90% of the calculated quantity of peracid had been consumed but peracid continued to be consumed for 3 to 6 additional hours. Similar results were obtained at 5–8°. The reaction mixture was poured into several volumes of cold water and the oily layer was dissolved in ether. The ether solution was washed with water until acid free (10 washes), dried, and the ether was evaporated, the last traces under high vacuum. The residue was a pale yellow oil which weighed 49 g.

Anal. Oxirane oxygen, 9.7%[12]; neut. equiv. 360; saponification equiv. 292; iodine number, 2.

Crystallization of the crude reaction product from two volumes of 80:20 acetone:water at −20° yielded 8 g. of white solid, which on recrystallization from the same volume of acetone at −20° yielded 3 g. of 9,12,15-triepoxystearic acid, m.p. 70.0–70.7°.

Anal. Calcd. for $C_{18}H_{30}O_5$: Oxirane oxygen, 14.7%; neut. equiv. 326. Found: Oxirane oxygen, 13.9%; neut. equiv. 322. The isolation of triepoxystearic acid could not always be repeated particularly in cases where the oxirane oxygen content of the crude reaction product was about 8.7, a value much closer to that calculated for a (diepoxy) (hydroxyacetoxy)stearic acid.

When the epoxidation reaction temperature was allowed to rise to about 60–70° during addition of peracetic acid and then held at 20–25° for 6 hr., the product obtained was a viscous, salvelike mass.

Anal. Oxirane oxygen, 0%; neut. equiv. 450; saponification equiv. 290; iodine number, 6.

Epoxidation of linolenic acid with perpelargonic acid. To a solution of 26 g. (0.15 mole) of perpelargonic acid in 120 ml. of ether, 13.9 g. (0.15 mole of double bond) of linolenic acid was added at 20–25° with stirring. Samples (1 ml.) were withdrawn periodically and peracid content was determined.

Reaction Time, Hr.	Moles of Peracid Consumed per Mole of Linolenic Acid
0	0
1	0.98
2	1.5
3	1.6
5	1.9
21	2.4
28	2.5
44	2.7
51	2.7

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(12) D. Swern, T. W. Findley, G. N. Billen, and J. T. Scanlan, *Anal. Chem.*, 19, 414 (1947).

(13) A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Hydrolysis and Rearrangement of 4-(1-Carbethoxy-2-oxo-cyclopentyl)crotonic Esters

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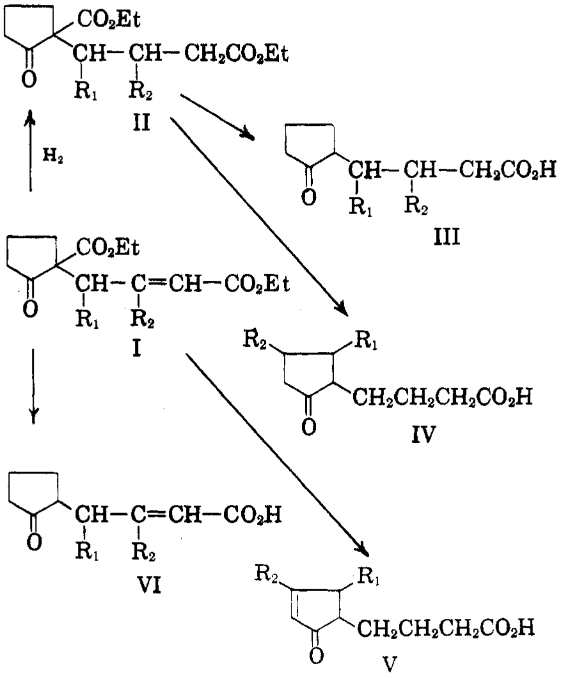
An earlier paper[1] described the discovery, incidental to our work on azulenes, that β-ketoesters of type II on acid hydrolysis undergo rearrangement and yield, not the expected ε-ketoacids III, but the isomeric ε-ketoacids IV. It appeared of interest to study the acid hydrolysis of the unsaturated β-ketoesters I from which the compounds of type II were prepared by hydrogenation.[2] Rearrangement during the acid hydrolysis of I would result in α,β-unsaturated cyclopentenones (V) which should be readily differentiable from the normal hydrolysis products, VI.



a $R_1, R_2 = H$
b $R_1 = CH_3, R_2 = H$
c $R_1 = H, R_2 = CH_3$

The results indicate that the driving force of this rearrangement depends both on structural factors and on the acid used. With dilute (50:50) hydrochloric acid,[4] Ia gave, *without rearrangement*, 4-(2-oxo-cyclopentyl)crotonic acid (VIa), whereas Ib gave a mixture of Vb and VIb, each of which was identified through its dinitrophenylhydrazone. On the other hand, Ic furnished, *with rearrangement*, exclusively Vc.

Hydrolysis with 10% sulfuric acid did not seem to promote the rearrangement as well as hydrochloric acid. Thus, hydrolysis of Ib now resulted in exclusive formation of VIb, *without rearrangement*, and Ic now gave what appeared to be a mixture consisting largely of VIc which could be isolated in crystalline form.

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(1) W. Herz, *J. Am. Chem. Soc.*, 78, 2529 (1956).

(2) The β-ketoesters(I) may be looked upon as analogs of certain compounds in which the conjugated double bond is located in an aromatic ring and which have been found to rearrange on treatment with acid.[3]

(3) F. Ramirez and A. P. Paul, *J. Am. Chem. Soc.*, 77, 1035 (1955); W. Herz, *J. Am. Chem. Soc.*, 78, 2529 (1956).

(4) The use of concentrated hydrochloric acid, employed earlier[1] for the hydrolysis of II, resulted in excessive decomposition. Even with dilute acid the yields were quite low.

EXPERIMENTAL[5]

Hydrolysis of Ia. A mixture of 20 g. of Ia and 120 ml. of dilute hydrochloric acid was refluxed overnight, cooled, and made basic with sodium carbonate. The neutral fraction was extracted with ether. The basic layer was acidified and the acid fraction was extracted with ether, dried, and distilled. The acid boiled at 158–165° (2 mm.), yield 3.1 g. There was a substantial amount of high-boiling residue.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.86; H, 7.38.

The infrared spectrum (carbon tetrachloride solution) exhibited bands at 1750 (cyclopentanone), 1710 (acid), and 1660 cm.$^{-1}$ (C=C), bonded acid OH in the —OH region, and was similar to the solution spectrum of crotonic acid.[6] The evidence cited below indicates it is 4-(2-oxocyclopentane)-2-butenoic acid (Va).

The semicarbazone was recrystallized from methanol and melted at 198–198.5°. The absence from its ultraviolet spectrum of a band above 220 mμ shows that the keto group is unconjugated.[7]

Anal. Calcd. for $C_{10}H_{15}N_3O_3$: C, 53.32; H, 6.71; N, 18.7. Found: C, 53.23; H, 6.62; N, 19.0.

The 2,4-dinitrophenylhydrazone, yellow needles from benzene, melted at 141–141.5°. The ultraviolet spectrum (λ_{max} 364 mμ, ϵ_{max} 23400) showed that the parent ketone was unconjugated.[8]

Hydrolysis of Ib. (A) *With hydrochloric acid.* The neutral fraction resulting from the hydrolysis of 17 g. of Ib with 120 ml. of dilute hydrochloric acid was insignificant. The acid fraction decomposed partially during distillation, b.p. 165–173° (1.5 mm.). The infrared spectrum (weak carbonyl at 1775, strong C=O at 1740 and 1700, C=C at 1650) and analysis indicated the presence of a mixture.

The semicarbazone, recrystallized from ethanol, melted at 203–204° (gas evolution). The low extinction coefficient of its ultraviolet spectrum (λ_{max} 262 mμ, ϵ_{max} 10,800) suggested the presence of a mixture of conjugated and unconjugated ketones.[7]

Anal. Calcd. for $C_{11}H_{17}N_3O_3$: C, 55.21; H, 7.16. Found: C, 54.92; H, 7.10.

Treatment of the mixture with 2,4-dinitrophenylhydrazine resulted in what appeared to be a mixture of dinitrophenylhydrazones. Fractional crystallization from ethanol permitted the isolation of orange needles, m.p. 201–201.5° from benzene, whose ultraviolet spectrum (λ_{max} 364 mμ, ϵ_{max} 20,000) indicated the absence of conjugation.[8]

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 5.01. Found: C, 53.47; H, 5.29.

The mother liquors of the orange dinitrophenylhydrazone were chromatographed and yielded a red dinitrophenylhydrazone, m.p. 132.5–133° whose ultraviolet spectrum (λ_{max} 387 mμ, ϵ_{max} 21,000), showed that it was conjugated.[8]

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 5.01. Found: C, 53.12; H, 5.10.

(B) *With sulfuric acid.* Hydrolysis of 10 g. of Ib with 100 ml. of 10% sulfuric acid resulted in 1.9 g. of an acid fraction, b.p. 165–175° (1.5 mm.) whose infrared spectrum in CCl_4 (cyclopentanone carbonyl at 1740, conjugated carboxyl near 1700, conjugated C=C at 1650 cm.$^{-1}$) indicated that it was primarily, if not exclusively, 4-(2-oxocyclopentyl)-2-pentenoic acid (Vb).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.08; H, 7.62.

This material gave only the orange dinitrophenylhydrazone of m.p. 201°.

Hydrolysis of Ic. (A) *With hydrochloric acid.* The acid fraction resulting from hydrolysis of 51 g. of Ic with 500 ml. of dilute hydrochloric acid boiled at 171–173° (1.8 mm.), wt. 8.7 g., n_D^{22} 1.5013. The infrared spectrum (strong broad band at 1710, combination of cyclopentenone carbonyl and carboxyl, C=C at 1632 cm.$^{-1}$) and the ultraviolet spectra of the derivatives indicated that it was an α,β-unsaturated ketone, *i.e.*, Vc.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.61; H, 7.54.

The semicarbazone was recrystallized from ethanol and melted at 201–202° (dec.). Its ultraviolet spectrum (λ_{max} 261.5 mμ, ϵ_{max} 21,100) showed that it was derived from an α,β-unsaturated ketone.[7]

Anal. Calcd. for $C_{11}H_{17}N_3O_3$: C, 55.21; H, 7.16; N, 17.6. Found: C, 55.07; H, 7.17; N, 17.4.

The dinitrophenylhydrazone, scarlet crystals from benzene, melted at 170–171.5°. The color and ultraviolet spectrum (λ_{max} 382 mμ, ϵ_{max} 21,200) showed that it was conjugated.[8]

Anal. Calcd. for $C_{16}H_{18}O_6N_4$: C, 53.03; H, 5.01; N, 15.4. Found: C, 52.69; H, 5.20; N, 15.2.

Catalytic hydrogenation of Vc (solvent ethanol, catalyst 5% palladium-on-charcoal), indicated the presence of one double bond. The product boiled at 166–170° (2 mm.). Attempts to prepare a semicarbazone and dinitrophenylhydrazone resulted in derivatives melting over a wide temperature range, presumably because of the formation of both *cis-* and *trans*-2-(3-carboxypropyl)-4-methylcyclopentanone during the reduction.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.01; H, 8.57.

(B) *With sulfuric acid.* Hydrolysis of 10 g. of Ic with 150 ml. of 10% sulfuric acid gave 1.8 g. of a viscous acid fraction, b.p. 165–175° (1.5 mm.), as well as a considerable amount of high-boiling residue. The infrared spectrum of the acid resembled that of the mixture obtained by hydrochloric acid treatment of Ib; it had two carbonyl bands, one at 1742 (cyclopentanone), the second, somewhat stronger, centered at 1705 cm.$^{-1}$ (combination of cyclopentenone and carboxyl band), as well as a fairly strong band at 1641 (conjugated C=C). It gave a mixture of dinitrophenylhydrazones which was chromatographed (solvent ethyl acetate). Ethyl acetate eluted an oily red dinitrophenylhydrazone which could not be crystallized; ethanol containing 3% acetic acid eluted a yellow dinitrophenylhydrazone, m.p. 147.5–148.5° after recrystallization from ethanol-water, whose color and ultraviolet spectrum (λ_{max} 362 mμ) showed that it was derived from 4-(2-oxocyclopentyl)-3-methyl-2-butenoic acid.

Anal. Calcd. for $C_{16}H_{18}O_6N_4$: C, 53.03; H, 5.01; N, 15.4. Found: C, 53.11; H, 5.17; N, 14.8.

On standing, the viscous mixture of acids deposited hard crystals which were separated, pressed on filter paper, and taken up in a small amount of methanol. Slow evaporation of the solvent in air gave crystals which were recrystallized from benzene and then melted at 107–108.5°. The infrared spectrum showed that this was 4-(2-oxocyclopentyl)-3-methyl-2-butenoic acid (VIc); it had a cyclopentanone band at 1742, conjugated carboxyl at 1695, and a relatively strong band (conjugated C=C) at 1642 cm.$^{-1}$

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.75; H, 7.53.

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[5] Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England. Infrared spectra were run by Mr. Dean S. Keeley and Mr. Joseph Kovacic on a Perkin-Elmer Model 21 double beam instrument. Ultraviolet spectra were determined by Mrs. Shirley Ann Pinner on a Beckman Model DK1 recording spectrophotometer.

[6] M. St. C. Flett, *J. Chem. Soc.*, 962 (1951); J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

[7] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, London, Edward Arnold Ltd., p. 102 (1954).

[8] Ref. 7, p. 107.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation for which I express my thanks.

NOTE ADDED IN PROOF: In a recent paper, D. K. Banerjee and T. R. Kastura, *J. Am. Chem. Soc.*, **79**, 926 (1957), describe, *inter alia*, the hydrolysis of Ib with essentially the same results as reported in the above.

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5,6-Dichloro-1-(3-dimethylaminopropyl)-benzimidazole Monohydrochloride Monohydrate

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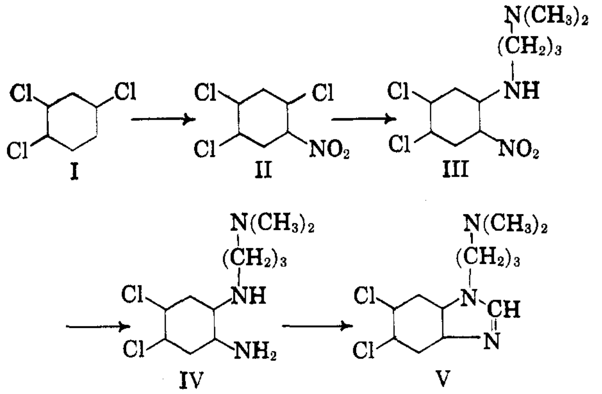
In the course of other work, a specimen of the title compound was desired. It was therefore synthesized by the following sequence of reactions.



2,4,5-Trichloro-1-nitrobenzene (II) was prepared by nitration of 1,2,4-trichlorobenzene (I) by a slight modification of the method of Barlow and Ing,[1] whereby the yield of crude product was raised to 90% of the theoretical; contrary to Cohn and Fischer,[2] it was readily recrystallized from hexane (3 vol.). This compound was condensed with *N,N*-dimethyl-1,3-propanediamine, essentially by Barlow's method,[3] to give III, which was isolated in crystalline form, both as the hydrochloride and as free base; of a long series of such compounds previously prepared,[1] the only one hitherto crystallized as the free base had been the 2-diethylaminoethyl analog. Compound III was then catalytically reduced to IV, and this was condensed with formic acid, in the presence of hydrochloric acid, to afford V, which was isolated as colorless crystals of its monohydrochloride monohydrate.

EXPERIMENTAL

2,4,5-Trichloro-1-nitrobenzene. Fuming nitric acid (240 ml.) was cooled in ice salt to −1.5°, and 50 ml. of 1,2,4-trichlorobenzene was added dropwise, with stirring, during 2 hr.; after stirring for a further 1 hr. at 0°, the suspension was poured onto 1 l. of crushed ice (in an ice bath) and allowed to warm slowly to room temperature overnight. The colorless crystalline product was filtered off, washed thoroughly with water, air-dried, and then dried under high vacuum. (The filtrate contained no oily material.) Yield, 88.7 g. (90% of the theoretical). It was best recrystallized from hexane (3 vol.); colorless crystals; yield of first crop, 69 g. (70% of the theoretical); m.p. 57–59°; lit. yield,[1] 50 to 60%; lit. m.p., 55°;[2] 57°;[1,4] 58°.[5,6]

N-(4,5-Dichloro-2-nitrophenyl)-N′,N′-dimethyl-1,3-propanediamine hydrochloride and free base. To 7.9 g. of dry pyridine was added 10.2 g. of *N,N*-dimethyl-1,3-propanediamine (3-dimethylaminopropylamine), followed by 25 g. of 2,4,5-trichloro-1-nitrobenzene. On swirling, the mixture became colder as the crystals all dissolved and then hotter as new crystals appeared. It was placed under a reflux condenser (Drierite tube), 100 ml. of dry toluene was added, and the suspension was boiled (glycerol bath at 116°) for 3.5 hr. The crystals (5.6 g.) were removed, and the filtrate was evaporated to dryness, affording a brown syrup which was dissolved in 315 ml. of hexane and extracted with 100 ml. of 2*N* hydrochloric acid followed by three portions of water. The aqueous layers were combined and evaporated to dryness, giving orange-colored crystals (23.1 g.). Recrystallization from absolute ethanol (5 vol.) afforded hygroscopic yellow crystals (which turn orange-colored in moist air) of the title compound; m.p. 195–197°. Its infrared absorption spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_{11}H_{15}Cl_2N_3O_2.HCl$: C, 40.20; H, 4.91; Cl, 32.37; N, 12.79. Found: C, 40.16; H, 4.64; Cl, 32.69; N, 12.82.

For isolation of the free base, the hydrochloride was dissolved in water, a slight excess of aqueous sodium bicarbonate solution was added, the cloudy solution was extracted several times with ether, and the combined ether extracts were dried with anhydrous sodium sulfate, filtered, and evaporated to dryness, affording a quantitative yield of yellow crystals which were dried at high vacuum; m.p. 34–35°. The material is readily soluble in ether, pentane, or heptane, but may be recrystallized by cautious addition of water to a solution in ethanol. Its infrared absorption spectrum (of the solid and of the melt) agreed with the proposed structure.

Anal. Calcd. for $C_{11}H_{15}Cl_2N_3O_2$: C, 45.22; H, 5.18; Cl, 24.27; N, 14.38. Found: C, 45.32; H, 5.00; Cl, 24.21; N, 14.32.

5,6-Dichloro-1-(3-dimethylaminopropyl)benzimidazole monohydrochloride monohydrate. To a solution of 7 g. of the previous free base in 70 ml. of absolute ethanol was added 3 g. of 10% palladized carbon, and the suspension was shaken with hydrogen (30 lb. per sq. in.) at room temperature until the yellow color had disappeared and uptake of hydrogen ceased. The suspension was then filtered, the colorless filtrate being collected directly in a flask containing 8 ml. of concentrated hydrochloric acid. This solution was evaporated to dryness under diminished pressure and two successive 100-ml. portions of absolute ethanol were added and evaporated off, giving a purplish flaky glass. This was dissolved in 50 ml. of 4*N* hydrochloric acid; a boiling stone and 4 ml. of 98% formic acid were added, and the solution was boiled under reflux during 2 hr. and then cooled. The solution was diluted with 250 ml. of water; 0.5 g. of Nuchar was added,

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(1) R. B. Barlow and H. R. Ing, *J. Chem. Soc.*, 713 (1950).

(2) P. Cohn and A. Fischer, *Monatsh.*, **21**, 267 (1900).

(3) R. B. Barlow, *J. Chem. Soc.*, 2225 (1951).

(4) A. F. Holleman and F. E. van Haeften, *Rec. trav. chim.*, **40**, 67 (1921).

(5) F. Beilstein and A. Kurbatow, *Ann.*, **192**, 228 (1878).

(6) H. H. Hodgson, *J. Soc. Dyers Colourists*, **42**, 365 (1926).