses were performed by Dr. S. M. Nagy and his associates. Except as noted, the drying agent employed was magnesium sulfate and solvents were removed under reduced pressure.

(25) All subsequent gas chromatographic analyses were carried out using this column.

3-Hydroxycyclooctanecarboxylic Acid Lactone (9). A solution of the keto ester **14b** (1.46 g) in methanol (15 ml) was cooled to 5° and to this was added 7.2 ml of a solution prepared from sodium borohydride (0.653 g) and 1 *N* sodium hydroxide (10 ml) which had been diluted to 25 ml with water. The addition required 0.5 hr and was carried out at 0–5° with stirring. The solution was stirred at room temperature for an additional 0.5 hr and then heated under reflux for 1 hr. The methanol was removed by distillation, and the cooled solution was acidified with 15% hydrochloric acid and stirred at room temperature overnight. The solution was extracted with four 20-ml portions of ether; the extracts were washed with water and dried, and the solvent was removed to yield 1.2 g of an oil. Distillation gave a white semisolid, bp 84–85° (0.2 mm), with physical characteristics identical with those of the major product of solvolysis of lactone **7**. The yield of lactone **9** could not be determined directly because of difficulties encountered in the distillation, but gas chromatographic analysis after esterification of the crude reaction product with diazomethane showed the presence of the lactone (61%) and an hydroxy ester (39%) which was presumably the *trans* isomer.

Lactone **9** was also prepared by hydrogenation of 2-bromo-3-hydroxycyclooctanecarboxylic acid lactone using 1% palladium on calcium carbonate as catalyst. The distilled product was identical with the material prepared in the manner outlined above, bp 89–91° (0.25 mm); infrared (CCl_4): 1775 cm^{-1}; nmr: 4.91 (1 H, multiplet) and 3.0–1.0 (13 H, multiplet).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.41; H, 9.25.

6-Oxo-1-cycloheptenecarboxylic Acid (16). A solution of dimethyl 7-hydroxy-2,7-cycloheptadienedicarboxylate (**15**) (34.5 g) in 20% aqueous hydrochloric acid (100 ml) was heated under reflux with stirring until an aliquot gave no color when treated with alcoholic ferric chloride solution (*ca.* 1 hr). The cooled solution was extracted with methylene chloride, and the organic layer was washed with water and dried. The oil obtained after removal of the solvent was dissolved in benzene and pentane was added to the cloud point. The crystals which formed were removed by filtration and dried. There was obtained 13 g (57%) of the keto acid **16**, mp 73.5–75.0°; infrared ($CHCl_3$): 3600–2400, 1705, and 1640 cm^{-1}; nmr: 11.5 (1 H, singlet), 7.36 (1 H, broad triplet), 3.66 (2 H, singlet), and 2.92–1.88 (6 H, multiplet); λ_{max}^{EtOH} 210 mμ (ϵ 7470).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.15; H, 6.38.

6-Hydroxy-6-methyl-1-cycloheptenecarboxylic Acid (17). To a solution of methylmagnesium iodide, prepared from magnesium (1.6 g) and methyl iodide (9.5 g) in anhydrous ether (120 ml), was added a solution of the keto acid **16** (5.0 g) in ether. As the addition proceeded, a precipitate formed. When the addition was complete, tetrahydrofuran (50 ml) was added and the mixture was heated under reflux for 5.5 hr. The cooled solution was poured into water and acidified with dilute hydrochloric acid, and the layers were separated. The aqueous layer was extracted with five 50-ml portions of ether, and the combined ether solutions were dried and evaporated to give a brown solid (4.1 g). The product was added to 80 ml of boiling benzene (not all went into solution), and the solution was allowed to stand overnight at 6°. White crystals (1.85 g, 34%) were obtained, mp 168–169°; infrared (KBr): 3450, 3600–2500, 1695, and 1640 cm^{-1}; nmr (CD_3SOCD_3): 11.3 (1 H, broad), 7.45 (1 H, triplet,) 5.4–4.0 (1 H, broad), 2.62 (2 H, singlet), 2.5–1.18 (7 H, multiplet), and 1.00 (3 H, singlet).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.23; H, 8.00.

3-Hydroxy-3-methylcycloheptanecarboxylic Acid Lactone (11). A solution of hydroxy acid **17** (1.0 g) in absolute ethanol (40 ml) was hydrogenated at room temperature and 1-atm pressure using 0.1 g of prereduced platinum oxide as catalyst. After 1 hr, 101% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration, and the solvent was removed at room temperature and reduced pressure. Essentially no lactone carbonyl absorption could be detected in the infrared spectrum of the product. The product was heated at 65° (100 mm), and a lactone carbonyl absorption appeared and reached a constant intensity after 2 hr. The oil was dissolved in ether, and the white precipitate which formed was removed by filtration. The ether solution was washed with saturated sodium bicarbonate solution and dried and the solvent removed. The solid residue was sublimed at 95° (14 mm) to give 400 mg (45%) of a waxy white solid with a camphoraceous odor, mp 57–59°; infrared (CCl_4): 1775 cm^{-1}; nmr: 2.70 (1 H, broad), 2.5–1.5 (10 H, multiplet), and 1.48 (3 H, singlet).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.91; H, 9.14.

These characteristics, the retention time on gas chromatographic analysis, and the mass spectrum were identical with those of lactone **11** isolated from the solvolysis mixture.

Methyl 4-cycloheptenecarboxylate (20b), prepared in 98% yield from 4-cycloheptenecarboxylic acid (**20a**) by esterification with methanol and sulfuric acid, had bp 35–37° (0.35 mm); n^{22}D 1.4668; infrared (CCl_4): 1745 and 1655 cm^{-1}; nmr: 5.93 (2 H, triplet), 3.76 (3 H, singlet), and 2.9–1.3 (9 H, multiplet).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.30; H, 9.17.

Methyl 4-Oxocycloheptanecarboxylate (21b). To sodium borohydride (0.95 g) in ether (30 ml) was added the unsaturated ester **20b** (6.7 g) and anhydrous zinc chloride (0.5 g). To the slurry was added boron trifluoride etherate (4.4 g) in ether (5 ml) over a period of 20 min. The mixture was stirred at room temperature for 2 hr and then water (5 ml) was added, followed by a solution of sodium dichromate dihydrate (11 g) and concentrated sulfuric acid (8.25 ml) in water (40 ml) over a period of 30 min. The two-phase solution was heated under reflux for 2 hr, and the layers were separated. The aqueous layer was extracted with three 100-ml portions of ether, and the combined ethereal extracts were washed with sodium chloride solution and then dried. Removal of solvent gave an oil which was distilled to give unreacted starting material (0.4 g) and 3.0 g (43%) of the keto ester, bp 75–77° (0.2 mm); infrared (CCl_4): 1735 and 1700 cm^{-1}; nmr 3.67 (3 H, singlet) and 3.0–1.3 (11 H, multiplet).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.28; H, 8.51.

Saponification of the ester by treatment with alcoholic sodium hydroxide solution at room temperature gave the corresponding acid in 59% yield, mp 59–60° (lit.[16] mp 58–59°); infrared ($CHCl_3$): 3400–2500 and 1705 cm^{-1}; nmr: 11.66 (1 H, singlet) and 2.85 (11 H, multiplet).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.25; H, 7.74.

4-Hydroxy-4-methylcycloheptanecarboxylic Acid Lactone (10). To a solution of methylmagnesium iodide prepared from magnesium (0.26 g) and methyl iodide (1.8 g) in ether was added a solution of keto acid **21a** (0.72 g) in tetrahydrofuran (10 ml) over a period of 30 min. The slurry was stirred for 2 hr at room temperature and then heated under reflux for 4 hr. The cooled solution was stirred with saturated aqueous ammonium chloride solution (50 ml), and the organic layer was separated. The aqueous layer was extracted with three 75-ml portions of ether, and the ethereal extracts were washed once with water, dried, and evaporated. This provided 0.65 g of a brown oil which showed no carbonyl absorption above 1710 cm^{-1} in the infrared spectrum. The oil was heated at 40–45° (100 mm) for 2 hr, and the whole mixture was esterified with diazomethane. Two peaks were evident when the product was analyzed by gas chromatography. The major product which also had the shorter retention time proved to be identical with the solvolysis product **10**.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.81; H, 9.13.