Preparation of II-Phenyl-[3]-quinque[4,3,4]phenyl (XIIIb).—A solution of 4-xenyllithium was prepared in the usual manner from 4.2 g. of *p*-bromobiphenyl (0.018 mole) and 0.28 g. of lithium metal (0.040 mole). Ketone XII (3.9 g., 0.012 mole), in 25 ml. of dry benzene, was added dropwise and the complex was decomposed with cold dilute sulfuric acid. The product was treated as described above for hydrocarbon XIIIa. Crystalline material was obtained at both the dienic and aromatic stage without the use of chromatography. The aromatic compound was recrystallized from isopropyl alcohol–benzene; yield 3.7 g. (68% from ketone XII), m.p. 182–184°, λ_{max}(isoöctane) 279 mμ (ϵ 5.6 $\times$ 10^4), 252 mμ (ϵ 4.1 $\times$ 10^4).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.42; H, 5.72; mol. wt. (cryoscopic), 468.

Preparation of 3-Xenyl Bromide.—The method used was essentially that of Huber, *et al.*[9] A slight modification of Huber's procedure afforded 3-xenyl bromide of high purity. Chromatography, employing an alumina column, followed by a second distillation produced a purer product. The 3-xenyl bromide, which had previously been reported as a liquid, was recrystallized from petroleum ether (30–60°); m.p. 9°. (Use of this 3-xenyl bromide did not, however, alleviate the problem of crystallization difficulties with polyphenyls containing *meta* links.)

Preparation of II-Phenyl-[3]-quinque[4,3,3]phenyl (XIIIc) and Its Dienic Precursor.—Ketone XII (3.24 g., 0.01 mole) was added slowly in dry benzene to a solution of 3-xenylmagnesium bromide prepared in the usual manner from 4.7 g. of 3-xenyl bromide (0.02 mole) and 0.5 g. of magnesium metal (0.02 mole). The addition complex was decomposed and the reaction product treated as described previously for hydrocarbon XIIIa. The diene was induced to crystallize in an ethanol–benzene mixture. It was recrystallized from ethanol–benzene (1:1) to a pale yellow solid; yield 3.0 g. (65%), m.p. 132–134°, λ_{max}(isoöctane) 248 mμ, inflections at 275 and 320 mμ.

Anal. Calcd. for $C_{36}H_{28}$: C, 93.88; H, 6.12. Found: C, 93.69; H, 5.84.

One gram of the diene in *p*-cymene was refluxed with palladium-on-charcoal. The aromatic product was treated in a manner similar to that employed in the synthesis of hydrocarbon XIIIa. The aromatic hydrocarbon was recrystallized from petroleum ether (60–80°)-benzene (1:1); yield 0.92 g. (99% from diene, 64% from ketone), m.p. 145–146°, λ_{max}(isoöctane) 248 mμ (ϵ 6.4 $\times$ 10^4).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.12; H, 5.57; mol. wt. (cryoscopic), 470.

Preparation of II-Phenyl-[3]-quinque[4,3,2]phenyl (XIIId).—Ketone XII (3.9 g., 0.012 mole), in dry benzene, was added slowly to an ethereal solution of 2-xenylmagnesium iodide that was prepared from 70 g. (0.025 mole) of 2-xenyl iodide and 0.6 g. of magnesium metal (0.025 mole). The complex was decomposed and the product treated as described for XIIIa. The crude diene was refluxed for 1 hour in *p*-cymene with palladium-on-charcoal. The product was treated in a manner similar to that described for hydrocarbon XIIIa. The polyphenyl was recrystallized from petroleum ether (60–80°)-benzene (1:1); yield 2.3 g. (42% from ketone XII), m.p. 172–174°, λ_{max}(isoöctane) 242 mμ (ϵ 4.8 $\times$ 10^4), inflection at 267 mμ.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.24; H, 5.90; mol. wt., (cryoscopic), 465.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract No. AF 33(616)-5063, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

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[9] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, THIS JOURNAL, **68**, 1111 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

The Baeyer–Villiger Oxidation of Bicyclic Ketones

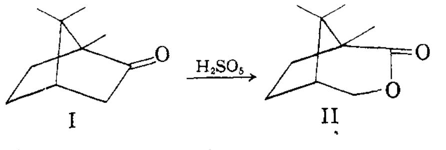
BY JERROLD MEINWALD[1] AND ELLIOTT FRAUENGLASS[2]

RECEIVED MARCH 5, 1960

The peracetic acid oxidation of bicyclo[2,2,1]heptanone-2 was carried out in buffered medium and in the presence of a strong acid catalyst. The primary product, in each case, was found to be the lactone of *cis*-3-hydroxycyclopentylacetic acid, corresponding to migration of the bridgehead carbon atom. The structure of this product was proved by direct comparison with an independently synthesized sample. The isomeric lactone, derived from *cis*-3-hydroxymethylcyclopentanecarboxylic acid, was also synthesized by an unambiguous route, and was not found in the Baeyer–Villiger reaction product. The oxidation of bicyclo[2,2,2]octanone was found to give rise to *cis*-4-hydroxycyclohexylacetic acid lactone, while bicyclo-[2,2,2]octen-5-one-2 suffered attack at the carbonyl group rather than at the double bond yielding a rearranged lactone derived from 2-hydroxycyclohexen-3-ylacetic acid. The factors determining the migrating group in these and related Baeyer–Villiger reactions are discussed briefly.

Introduction.—In 1899, Baeyer and Villiger reported the first examples of the peracid oxidation of ketones to esters or lactones.[3] Since that time this type of oxidation has found a wide variety of important synthetic and degradative applications.[4] Thus, peracids have been used to synthesize a variety of steroid and terpene lactones, as well as lactones involving medium and large rings which are virtually unobtainable by any other means.

Although the general mechanistic features of this oxidative rearrangement are understood,[4] the original observation of Baeyer and Villiger that persulfuric acid transforms camphor (I) into α-campholide (II) (see eq. 1) has been difficult to understand since this reaction course implies that the migration of a primary group (methylene) has taken precedence over the migration of a tertiary group (the bridgehead carbon). This implication, which



(1)

is hard to reconcile with the more generally observed rule that in an unsymmetrical ketone the group which can better accommodate the positive charge will migrate, has been rationalized by Murray, Johnson, Pederson and Ott on the basis of a

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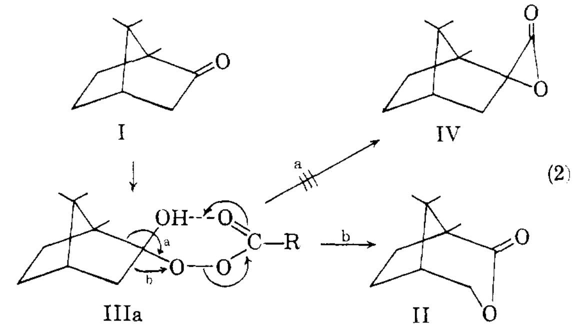
[1] Fellow of the Alfred P. Sloan Foundation.

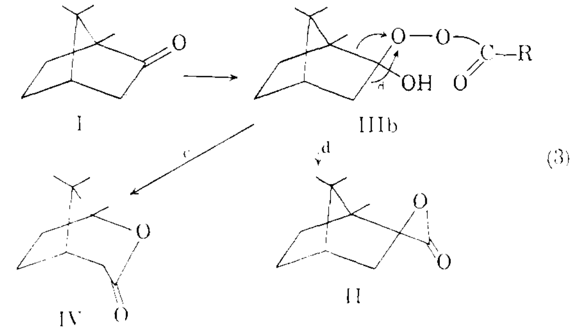
[2] Monsanto Fellow, 1959.

[3] A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899).

[4] For a convenient survey of this reaction see the review by C. H. Hassall in R. Adams, "Organic Reactions," Vol. 9, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 73.

steric argument.[5] Thus, camphor was presumed to give rise exclusively to the hydroxyperester IIIa, which could give α-campholide *via* a relatively unstrained transition state (chair conformation), while migration of the bridgehead would require a boat form transition state (see eq. 2). This argument ignores the fact that addition of the peracid to the camphor carbonyl group in the opposite steric sense would give the epimeric hydroxyperester IIIb, *which could then give the electronically favored product IV via the sterically favored transition state (chair conformation)*, as shown in eq. 3.



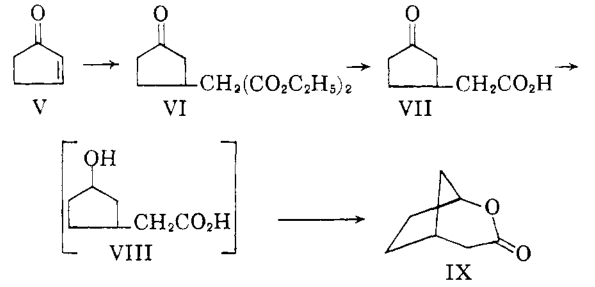


Since it has recently been shown that in the trifluoroperacetic acid oxidations of ketones there is rapid equilibration with the corresponding hydroxyperesters, and that the peroxide heterolysis plus migration is the rate-determining step,[6] it becomes clear that the above rationalization of the course of the camphor oxidation is somewhat oversimplified. That it is, in fact, also based on misleading data was demonstrated recently in a careful study by Sauers,[7] who showed that camphor actually gives rise to the expected lactone IV, rather than α-campholide, when oxidized with *buffered* peracetic acid. In the presence of added sulfuric acid, the reaction becomes more indiscriminate and 30% of α-campholide is formed. Since the lactone IV happens to be unstable under these strongly acidic conditions, it was not found in the original work of Baeyer and Villiger.

In connection with the presumed anomaly of the camphor oxidation, we undertook a study of the Baeyer–Villiger oxidation of some simple, bicyclic ketones. In the course of this work, the peracetic acid oxidations of bicyclo[2,2,1]heptanone-2 (XIV), bicyclo[2,2,2]octanone-2 (XV) and bicyclo[2,2,2]-octen-5-one-2 (XX) have been carried out. The results of these studies, and their relations to earlier work in this field, will now be presented.

Experimental Results.—In anticipation of both possible outcomes for the Baeyer–Villiger oxidation of bicyclo[2,2,1]-heptanone-2, independent syntheses for the lactones to be expected from both bridgehead and methylene migration were sought. The bridgehead migration product, *cis*-3-hydroxycyclopentylacetic acid lactone (IX), was obtained as outlined in Chart 1.

CHART 1



Cyclopentenone (V) was prepared conveniently from cyclopentadiene, *via* 3-chlorocyclopentene, as described recently by Alder and Flock.[8] The Michael addition of diethyl malonate to cyclopentanone gave the desired adduct VI in 90% yield. Acid-catalyzed hydrolysis and decarboxylation of VI could be conveniently carried out in one step, to give cyclopentanone-3-acetic acid (VII) in 80% yield. This acid, dissolved in aqueous base, readily took up one molar equivalent of hydrogen over Raney nickel catalyst to give the expected hydroxyacid VIII in 96% yield. The resultant crude VIII was subjected directly to treatment with acetic anhydride and sodium acetate in refluxing benzene. Careful distillation of the product gave *cis*-3-hydroxycyclopentylacetic acid lactone (IX), m.p. 56–58°, in about 35% yield. Before this reaction sequence was worked out, several rather similar synthetic routes were pursued less successfully. Thus, basic hydrolysis of the malonic ester adduct VI, followed by thermal decarboxylation was not satisfactory. High pressure catalytic hydrogenation of the malonic ester adduct proceeded well to give the expected hydroxydiester, and base hydrolysis gave the hydroxy diacid in good yield. However, thermal decarboxylation was complicated by simultaneous lactonization, giving rise to the desired product in a difficultly purifiable form.

The successful route to *cis*-3-hydroxymethylcyclopentane carboxylic acid lactone (XIII) is outlined in Chart 2. The anhydride of *cis*-cyclopentane-1,3-dicarboxylic acid (X) was obtained by treatment of the diacid with acetyl chloride.[9] Several attempts to reduce the anhydride directly to the corresponding lactone with lithium aluminum hydride were unrewarding. Similar attempts at selective reduction of the corresponding half ester-half acid chloride with sodium borohydride also failed. Finally, the anhydride was converted

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[5] M. F. Murray, B. A. Johnson, R. L. Pederson and A. C. Ott, THIS JOURNAL, **78**, 981 (1956).

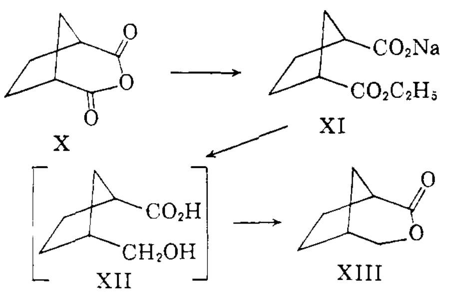
[6] M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *ibid.*, **80**, 6393 (1958); M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6398 (1958).

[7] R. R. Sauers, *ibid.*, **81**, 925 (1959).

[8] K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

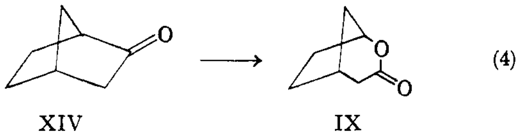
[9] K. Alder and W. Roth, *ibid.*, **90**, 1835 (1957).

CHART 2



into the half ester, half sodium salt XI, which gave the expected hydroxy acid XII using the sodium borohydride–aluminum chloride procedure of Brown and Subba Rao.[10] The crude hydroxy acid XII was lactonized directly using acetic anhydride and sodium acetate in benzene. The final lactone was difficult to purify, and was isolated only in low yield.

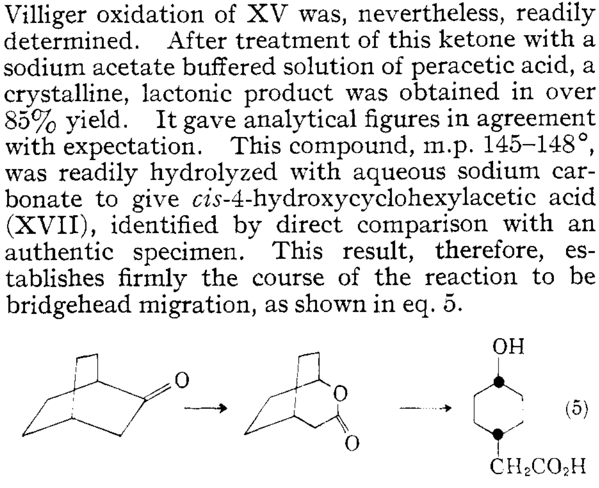
Bicyclo[2,2,1]heptanone (XIV) was prepared conveniently by the catalytic dehydrogenation of *exo*-norborneol, in an adaptation of Alder's procedure for the dehydrogenation of *endo*-norborneol.[11] The oxidation of this ketone with either commercially available peracetic acid solution (containing a small amount of sulfuric acid), or with a solution of this acid buffered with sodium acetate, gave a good yield of *cis*-3-hydroxycyclopentylacetic acid lactone (IX) (eq. 4). The product was identified by direct infrared comparison with the authentic synthetic sample.[12] The infrared spectrum of the unpurified Baeyer–Villiger product was found to lack several strong absorption bands characteristic of the isomeric lactone XIII indicating a high degree of specificity in the oxidative rearrangement.[12a]



(4)

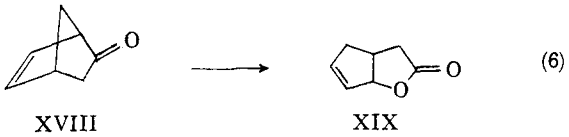
Finally, oxidation of bicyclo-[2,2,1]-heptanone-2 in strongly acidic medium was found to proceed rapidly at room temperature, again giving IX in excellent yield. Thus, under all conditions studied, *chiefly bridgehead migration occurs.*

Bicyclo[2,2,2]octanone (XV) and bicyclo[2,2,2]-octen-5-one-2 (XX) were prepared as described earlier by Wildman and Saunders.[13] Attempted syntheses of the expected oxidation product of XV, *cis*-4-hydroxycyclohexylacetic acid lactone (XVI), were unsuccessful. The hydroxy acid XVII was prepared essentially as described by Ungnade and Morriss.[14] However, neither acetic anhydride nor dicyclohexylcarbodiimide[15] brought about lactonization. The course of the Baeyer–Villiger oxidation of XV was, nevertheless, readily determined. After treatment of this ketone with a sodium acetate buffered solution of peracetic acid, a crystalline, lactonic product was obtained in over 85% yield. It gave analytical figures in agreement with expectation. This compound, m.p. 145–148°, was readily hydrolyzed with aqueous sodium carbonate to give *cis*-4-hydroxycyclohexylacetic acid (XVII), identified by direct comparison with an authentic specimen. This result, therefore, establishes firmly the course of the reaction to be bridgehead migration, as shown in eq. 5.

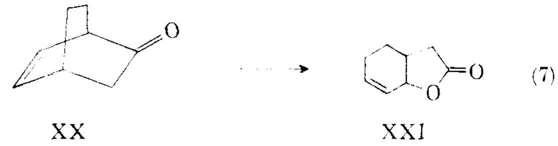


(5)

Finally, we wish to report the course of the peracetic acid oxidation of bicyclo[2,2,2]octen-5-one-2 (XVIII), a substrate which offers the possibility of competition between epoxidation of the double bond and attack of the ketonic function. In an earlier study from this Laboratory, it was shown that dehydronorcamphor (bicyclo[2,2,1]hepten-5-one-2) (XVIII) gives rise to the rearranged, unsaturated lactone XIX (see eq. 6) under these conditions, reflecting the deactivation of the β,γ-double bond by the nearby carbonyl group.[16] In the present work it was found that even in the case of the homologous bicyclooctenone, peracetic acid preferentially attacks the carbonyl group, giving the rearranged, unsaturated lactone XXI, as shown in eq. 7, in 80% yield. The structure of the final product was ascertained by its infrared spectrum (λ_{max} 5.65 μ), elementary analysis and proton magnetic resonance spectrum (showing the presence of two olenfinic protons), as well as by catalytic hydrogenation, which gave rise to the expected hydrogenolysis product (cyclohexylacetic acid) in addition to the corresponding saturated lactone. The structure of this unsaturated lactone was confirmed by the recent work of Klein, who published the infrared spectrum of XXI, prepared independently in connection with



(6)



(7)

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(10) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 2582 (1956).

(11) K. Alder, H. Wirtz and H. Koppelberg, *Ann.*, **601**, 138 (1956).

(12) Professor G. Ourisson has informed us that he has reached this same conclusion on the basis of degradative evidence. For the details of this work, which now have been published, see A. Rassat and G. Ourisson, *Bull. soc. chim. France*, 1133 (1959).

(12a) NOTE ADDED IN PROOF.—Professor R. R. Sauers recently has found a small amount of a second lactonic product from this reaction. Our own analytical method would not have found less than 5% of XIII. We are grateful to Dr. Sauers for communicating his results prior to publication.

(13) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

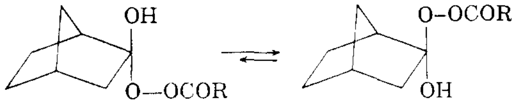
(14) H. E. Ungnade and F. V. Morriss, THIS JOURNAL, **70**, 1898 (1948).

(15) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

(16) J. Meinwald, M. C. Seidel and B. C. Cadoff, THIS JOURNAL, **80**, 6303 (1958).

another problem.[17] It is thus apparent that XX behaves in a manner completely analogous to XVIII in its reaction with peracetic acid, both ketones giving lactones derived from Baeyer–Villiger oxidation involving bridgehead migration, with simultaneous or subsequent rearrangement to the more stable allylic lactonic isomer.[16]

Conclusions.—It would be unjustified to try to make any sweeping generalizations concerning the course of Baeyer–Villiger oxidations of bicyclic ketones on the basis of the above results. It is apparent, however, that in each of the three cases studied the electronically favored group (situated at the bridgehead) was found to migrate to the electron-deficient oxygen atom. This result is most striking when the acid-catalyzed reactions of camphor and bicyclo[2,2,1]heptanone-2 (XIV) are compared. It is at first hard to see why, if camphor gives rise to *both* II and IV under acidic conditions due to a compression of the scale for the activation energies in the rearrangement of the intermediate IIIa, XIV does not behave analogously to give both IX and XIII. The simplest rationalization of these observations would seem to be that camphor gives the electronically unfavored lactone IV from intermediate IIIa by path b (eq. 2), which is sterically favorable, but not from intermediate IIIb by path d, which would be both electronically and sterically unfavorable. It is important to note at this point that at equilibrium, IIIa should predominate over IIIb.[18] The analogous intermediates in the case of XIV are shown as XXIIa and XXIIb. Because of the absence of the methyl groups of camphor, the equilibrium position here would clearly be reversed, favoring XXIIb.[19] Since XXIIa is the only intermediate which could have given XIII (analogous to II) *via* a transition state in the chair conformation, and since steric factors dictate that the concentration of XXIIa would be much less than that of IIIa under comparable conditions, the failure of XIV to give detectable amounts of XIII seems to be attributable to these steric differences. More generally, it becomes clear that the nature of the migrating group in this type of rearrangement will depend on both electronic and steric factors, involving a fairly subtle balance between equilibrium concentrations of the possible intermediates, and competitive rates for the rearrangement of each intermediate in either of two directions. It is, therefore, not surprising that no simple rule can be use to predict products with accuracy.



XXIIa XXIIb

Experimental

3-Ketocyclopentylmalonic Ester (VI).—Following the procedure of Bartlett for the addition of diethyl malonate to cyclohexenone,[20] a solution of 35.0 g. of diethyl malonate in 70 ml. of absolute ethanol containing 0.2 g. of sodium was prepared. To this solution, 16.6 g. of cyclopentenone[8] was added in a nitrogen atmosphere, and with continuous stirring and cooling in an ice–salt-bath. The addition required 30 minutes, after which 2 ml. of acetic acid was added and the mixture was allowed to come to room temperature. The alcohol was distilled off under reduced pressure, and the residue was taken up in ether and washed with water. After drying of the solution and removal of the solvent, vacuum distillation gave 44.3 g. (90%) of VI, b.p. 181–187° (0.5 mm.), $n^{20}\text{D}$ 1.4562.

Anal. Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.68; H, 7.60.

3-Ketocyclopentylacetic Acid (VII).—A mixture of 9.22 g. of VI and 75 ml. of 8% hydrochloric acid was allowed to reflux for 18 hours. The bath temperature was adjusted so that the ethanol formed could distil over. At the end of this time carbon dioxide evolution was essentially complete. Ether extraction followed by distillation yielded 5.10 g. (80%) of VII, b.p. 127–128° (0.2 mm.), 91–95° (0.03 mm.), $n^{25}\text{D}$ 1.4768.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.09; H, 7.37.

A semicarbazone was prepared in the usual way and recrystallized from ethanol. It showed a melting point of 205° dec. (lit.[21] 198°).

3-Hydroxycyclopentylacetic Acid (VIII).—In a 500-ml. Parr bomb, 6.35 g. of VII, dissolved in 125 ml. of 1 *N* sodium hydroxide, was shaken with about 5 g. of Raney nickel under 50 p.s.i. of hydrogen. In 3 hours, 100% of the theoretical amount of hydrogen was taken up. The catalyst was removed by filtration, and the resulting solution was acidified with hydrochloric acid and extracted with ether to give 6.20 g. (96%) of crude VIII.

Attempts to use Adams catalyst, with or without added iron salts, or Raney nickel in ethanol failed. In these cases an initially rapid hydrogen uptake quickly fell off before the hydrogenation was complete.

***cis*-3-Hydroxycyclopentylacetic Acid Lactone (IX).**—A mixture of 4.68 g. of crude VIII, 100 ml. of benzene, 6.2 ml. of acetic anhydride and 1.0 g. of sodium acetate was refluxed vigorously under a nitrogen atmosphere for 26 hours. After stirring the reaction mixture with water to hydrolyze the excess acetic anhydride, the mixture was taken up in ether, washed with aqueous sodium bicarbonate and with water, and dried. The solvents were distilled off through a 15-cm. glass helix-packed column to give 3.2 g. of crude, residual product. Vacuum distillation yielded 1.50 g. (37%) of IX, b.p. 77° (0.25 mm.), m.p. 56–58° (sealed capillary). The infrared spectrum of this material was superimposable on that of the Baeyer–Villiger product obtained from XIV (see below).

***cis*-Cyclopentane-1,3-dicarboxylic Acid.**—A convenient preparation of this diacid was found to be a modification of a procedure originally described by Birch, *et al.*[22] A mixture of 30.0 g. of norbornene,[23] 200 ml. of 30–60° petroleum ether and 400 ml. of water was cooled in an ice-bath and stirred while 139 g. of crystalline potassium permanganate was added slowly. Stirring was continued overnight at room temperature, and finally the mixture was refluxed for 5 hours. Sulfur dioxide was then bubbled through the suspension, and the resulting solution was acidified with hydrochloric acid. Extraction with ether gave 33.3 g. (66%) of product, m.p. 119–123°. One recrystallization from water raised the melting point to 123–124° (lit.[22] 119.9–120.6°).

***cis*-Cyclopentane-1,3-dicarboxylic anhydride** m.p. 163–164° (lit.[24] 160–161.5°), was prepared in 84% yield following the method described by Alder.[9]

Sodium Ethyl *cis*-Cyclopentane-1,3-dicarboxylate (XI).—A solution of 25.5 g. of X in 100 ml. of absolute ethanol was prepared, and to it a solution of 3.98 g. of sodium in 50 ml. of absolute ethanol was added slowly. The resulting mixture was evaporated to dryness, and the residue dried

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[17] J. Klein, THIS JOURNAL, **81**, 3611 (1959).

[18] *Cf.* G. Vavon and M. de Botton, *Compt. rend.*, **237**, 729 (1953); M. de Botton, *Bull. soc. chim. France*, 816 (1955).

[19] *Cf.* A. C. Cope, E. Ciganek and N. A. LeBel, THIS JOURNAL, **81**, 2799 (1959).

[20] P. D. Bartlett and G. F. Woods, *ibid.*, **62**, 2933 (1940).

[21] E. H. Farmer, *J. Chem. Soc.*, **123**, 3330 (1923).

[22] S. F. Birch, W. J. Oldham and E. A. Johnson, *ibid.*, 818 (1947).

[23] The authors are indebted to the du Pont Co. for a generous gift of norbornene.

[24] P. C. Guha and S. K. Banganathan, *Ber.*, **69**, 1199 (1936).

at 80° in a vacuum oven to yield 35.0 g. (93%) of XI as a deliquescent solid, m.p. 105–106° (sintering at 100°). This crude product was used directly for the following reduction and lactonization.

***cis*-3-Hydroxymethylcyclopentanecarboxylic Acid Lactone (XIII).**—A mixture of 4.00 g. of sodium borohydride and 20.50 g. of XI was stirred in 120 ml. of dry diglyme for 30 minutes. A solution of 4.70 g. of aluminum chloride in 20 ml. of dry diglyme was added slowly, and stirring was continued for 30 minutes. The temperature was then raised to 140°, and the mixture was stirred for an additional 80 minutes. The cooled reaction mixture was quenched with 200 g. of ice and 20 ml. of hydrochloric acid. Ether extraction, followed by drying and distillation of the solvents at reduced pressure, gave 13.55 g. (96%) of crude XII.

A mixture of 1.0 g. of sodium acetate, 42 ml. of benzene, 14.3 ml. of acetic anhydride and 11.0 g. of crude XII was refluxed for 4 hours. The mixture was cooled and stirred with water for 15 minutes to hydrolyze the excess acetic anhydride. The mixture was then taken up in ether and washed with aqueous sodium bicarbonate. The solvents were distilled through a helix-packed column to yield 11.1 g. of crude product, vacuum distillation of which gave 3.45 g. (36%) of XIII as a semi-solid, b.p. 135–136° (20 mm.). An analytical sample, m.p. 88–91° (sealed capillary), was obtained after several successive sublimations.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.95; H, 8.20.

Bicyclo[2,2,1]heptanone-2 (XIV).—Adopting the procedure described for the dehydrogenation of *endo*-norborneol,[11] 29.0 g. of *exo*-norborneol[25] was dissolved in 100 ml. of paraffin oil, and 5 g. of Raney nickel and one pellet of potassium hydroxide were added. The mixture was heated at 140–160° and stirred under a slow stream of carbon dioxide. The product was sublimed directly from the reaction mixture. Yields of crude XIV varied from 50 to 80%. The initial half of the sublimate consisted of pure XIV (m.p. 89–92°, lit.[11] 90–92°), while the remainder contained about 5% of starting material.

Buffered Baeyer–Villiger Oxidation of XIV.—Using the procedure of Sauers for the case of camphor,[7] 2.0 g. of XIV was dissolved in 10 ml. of acetic acid containing 1.0 g. of sodium acetate. To this mixture, 10 ml. of 28% peracetic acid was added dropwise. After standing for 5 days at room temperature in the dark, the mixture was neutralized by pouring into 100 ml. of 20% aqueous sodium carbonate. The basic solution was extracted with ether, dried over magnesium sulfate, and distilled to yield 2.0 g. (88%) of crude *cis*-3-hydroxycyclopentylacetic acid lactone (IX), m.p. *ca.* 0°. The infrared spectrum of this material was identical with that of pure IX obtained synthetically as described above.

In an unbuffered oxidation, the same lactonic product was obtained quantitatively. Resublimation of this product at 85–90° (12 mm.) gave an analytical sample, m.p. 54–56° (sealed capillary).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.97. Found: C, 66.94; H, 8.26.

Acid-catalyzed Beayer–Villiger Oxidation of XIV.—A solution of 1.6 ml. of concentrated sulfuric acid, 1.00 g. of XIV and 4.0 ml. of acetic acid was cooled to 0° and 1.9 ml. of 40% peracetic acid was added dropwise. After the mixture had stood for 2 hours in the dark, 100 ml. of ether was added, and the solution was poured into a cold solution of 8.6 g. of carbonate in 90 ml. of water. The ether layer was separated, and the aqueous layer extracted with additional ether. The combined ether extracts were washed with aqueous sodium bicarbonate and with water. Drying over magnesium sulfate and careful distillation yielded 1.0 g. (97%) of crude product. The infrared spectrum of this material was essentially that of pure IX. No absorption bands characteristic of either XIII or XIV were detectable.

Bicyclo[2,2,2]octen-5-one-2 (XX) and Bicyclo[2,2,2]-octanone-2 (XV).—These ketones were prepared essentially as described by Wildman and Saunders.[13]

***cis*-4-Hydroxycyclohexylacetic acid XVII** was obtained following the route of Ungnade and Morriss.[14] The step involving oxidation of the mixture of stereoisomeric hydroxy acids was carried out using the Jones procedure.[26]

Baeyer–Villiger Oxidation of Bicyclo[2,2,2]octanone.—A mixture of 2.0 g. of XV, 19 ml. of glacial acetic acid and 1.0 g. of sodium acetate was prepared and cooled. To this mixture, 10 ml. of 28% peracetic acid was added dropwise. After standing at room temperature in the dark for 5 days, the mixture was neutralized with sodium carbonate solution and worked up in the usual way to give 2.0 g. (89%) of crude material, m.p. 140–145° (sealed capillary). Recrystallization from hexane, followed by sublimation, gave an analytical sample, m.p. 145–148°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.56; H, 8.63.

Hydrolysis of XVI.—A mixture of 200 mg. of the above product and 3 equivalents of sodium carbonate dissolved in 3 ml. of water was refluxed overnight. From the reaction mixture, 192 mg. (85%) of XVII, m.p. 139–140.5°, was isolated after the usual work-up. This product gave no melting point depression when mixed with an authentic sample, m.p. 137.5–138.5°, prepared as described above.

Baeyer–Villiger Oxidation of Bicyclo[2,2,2]octen-5-one-2.—A mixture of 2.2 g. of XX, 10 ml. of glacial acetic acid and 1.0 g. of sodium acetate was treated with 5.0 ml. of 28% peracetic acid. After standing in the dark for 3 days, the mixture was worked up as described previously to give 2.5 g. of crude, lactonic product. Distillation yielded 1.96 g. (80%) of XXI, b.p. 130–132° (8 mm.), n^{20}_{D} 1.4983. The infrared spectrum of this product agreed well with that reported by Klein.[17]

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.38; H, 7.29.

Base hydrolysis of this lactone, followed by acidification of the reaction mixture, led to 80% recovery of regenerated starting material.

The proton magnetic resonance spectrum of this lactone was recorded at 60 mc. in carbon tetrachloride by Varian Associates, Palo Alto, Calif. Using tetramethylsilane as an internal reference, peaks in the 356 c.p.s. region could be assigned to two olefinic hydrogens, and a 283 c.p.s. absorption to a proton bonded to a carbon bearing both an oxygen and a doubly-bonded carbon.

Catalytic Hydrogenation of XXI.—A mixture of 10 mg. of Adams catalyst and 10 ml. of acetic acid was prereduced, and to the catalyst 0.54 g. of XXI was added. After two hours of stirring, hydrogen uptake stopped at a value corresponding to about 30% hydrogenation and 70% hydrogenolysis. The solution was made basic and extracted with ether to yield 0.13 g. (25%) of 2-hydroxycyclohexylacetic acid lactone, m.p. 4–6.5° (lit.[27] 13.5–15°). The infrared spectrum of this product is identical with that reported by Klein.[17]

The basic, aqueous solution was acidified with hydrochloric acid and extracted with ether to give 0.29 g. (55%) of cyclohexylacetic acid. The infrared spectrum of this product was identical with that reported,[28] and an amide, m.p. 166–168° (lit.[29] 166–168°), was formed readily.

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