instrument employing sodium chloride optics and CCl_4 solutions of freshly purified materials in matched 1.0-mm. sodium chloride cells unless otherwise indicated.

A study of the effect of dilution on the split carbonyl band in the infrared spectrum of α-morpholino-*p*-phenylacetophenone gave the results: 9.21 mg./ml. CCl_4 in a 1.0-mm. cell, $\gamma_{1C=O}$, 1700/62, $\gamma_{2C=O}$, 1686/70 (a_2/a_1 = 1.13); 3.78 mg./ml. CCl_4 in a 1.0 mm. cell, $\gamma_{1C=O}$ 1702–38, $\gamma_{2C=O}$, 1686/47 (a_2/a_1 = 1.23); 0.75 mg./ml. CCl_4 in a 5.0-mm. cell, $\gamma_{1C=O}$, 1701/46, $\gamma_{2C=O}$, 1684/56 (a_2/a_1 = 1.21).

LINCOLN, NEBR.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Reaction of 1,5-Diketones with Sulfuric Acid

BY WILLIAM G. DAUBEN AND JAMES W. MCFARLAND[1]

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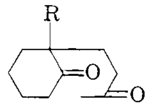
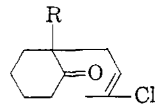
It has been found that certain 1,5-diketones upon treatment with sulfuric acid give rise to products with bridged bicyclic structures rather than the expected fused ring systems. The strain in certain 3,2,1-bicyclic systems is discussed.

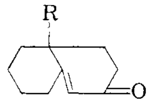
There are two general synthetic routes which have been employed to fuse an additional carbocyclic ring to a cyclic ketone. The first procedure, that of Robinson,[2] is the cyclization of a 1,5-diketone, such as Ia, with dilute acid or base. The second procedure, discovered by Wichterle[3] and widely employed by Prelog,[4,5] is the cyclization of a 2-(3′-chlorocrotyl)-cyclonone, such as IIa, with concentrated sulfuric acid. Although the reaction conditions of these two processes are very different, in both reactions the octalone IIIa is obtained in good yield. It has been proposed that the vinyl chloro group acts as a disguised ketone and upon treatment with strong acid gives rise to the same 1,5-diketone employed in the Robinson reaction.



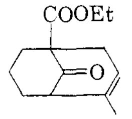
Ia, R = H
b, R = COOEt



IIa, R = H
b, R = COOEt



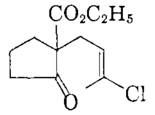
IIIa, R = H
b, R = COOEt



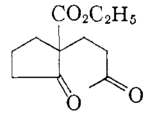
IV

One particular facet of these reactions which is of special interest arises when the potential angular grouping is carbethoxy. In this case, Ib under Robinson conditions[2] yields the expected octalone IIIb, while IIb under Wichterle conditions[4] gives rise to the bicyclic ketone IV. If the vinyl chloro group is acting as a disguised carbonyl group, then the strongly acidic conditions used in the Wichterle reaction must be a controlling factor directing ring closure to a bicyclic system. Such now has been found to be the case since Ib upon reaction with concentrated sulfuric acid yields bicyclic ketone IV in good yield.

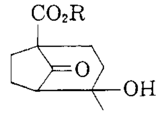
In contrast to the excellent reaction of IIb with sulfuric acid, Prelog and Zimmermann[5] found that ethyl 2-(3′-chlorocrotyl)-cyclopentanone-2-carboxylate (V) yielded only an intractable mixture of materials. In this reaction, the presumed intermediate would be ethyl 2-(3′-oxobutyl)-cyclopentanone-2-carboxylate (VI) whose reaction has now been studied. When the diketone VI was allowed to react with 95% sulfuric acid, a solid isomeric product ($C_{12}H_{18}O_4$) was obtained in good yield. The material could be hydrolyzed in either dilute acid or base to a carboxylic acid which, in turn, upon treatment with diazoethane was reconverted to the original ester. The infrared spectrum of the ester in carbon tetrachloride showed a single strong band at 1740 cm.$^{-1}$ and in chloroform showed two bands at 1732 and 1720 cm.$^{-1}$. The spectrum of the acid in chloroform possessed bands at 1750 and 1719 cm.$^{-1}$. These data indicate the presence of a cyclopentanone and a carboxyl function. No direct chemical evidence for the carbonyl group could be obtained since the product would not react with 2,4-dinitrophenylhydrazine, semicarbazide or thiosemicarbazide, even under forcing conditions. The fourth and remaining oxygen function was shown to be a hydroxy group by the presence of a weak but definite band at 3450 cm.$^{-1}$ in the infrared spectrum, and by the presence of one active hydrogen as determined by the Zerewitinoff reaction.



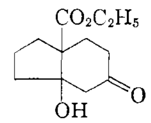
V



VI



VII, R = C_2H_5
VIII, R = H



IX

Based upon these data and assuming no deep seated rearrangement, there are two possible formulations for the reaction product, VII and IX.

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[1] United States Rubber Co. Fellow in Chemistry, 1955–1956; Dow Chemical Co. Fellow in Chemistry, 1956–1957.

[2] E. C. DuFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[3] O. Wichterle, J. Prochazka and J. Hofman, *Coll. Czech. Chem. Comm.*, **13**, 300 (1948).

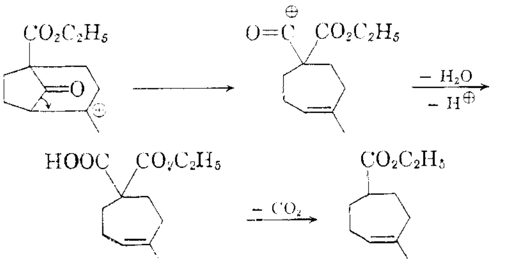
[4] V. Prelog, P. Barman and M. Zimmermann, *Helv. Chim. Acta*, **32**, 1284 (1949).

[5] V. Prelog and M. Zimmermann, *ibid.*, **32**, 2360 (1949).

However, the chemical reactivity of the material clearly establishes the correctness of structure VII. It was found that upon oxidation by the Kuhn–Roth procedure the ester possessed two C-methyl groups, and the parent acid VIII possessed one such function. Further, the stability of the tertiary hydroxy function to the strong dehydrating conditions would not be expected of structure IX, whereas the bicyclic nature of VII could endow such stability to an alcoholic grouping. The stability of the hydroxyl function, and the unreactivity of the carbonyl group will be discussed in more detail later.

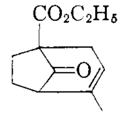
Since the reaction of VI with sulfuric acid led to a single product in high yield, the Wichterle reaction of V was reinvestigated. A mixture of neutral and acidic products was obtained. Fractional distillation of the neutral portion gave two distinct fractions, a lower boiling one in 2.6% yield, and a higher boiling one in 32% yield. A solid compound was obtained from the acidic fraction in 6.8% yield.

The lower boiling neutral fraction had the composition $C_{11}H_{18}O_2$, and possessed two C-methyl groups (Kuhn–Roth), one double bond (microhydrogenation) and one ethoxyl group (Zeisel). The infrared spectrum of the material exhibited a band at 1732 cm.$^{-1}$ which is characteristic of a non-conjugated ester. From these data and the plausible reaction mechanism shown in the diagram, the product was assigned the structure of ethyl 4-methyl-Δ^4-cycloheptenecarboxylate (X).

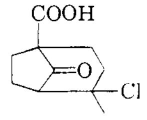


X

Analyses of the higher boiling neutral fraction established a composition of $C_{12}H_{16}O_3$, and, in addition, the material possessed two methyl groups (Kuhn-Roth), one double bond (microhydrogenation) and one ethoxy group (Zeisel). Bands of 1760 and 1727 cm.$^{-1}$ in the infrared spectrum indicate cyclopentanone and ester features in the structure. The ultraviolet spectrum displayed a maximum only at 294 mμ (ϵ 76) which demonstrates that there is no conjugated system. The compound reacted readily with thiosemicarbazide to give a characteristic derivative. These data indicate that the product is ethyl 4-methyl-Δ^3-bicyclo-[3:2:1]octene-8-on-1-carboxylate (XI), the five-membered ring analog to the series of compounds studied by Prelog and his co-workers.[4] When XI was treated with 90% sulfuric acid, the ketol-ester VII was obtained, thus demonstrating the relationship between the two compounds. In addition, the reaction of XI with 6 *N* hydrochloric acid gave VIII as the product. Saponification of XI, however, gave an oily material which could not be characterized.



XI

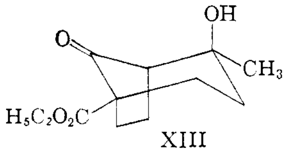


XII

The solid acidic product had the composition $C_{10}H_{13}O_3Cl$, and possessed one C-methyl group (Kuhn–Roth). No double bond was present because the acid would not reduce solutions of bromine or potassium permanganate. The infrared spectrum of the material exhibited bands at 1760 (cyclopentanone) and at 1704 cm.$^{-1}$ (acid). The ultraviolet spectrum showed a maximum only at 290 mμ (ϵ 22) which is indicative of a non-conjugated ketone. However, the acid did not react with 2,4-dinitrophenylhydrazine, semicarbazide or thiosemicarbazide. The reaction of this acid with 6 *N* hydrochloric acid to give VIII, however, permits one to formulate its structure as 4-chloro-4-methylbicyclo[3:2:1]octan-8-on-1-carboxylic acid (XII).

These studies afford some interesting observations on the chemistry of bicyclo[3:2:1]octane systems. Of primary importance in determining the structure of the ketol-ester VII was the question of the surprising stability of the tertiary hydroxyl group under conditions known to cause elimination in the bicyclo[3:3:1]nonane system. The ease with which XI was converted to VII by 90% sulfuric acid, however, would seem to indicate that a double bond in such a bicyclic system introduces considerable strain, a strain released by hydration of the double bond. In line with this hydration of a double bond are the results of Newman and Yu[6] who found that by treating Δ^2-bicyclo[2:2:2]-octene with 80% sulfuric acid, 2-bicyclo[3:2:1]-octanol was obtained.

It is interesting to note that while the ketone function of the ketol-ester VII is inert to a reagent such as thiosemicarbazide, XI reacts with no apparent difficulty. The difference in reactivity must be due to the additional substituent at the C-4 position. It is evident that in forming a thiosemicarbazone the C-8 carbon atom must expand its sp^2 orbitals to sp^3 at some point during the course of reaction. Consideration of the most probable conformation of the ketol-ester XIII shows that the addition of any reagent to the carbonyl group creates a 1,3-diaxial repulsive interaction between the substituents on C-4 and C-8. Apparently, in this case the interaction is strong enough to prevent reaction under normal conditions.



XIII

Experimental[7]

Ethyl 2-(3′-oxobutyl)-cyclohexanon-2-carboxylate (Ib) prepared in the manner described by Dreiding and Tomasewski.[8]

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(6) M. S. Newman and Y. T. Yu, THIS JOURNAL, **74**, 507 (1952).

(7) All melting points and boiling points reported here are uncorrected. The ultraviolet spectra were all taken in 95% ethanol. Only

Ethyl 4-Methyl-Δ^3-bicyclo[3:3:1]nonen-9-on-1-carboxylate (IV) and the Corresponding Acid.—Sulfuric acid (95%, 5.0 cc.) was added dropwise with swirling and cooling to 4.51 g. (0.0188 mole) of Ib. The resulting red-brown solution was allowed to stand for 36 hours at room temperature after which time it was poured cautiously into 200 cc. of saturated sodium bicarbonate solution. The basic aqueous solution was extracted three times with 25-cc. portions of ether. The combined ethereal extracts were dried and the solvent was removed. The residual oil was fractionally distilled to yield 2.43 g. (58%) of IV, b.p. 96–98° (0.3 mm.), n^{25}D 1.4921, λ_{max} 287 mμ (ϵ 55); ν_{max} 1720 , 1730 cm.$^{-1}$ [lit.[4] b.p. 82–84° (0.1 mm.), λ_{max} 292 mμ (ϵ 50)].

The basic aqueous solution from which the keto-ester had been extracted was acidified with sulfuric acid, and then was extracted three times with 25-cc. portions of ether. The combined extracts were dried and the solvent was removed to yield 425 mg. (12%) of crude 4-methyl-Δ^3-bicyclo[3:3:1]nonen-9-one-1-carboxylic acid. This product was twice recrystallized from hexane–chloroform; m.p. 140–141°, λ_{max} 290 mμ (ϵ 49) [lit.[4] m.p. 139°, λ_{max} 293 mμ (ϵ 32)].

Anal. Calcd. for $C_{11}H_{14}O_3$ (194.22): C, 68.02; H, 7.27. Found: C, 67.87; H, 7.18; neut. equiv., 191; C-methyl (Kuhn–Roth), 0.45 per mole.

The acid also was obtained from IV in the following manner. A solution of 525 mg. (2.36 mmoles) of IV, 0.65 g. of potassium hydroxide and 6 cc. of methanol was heated under reflux for 4 hours. The solution was poured into 50 cc. of water, and was acidified with hydrochloric acid. The aqueous solution was extracted three times with 20-cc. portions of ether. The combined extracts were dried, and the solvent was removed to give 374 mg. of a crystalline red-brown residue. The material was recrystallized from hexane–chloroform to give 166 mg. (36%) of 4-methyl-Δ^3-bicyclo[3:3:1]nonen-9-one-1-carboxylic acid, m.p. 140–142°; mixed m.p. with acid obtained previously, 140.5–142°.

The thiosemicarbazone of IV was obtained by dissolving 100 mg. (1.10 mmoles) of thiosemicarbazide and 22 mg. (1.00 mmole) of IV in 5 cc. of hot 80% methanol, and allowing the resulting solution to stand at room temperature for 18 hours. The crystalline thiosemicarbazone was filtered; yield 256 mg. (87%), m.p. 209–210° dec.

Anal. Calcd. for $C_{14}H_{21}O_2N_3S$ (295.40): C, 56.92; H, 7.17; N, 14.23; S, 10.86. Found: C, 57.20; H, 6.88; N, 14.40; S, 10.70.

Ethyl 2-(3′-Oxobutyl)-cyclopentanone-2-carboxylate (VI).—A solution of 49.6 g. (0.318 mole) of ethyl cyclopentanon-2-carboxylate, 30.0 cc. (25.5 g., 0.354 mole) of anhydrous methyl vinyl ketone, 12.0 cc. of triethylamine and 200 cc. of dry benzene was allowed to stand at room temperature for 7 days. The volatile components were then removed and the product VI was fractionally distilled, b.p. 140–142° at 2.5 mm., n^{25}D 1.4641, yield 66.3 g. (92%) (lit.[9] b.p. 139° at 3 mm.).

Anal. Calcd. for $C_{12}H_{18}O_4$ (226.26): C, 63.70; H, 8.02; OC_2H_5, 19.92. Found: C, 63.84; H, 8.14; OC_2H_5, 20.28.

The disemicarbazone was made in the usual manner, m.p. 178–179° (lit.[9] 178–179°).

Ethyl 4-Hydroxy-4-methylbicyclo[3:2:1]octan-8-on-1-carboxylate (VII).—While cooling in an ice-bath, 1.0 g. of 95% sulfuric acid was added dropwise with swirling to 500 mg. (2.21 mmole) of VI. The resulting solution was allowed to stand at room temperature overnight, and then was poured into 10 cc. of ice and water. The aqueous solution was neutralized with sodium bicarbonate, and the solid product was filtered and washed with water; yield 375 mg. (75%), m.p. 53–56°. Two recrystallizations from methanol-water gave pure VII, m.p. 61–62°, λ_{max} 211 mμ (ϵ 170); γ_{max} 3450, 1732, 1720 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{18}O_4$ (226.26): C, 63.70; H, 8.02; OC_2H_5, 19.92. Found: C, 63.42; H, 8.19; OC_2H_5, 19.40; mol. wt. (Rast), 240; C-methyl (Kuhn–Roth): 2.0 per mole; active hydrogen (Zerewitinoff): 0.95 per mole.

Compound VII does not discolor solutions of either bromine or potassium permanganate under the usual conditions of testing unsaturation. All attempts to make a 2,4-dinitrophenylhydrazone, semicarbazone or thiosemicarbazone derivative failed.

4-Hydroxy-4-methylbicyclo[3:2:1]octan-8-on-1-carboxylic Acid (VIII). (a).—With heating on a steam-bath for 30 minutes, 505 mg. (2.23 mmoles) of VII dissolved in 10 cc. of 6 *N* hydrochloric acid. Upon cooling, the solution gave 270 mg. (61%) of VIII. The material was twice recrystallized from chloroform–carbon tetrachloride; m.p. 176–177°, λ_{max} 211 mμ (ϵ 150); ν_{max} 1750–1719 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{14}O_4$ (198.24): C, 60.59; H, 7.12. Found: C, 60.45; H, 6.98; neut. equiv., 198; C-methyl (Kuhn–Roth), 0.78 per mole.

Compound VIII did not discolor either bromine or permanganate solutions. All attempts to make a 2,4-dinitrophenylhydrazone, semicarbazone or thiosemicarbazone failed.

(b).—A solution of 243 mg. (1.07 mmole) of VII and 7.0 cc. of 2 *N* sodium hydroxide was stirred at room temperature for 24 hours. A small amount of amorphous, insoluble material was filtered, and the filtrate was acidified. The aqueous solution was extracted with ether three times, and the combined extracts were dried. The solvent was removed to give a waxy solid which was twice recrystallized from chloroform–carbon tetrachloride; m.p. 175–176°. No depression of the melting point was observed when this acid was mixed with that obtained in (a).

The Reconversion of VIII to VII.—Using the method described by McKay and his co-workers,[10] diazoethane was passed through a solution of 194 mg. (1.00 mmol.) of VIII and 10 cc. of ether. After standing at room temperature for 15 minutes, the solution was treated with a few drops of glacial acetic acid to destroy the excess diazoethane. The ether was distilled, and the oily residue was then recrystallized from methanol–water to give 89 mg. (39%) of VII, m.p. 61–62°, mixed m.p. 61–62°.

Ethyl 2-(3′-Chlorocrotyl)-cyclopentanone-2-carboxylate V) was prepared by the procedure of Prelog and Zimmermann.[5]

The Reaction of V with Sulfuric Acid.—With cooling and swirling, 14 cc. of 95% sulfuric acid was added dropwise to 13.1 g. (0.0533 mole) of V. Caution had to be observed about half-way through the addition of the acid because the evolution of hydrogen chloride became so vigorous that the reactants were in danger of foaming over the walls of the reaction flask. When the addition was complete, the resulting solution was allowed to stand at room temperature for 7 days. The solution was poured into 700 cc. of ice and water, and was then neutralized with sodium bicarbonate. The neutral organic was extracted from the aqueous solution using three 80-cc. portions of ether. The combined extracts were dried, and the solvent was removed to give an oily residue which was fractionally distilled into X and XI.

Compound X was presumed to be ethyl 4-methyl-Δ^4-cycloheptencarboxylate plus about 5% of an α,β-unsaturated isomeric ester, yield 250 mg. (2.6%), b.p. 78–80° (2.0 mm.), n^{25}D 1.4640, λ_{max} 232 mμ (ϵ 510), γ_{max} 1732 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{18}O_2$ (182.25): C, 72.49; H, 9.95; OC_2H_5, 24.78. Found: C, 72.29; H, 9.80; OC_2H_5, 24.22; double bonds (microhydrogenation, Pd–C in 95% ethanol), 1.04 per mole; C-methyl (Kuhn–Roth), 1.64 per mole.

Compound XI was ethyl 4-methyl-Δ^3-bicyclo[3:2:1]-octene-8-on-1-carboxylate; yield 3.53 g. (32%), b.p. 111–115° (1.2–1.6 mm.), n^{25}D 1.4826, λ_{max} 294 mμ (ϵ 76); γ_{max} 1760, 1727 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{16}O_3$ (208.25): C, 69.20; H, 7.75; OC_2H_5, 21.64. Found: C, 69.42; H, 8.02; OC_2H_5, 21.69; double bonds (microhydrogenation, Pd–C in 95% ethanol), 0.91 per mole; C-methyl (Kuhn–Roth), 1.74 per mole.

The aqueous solution from which the neutral organic products had been extracted was acidified with sulfuric acid, and was extracted four times with 70-cc. portions of ether.

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the definitive peaks of the infrared spectra are recorded. The analyses were performed by the Microanalytical Laboratory, College of Chemistry, the University of California.

(8) A. S. Dreiding and A. J. Tomasewski, THIS JOURNAL, **77**, 168 (1955).

(9) J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825 (1949).

(10) A. F. McKay, THIS JOURNAL, **71**, 1968 (1949); A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Res.*, **B28**, 683 (1950).

The combined extracts were dried, and the solvent was removed to give 3.38 g. of a white powder, m.p. 130–155°. Two recrystallizations from chloroform–carbon tetrachloride gave 788 mg. (6.8%) of 4-chloro-4-methylbicyclo-[3:2:1]octan-8-one-1-carboxylic acid (XII), m.p. 180–182°. One more recrystallization gave an analytical sample, m.p. 182–183°, λ_{max} 290 mμ (ϵ 22); ν_{max} 1760, 1704 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{13}O_3Cl$ (216.66). C, 55.43; H, 6.05; Cl, 16.37. Found: C, 55.31; H, 5.90; Cl, 16.14; C-methyl (Kuhn–Roth), 0.76 per mole.

Attempts to make a 2,4-dinitrophenylhydrazone, semicarbazone or thiosemicarbazone derivative of XII all failed.

The Thiosemicarbazone of XI.—A solution of 265 mg. (1.27 mmoles) of XI, 116 mg. (1.27 mmoles) of thiosemicarbazide and 7 cc. of 95% ethanol was heated under reflux for 4 hours. Rapid cooling of the reaction solution gave 182 mg. (51%) of the thiosemicarbazone as leaflets, m.p. 191–193.5°. (When the cooling occurred more slowly, a dimorphic form of the product was obtained: prisms, m.p. 185–188°.) Two recrystallizations from 95% ethanol gave an analytic sample, m.p. 193–195°.

Anal. Calcd. for $C_{13}H_{19}O_2N_3S$ (281.37): C, 55.49; H, 6.81; N, 14.93; S, 11.40. Found: C, 55.58; H, 6.63; N, 14.86; S, 11.20.

The Conversion of XI to VII.—With swirling and cooling in an ice-bath 536 mg. (2.58 mmoles) of XI was treated with 1.0 cc. of chilled 90% sulfuric acid (dropwise addition). The resulting solution was allowed to stand at room temperature overnight, and was then poured into 100 cc. of saturated sodium bicarbonate solution cautiously. The solid organic material was filtered to give 189 mg. of a product, melting 45–51°. Recrystallization from methanol–water gave 58 mg. (10%) of VII, m.p. 58–60°, mixed m.p. 60.5–62°.

The aqueous solution was extracted three times with 20-cc. portions of chloroform. The combined extracts were dried, and the solvent was removed to give 313 mg. of an oil which would not crystallize from various solvents. The infrared spectrum of the material, however, showed it to be largely VII.

Hydrolysis of XI by 6 *N* Hydrochloric Acid.—A mixture of 270 mg. (1.30 mmoles) of XI and 5.5 cc. of 6 *N* hydrochloric acid was stirred at room temperature for 48 hours. The resulting solution was extracted three times with 10-cc. portions of chloroform. The combined extracts were dried, and the solvent was removed to give 151 mg. of oily and solid products. Recrystallization from chloroform–hexane gave 52 mg. (20%) of VIII, m.p. 177–178°, mixed m.p. 174–176°.

The Saponification of XI.—A solution of 549 mg. (2.64 mmoles) of XI and 10 cc. of 10% potassium hydroxide in methanol was heated under reflux for 3 hours. The reaction solution was poured into 100 cc. of water, and was acidified with hydrochloric acid. The aqueous solution was extracted three times with 15-cc. portions of chloroform. The combined extracts were dried, and the solvent was removed to yield 167 mg. of an oily product. The infrared spectrum of this material exhibits only one band at 1700 cm.$^{-1}$ in the carbonyl stretching region. Apparently the cyclopentanone feature of the structure had been lost. Attempts to obtain a crystalline product from the oil all failed.

The Conversion of XII to VIII.—The acid XII (168 mg., 0.775 mmole) was dissolved in 5 cc. of 6 *N* hydrochloric acid by heating on a steam-bath for 3 hours. When cool, the solution was extracted four times with 5-cc. portions of chloroform. The combined extracts were dried, and the solvent was removed to give a solid material which was recrystallized from chloroform–carbon tetrachloride; yield 25 mg. (16%), m.p. 176–178°, mixed m.p. with VIII 175–177°, mixed m.p. with starting chloro-acid 149–165°.

The Attempted Periodic Acid Oxidation of VIII.—The acid (173 mg., 0.875 mmole) was dissolved in 40 cc. of 0.1 *N* sodium bicarbonate solution, while 310 mg. (1.35 mmol.) of periodic acid was dissolved in another 40 cc. of 0.1 *N* sodium bicarbonate solution. These two preparations were rapidly mixed, and the resulting solution was made acid to congo red paper by the addition of hydrochloric acid. The volume was brought to exactly 100.0 cc., and a sample was removed for quantitative determination of the periodic acid concentration.

The analytical procedure was: A 5.02-cc. sample was withdrawn from the reaction solution, and was added to 9.90 cc. of a 0.0109 *M* sodium arsenite solution to which an excess of sodium bicarbonate had been added. Starch indicator was added along with 0.5 cc. of a 20% potassium iodide solution. The excess arsenite was then titrated against a 0.00960 *M* iodine solution. The results of this analysis done at various intervals are:

Hours	0	4	28	100	192
I_2, cc.	3.72	3.82	3.78	3.87	3.80

The remaining solution in the reaction flask was extracted three times with 15-cc. portions of chloroform. The combined extracts were dried, and the solvent was removed to give 107 mg. (81%) of unreacted starting material.

The Attempted Conversion of VII to Ethyl 5,6,7,8-Tetrahydroindan-5-on-8-carboxylate.—A solution of 1.00 g. (4.43 mmol.) of VII, 1.00 g. of aluminum *t*-butoxide and 20 cc. of dry benzene was heated under reflux for 48 hours. When cool, the solution was poured into 100 cc. of water. The resulting mixture was extracted three times with 25-cc. portions of ether. The combined extracts were dried, and the solvent was removed to give 0.90 g. (90%) of crude starting material. One recrystallization from methanol–water afforded material melting at 60–62°; the mixed m.p. was 60–62°.

The Attempted Conversion of Ethyl 5,6,7,8-Tetrahydroindan-5-on-8-carboxylate to VII.—With cooling and swirling, 400 mg. (1.92 mmoles) of the indanone was treated dropwise with 1.3 g. of 90% sulfuric acid. The resulting solution was allowed to stand at room temperature for 2 days after which it was poured cautiously into 75 cc. of saturated sodium bicarbonate solution. The basic aqueous solution was extracted three times with 15-cc. portions of ether. The combined extracts were dried, and the solvent was removed to give an oil. The infrared spectrum of the product showed it to be identical with the starting material; yield 352 mg. (88%).

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