[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Diethyl Oxalo-phenoxyacetate, Diethyl Oxalo-(S-phenylmercapto)-acetate and Related Compounds

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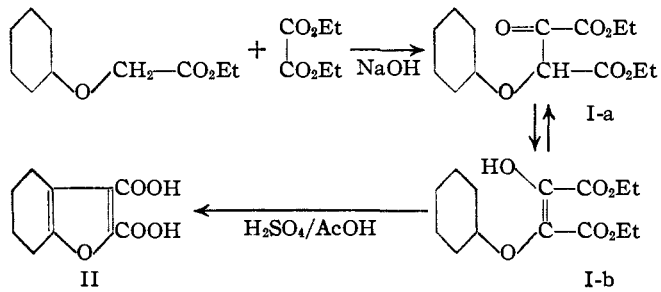
Coumaranone-2,3-dicarboxylic acid was first reported[3] in 1937 by two rather similar syntheses, both starting from isatin. The low yields (2–4%) of these workers were subsequently improved in this Laboratory[4] to as high as 30.5%. While this latter paper was being written, a new synthesis of the acid, capable of extension to certain related compounds and homologs, was also reported.[5]

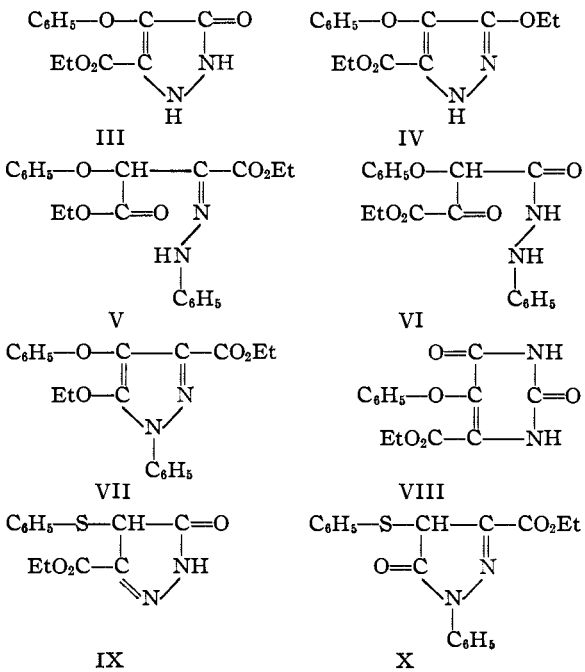
This Koelsch and Whitney synthesis was based upon sulfuric–acetic acid cyclization of a condensation product of phenoxyacetic acid with diethyl oxalate. This intermediate, although formulated as diethyl α-hydroxy-α-phenoxymaleate, was not purified, analyzed or (except for ring closure) otherwise characterized. Furthermore, the low yields (43–44%) of coumarone-2,3-dicarboxylic acid obtained on its cyclization suggested that extensive diversionary reactions might simultaneously be taking place. Since no other report on this intermediate ester occurs in the literature, and since we desired to extend the method to the preparation of various thianaphthene derivatives, a more extensive knowledge of the corresponding intermediate esters seemed desirable.

The identity of samples of coumarone-2,3-dicarboxylic acid produced from isatin[3,4] and from phenoxyacetic acid[5] has hitherto been assumed on the basis of their compositions, origin, and general accord of melting points. In the course of a satisfying confirmation of the Koelsch and Whitney synthesis, we therefore seized the opportunity to establish by direct comparison the identity of the dimethyl esters derived from both methods.

We have prepared and purified the Koelsch and Whitney intermediate which we prefer to designate as diethyl oxalo-phenoxyacetate (I). It reacts as a tautomeric mixture of structures I-a and I-b. Although we did not seek to study the mechanism of the ring closure it is a fact that the ester undergoes cyclization to coumarone-2,3-dicarboxylic acid (II) or its immediate relatives. Although attempts were made to effect isomerization of the ester to a *trans* stereoisomer of I-b by means of light and catalysts, and while material so processed showed a lower refractive index and failed to yield coumarone derivatives under cyclization conditions successful with ordinary samples, yet no certain evidence of the existence of the *trans* configuration was obtained.



The enolic tautomer (I-b) is supported by its color reaction with ferric chloride, by formation of a copper enolate, by its reaction with hydrazine hydrate to form a corresponding pyrazolone derivative (III), by its condensation with urea to a substituted pyrimidine (VIII), and by its ring closure to coumarone-2,3-dicarboxylic acid (II).



The ketonic tautomer (I-a) is evidenced by its loss of carbon monoxide on heating with consequent formation of diethyl phenoxymalonate (XI), and by formation at ordinary temperature of a phenylhydrazone (V) readily converted on heating to a pyrazole derivative (VII).

(1) This paper is constructed from part of a dissertation submitted by Robert T. Olsen to the Faculty of the Massachusetts Institute of Technology in September, 1942, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Titoff, Müller and Reichstein, *Helv. Chim. Acta*, **20**, 883–892 (1937).

(4) Huntress and Hearon, THIS JOURNAL, **63**, 2762–2766 (1941).

(5) Koelsch and Whitney, *ibid.*, **63**, 1762 (1941).

Attempts to saponify diethyl oxalo-phenoxyacetate (I) with aqueous ammonium hydroxide or with absolute ethanolic potassium hydroxide led to hydrolytic cleavage of the C_2–C_3 unsaturation with consequent formation of phenoxyacetic and oxalic acid (or their derivatives). This saponification and cleavage (without oxidation) also occurred slowly in moist air. On treatment with concentrated ammonium hydroxide the ester (I) yielded neutral ammonium oxalate whose formation (rather than ammonium oxamate or oxamide) shows that saponification occurred prior to cleavage. Since investigation of the mother liquor from cyclization of the ester also showed the presence of oxalic acid, cleavage occurring in this reaction medium doubtless comprises a side reaction diminishing the yield of coumarone derivatives.

By condensation of ethyl (S-phenylmercapto)-acetate with diethyl oxalate in a manner similar to that used for I, a product (XII) presumably analogous to it was obtained. This diethyl oxalo-(S-phenylmercapto)-acetate could not, however, be distilled as such because of loss of carbon monoxide and formation of diethyl S-phenylmercaptomalonate (XIII). Moreover, in moist air it suffered C_2–C_3 fission even more readily than ester I, and all attempts to cyclize it to thianaphthene-2,3-dicarboxylic acid were unsuccessful. With hydrazine hydrate and with phenylhydrazine, it gave in rather low yields pyrazolone derivatives IX and X, respectively.

Experimental Work

Diethyl Oxalophenoxyacetate (I).—Diethyl oxalate (123 g., 0.84 mole) in dry ether (200 ml.) was slowly added to dry sodium ethoxide prepared from freshly cut sodium (14.1 g., 0.61 mole) and the resultant yellow solution was refluxed for twenty minutes. A solution of ethyl phenoxyacetate (100 g., 0.56 mole) in dry ether (175 ml.) was then added and the entire mixture refluxed under anhydrous conditions for twenty-two hours. The resulting red solution was poured onto ice (400 g.), the red aqueous layer separated, and the ether layer further extracted with water (two 30-ml. portions). The combined aqueous extracts were acidified under fresh ether with concentrated hydrochloric acid (45 ml.). This ether layer was separated and the aqueous phase further extracted with ether (110, 60 and 40 ml.), after which the combined ether layers were dried over Drierite/calcium carbonate. After removal of the solvent under reduced pressure the residual liquid was fractionated. The resultant ester was a pale yellow liquid, b. p. 135–140° cor. at 2 mm.; yield, 111.6 g. or 71.7% of theoretical based on ethyl phenoxyacetate; d^{20}_4 1.1855; $n^{20}D$ 1.5092.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 59.90; H, 5.74. Found: C, 59.8, 59.9; H, 5.82, 6.01.

This ester is insoluble in water or aqueous 1% sodium bicarbonate. It dissolves, however, in aqueous 1% sodium hydroxide or sodium carbonate and in alcohol gives with ferric chloride a brilliant permanent red-violet coloration. It is soluble in cold 95% ethanol, acetone, ether or benzene but only sparingly soluble in cold ligroin. The pure compound does not reduce ammoniacal silver nitrate or Fehling solution, but is rapidly oxidized by potassium permanganate in acetone. On shaking with aqueous cupric acetate for twenty-two hours, the ester yields a precipitate of green crystals. These could be recrystallized from hot benzene but on attempting to dry the product at 120° gradual decomposition ensued until after thirty-three days a constant weight of 28.5% its original value was attained. No satisfactory analysis of its copper content could be obtained.

Effect of Heat on the Ester (I).—The ester (12.4 g.) on heating at 130–195° and 33 mm. pressure for thirty minutes survived without change. At 200°, however, loss of carbon monoxide was complete within five minutes, leaving 8.2 g. (74% yield) of diethyl phenoxymalonate (XI), b. p. 201.5–204.5° at 34 mm. Recrystallization of the seeded distillate gave 69.5% recovery of long white needles, m. p. 51–52° (recorded[6] 52–53°). This material no longer gave any color with ferric chloride. Its identity was further confirmed by conversion to phenoxymalono-(di)amide, m. p. 212.5–213.0° uncor. (recorded,[6] 214–215° uncor.).

Behavior of the Ester (I) with Alkaline Media. (A) With Ammonium Hydroxide.—The ester (0.422 g.) dissolved in concentrated aqueous ammonium hydroxide, sealed in glass and heated at 100° for twenty-one hours, gave ammonium oxalate (0.104 g. = 55.6% yield), but another run similarly heated for sixty-five hours gave 88% yield. These crystals were purified by precipitation from water with four volumes of 95% ethanol. On heating their solution in aqueous 3% sodium hydroxide ammonia was evolved but addition of ferric chloride to an aqueous solution of the salt gave no coloration.

Anal. Calcd. for $C_2H_8O_4N_2$ (neutral ammonium oxalate): N, 22.6. Found: N, 22.0, 22.3. Calcd. for $C_2H_6O_3N_2$ (ammonium oxamate): N, 26.4.

(B). With Alcoholic Potassium Hydroxide.—Attempts to saponify the ester using aqueous 1 *N* sodium hydroxide for two hours at 100° gave an average saponification equivalent of 85.6 and the same value was obtained by similar treatment for three, four and five hours. Since the value corresponding to hydrolysis of the two ester groups would be 280/2 = 140, this observation indicated that additional changes were being effected by the alkali.

Further study of the reaction using a larger sample of ester (2.80 g. = 0.01 mole) with potassium hydroxide (1.20 g., 0.02 mole) in absolute ethanol at 25° for sixteen hours led to a mixture of potassium salts, whose metal content (24.5%) corresponded to a mixture of equal moles of potassium phenoxyacetate and potassium hydrogen oxalate (24.5%). This composition was confirmed by isolation of both phenoxyacetic acid and oxalic acid, their respective identities being demonstrated by comparison of melting point and mixed melting points with authentic samples. Examination of the potassium salt mixture with the polarizing microscope supported this view.

Behavior of Ester (I) with Water.—Exposure of a sample of ester to moist air led to the appearance in two days of colorless crystals of oxalic acid whose quantity increased with time. In another experiment a wet benzene solution of the ester agitated by an air stream for twenty-five days gave 31.6% of oxalic acid dihydrate.

Behavior of Ester (I) on Cyclization.—A sample of ester was cyclized with sulfuric/acetic acid mixture according to the method of Koelsch and Whitney.[5] After separation of the coumarone-2,3-dicarboxylic acid there was isolated from the filtrate a considerable amount of oxalic acid (as dihydrate).

Behavior of Ester (I) with Hydrazine Hydrate.—The ester (4.7 g., 0.017 mole) mixed with hydrazine hydrate (0.90 g., 0.017 mole of 93.8% concentration) in 95% ethanol (12 ml.) was heated in a sealed tube at 100° for forty hours. Subsequent addition of water (100 ml.) to the warm solution precipitated 2.21 g. of 5-carbethoxy-4-phenoxypyrazolone-3 (III), m. p. (after purification) 208–209° uncor.; 213.5–214.5° cor.; yield 53%.

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: N, 11.30. Found: N, 11.6, 11.7.

Heating for twenty hours and sixty-five hours gave yields of 33 and 69%, respectively. The product was soluble in

(6) Niederl and Roth, THIS JOURNAL, **62**, 1156 (1940).

dilute aqueous alkali from which it reprecipitated on acidification; it gave in alcohol solution with ferric chloride a permanent red-brown enol test; in dry ether solution it reacted with diazomethane with slow evolution of nitrogen. This behavior certified its enolic character and together with its analysis distinguished it from 5-carbethoxy-4-phenoxy-3-ethoxypyrazole (IV) ($C_{14}H_{16}O_4N_2$; N, 10.14%) which might conceivably have resulted from a different type of ring closure.

Behavior of Ester (I) with Phenylhydrazine. (A) At Ordinary Temperature.—The ester (0.30 g., 0.0028 mole) with phenylhydrazine (0.65 g., 0.0023 mole) in absolute ethanol (6 ml.) began within thirty seconds to precipitate a phenylhydrazone (V). After fifteen minutes of shaking, the yield of solid was 0.55 g. (64.6% theoretical). Recrystallization from hot 95% ethanol gave a product of m. p. 120.0–120.1° uncor.; 121.5–121.6° cor.

Anal. Calcd. for $C_{20}H_{22}O_5N_2$: N, 7.57. Found: N, 8.02, 8.09.

Although these values were high and seemed to be in better accord with a mono-(phenylhydrazide) (VI) ($C_{18}H_{18}O_5N_2$: N, 8.19), the phenylhydrazone character was assured both by the lack of enolic behavior and since only such a structure could be precursor to that obtained on heating (see below).

The phenylhydrazone was insoluble in hot water, hot aqueous 1% sodium hydroxide, or cold 95% ethanol, but readily soluble in hot 95% ethanol or cold ether. It gave no color with alcoholic ferric chloride and in dry ether did not react with diazomethane.

(B) On Heating.—The ester (2.80 g., 0.01 mole) with phenylhydrazine (1.08 g., 0.01 mole) in absolute ethanol (10 ml.) was refluxed for thirty-five minutes. The phenylhydrazone initially precipitated dissolved during the heating. Water (4 ml.) was added to the hot solution until clouding occurred and the mixture was cooled. The supernatant liquid was decanted from the residual oil and diluted with 95% ethanol (13 ml.). After stirring at 0° for an hour, the yellow needles of 1-phenyl-3-carbethoxy-4-phenoxy-5-ethoxypyrazole (VII) (yield, 1.1 g., 31.2%) were recrystallized from 65% ethanol and then gave m. p. 82.5–83.5° uncor., 83.5–84.5° cor.

Anal. Calcd. for $C_{20}H_{20}O_4N_2$: N, 7.96; mol. wt., 352. Found: N, 7.98, 8.12; mol. wt. (Rast), 344.

This compound was insoluble in hot water or aqueous 1% sodium hydroxide; it was fairly soluble in cold methanol and very soluble in hot ethanol or cold acetone, ethyl acetate, ether, benzene or chloroform.

Behavior of Ester (I) with Urea.—The ester (2.80 g., 0.01 mole) and urea (0.60 g. = 0.1 mole) in glacial acetic acid (5 ml.) at 100° was treated with hydrogen chloride gas for thirty-five minutes. After standing overnight at room temperature, the resultant crystals were removed, washed with cold benzene and dried at 120° for one hour. The yield of product was small (15.8% of theory) but repetition of the hydrogen chloride treatment and two days' standing at 0° gave no further solid. Recrystallization of the crude from hot 60% ethanol gave 2,6(4)-dioxotetrahydro-4(6)-carbethoxy-5-phenoxypyrimidine (VIII), m. p. 252.0–252.5° uncor. (when heated from 251° uncor.), m. p. 258.0–258.5° cor. (when heated from 257° cor.).

Anal. Calcd. for $C_{13}H_{12}O_5N_2$: C, 56.6; H, 4.38; N, 10.16. Found: C, 56.6, 56.5; H, 4.52, 4.48; N, 10.3, 10.0.

The compound was insoluble in water or aqueous 5% sodium bicarbonate, but soluble (without gas evolution) in aqueous 1% sodium hydroxide or sodium carbonate. It was sparingly soluble in cold 95% ethanol but dissolved on heating. It was insoluble in cold benzene.

Its preparation above was essentially that of Wheeler[7]; attempts to obtain it from the ester (I) with urea and ethanolic sodium ethoxide by the Johnson and Guest[8] method were fruitless.

(7) Wheeler, *Am. Chem. J.*, **38**, 358–366 (1907).

(8) Johnson and Guest, *ibid.*, **42**, 286 (1909).

Diethyl Oxalo-(S-phenylmercapto)-acetate (XII).—Diethyl oxalate (96.2 g., 0.659 mole) in dry ether (100 ml.) was slowly added to sodium ethoxide (from 11.5 g. (0.5 mole) of sodium) in dry ether (100 ml.) and the mixture treated with ethyl S-phenylmercaptoacetate[9] (85.0 g., 0.434 mole) in 150 ml. dry ether in the general manner described for the analogous diethyl oxalo-phenoxyacetate (I). Particular attention was given to thorough washing of the aqueous and ether solutions of the sodium salt and ester, respectively. Solvent ether was removed at reduced pressure below 40° and a small forerun, b. p. 52–57°, was removed at 2 mm. The main product, however, could not be distilled without decomposition and was used directly. The undistilled oil amounted to 118.1 g. (91% theoretical) and showed $n^{24}D$ 1.5353.

The ester was insoluble in water or aqueous 1% sodium bicarbonate. It dissolved, however, in aqueous 1% sodium hydroxide or carbonate from which it was reprecipitated with acid. With ferric chloride in 95% ethanol it gave a wine-red coloration permanent for several hours. It reacted with etheral diazomethane after which no ferric chloride color resulted. With aqueous cupric acetate it yielded a khaki-colored copper salt soluble in chloroform. The ester did not reduce Fehling solution either hot or cold.

Behavior of Diethyl Oxalo-(S-phenylmercapto)-acetate (XII) on Heating.—On heating the ester (19.5 g., 0.066 mole) at 170° and 50 mm. pressure, carbon monoxide was readily evolved. Fractional distillation of the residual liquid gave 16.0 g. (90% yield) of diethyl S-phenylmercaptomalonate (XIII) as a pale yellow liquid, b. p. 203–205° cor. at 23 mm., $n^{24.5}$ 1.5207, m. p. < −20°.

Anal. Calcd. for $C_{13}H_{16}O_4S$: S, 11.9; sapon. equiv., 134.0. Found: S, 11.8, 12.0; sapon. equiv., 136.4.

The above diethyl S-phenylmercaptomalonate (2.68 g., 0.01 mole) was further confirmed by amidation with a mixture of concentrated aqueous ammonium hydroxide (25 ml.) and absolute ethanol (15 ml.) saturated with ammonia gas at 0°. This mixture was placed in a stoppered flask and kept at 50° for three and one-fourth hours. The resultant S-phenylmercaptomalon(di)amide weighed 1.30 g. (71.5% yield) and showed m. p. 252 uncor. (261° cor.) with decomposition.

Anal. Calcd. for $C_9H_{10}O_2N_2S$: N, 13.33; S, 15.24. Found: N, 13.02, 13.13; S, 15.03, 15.09.

The diethyl S-phenylmercaptomalonate upon saponification with ethanolic potassium hydroxide at 30° for one and one-half hours, and subsequent acidification gave S-phenylmercaptoacetic acid, m. p. 62–63° uncor., recorded[10] 62°.

Behavior of Diethyl Oxalo-(S-phenylmercapto)-acetate (XII) with Hydrazine Hydrate.—A sample of ester (1.48 g., 0.005 mole) mixed with hydrazine hydrate (0.41 g., 0.0075 mole) in absolute ethanol (5 ml.) was refluxed eighteen and one-half hours. Filtration and evaporation of solvent gave 0.31 g. (23.5% yield) of 5-carbethoxy-4-(S-phenylmercapto)-pyrazolone-5 (IX). After recrystallization from hot 50–60% ethanol this showed m. p. 207.5–207.7° uncor., 213.0–213.2° cor., gave with alcoholic ferric chloride an orange color, and with ethereal diazomethane evolved nitrogen.

Anal. Calcd. for $C_{12}H_{12}O_3N_2S$: N, 10.60; S, 12.12. Found: N, 10.2, 10.4; S, 12.1, 12.0.

Behavior of Diethyl Oxalo-(S-phenylmercapto)-acetate (XII) with Phenylhydrazine.—The ester (1.50 g., 0.0051 mole) with phenylhydrazine (0.75 g., 0.0069 mole) in absolute ethanol (2.5 ml.) was heated in a sealed tube at 100° for thirteen hours giving 0.52 g. (30% yield) of 1-phenyl-3-carbethoxy-4-(S-phenylmercapto)-pyrazolone-5 (X) colorless needles from 85% ethanol, m. p. 179.0–179.2° uncor., 183.5–183.7° cor. This product gives no color reaction with alcoholic ferric chloride, but is slowly soluble in aqueous 10% sodium carbonate and does evolve nitrogen with ethereal diazomethane.

(9) Claësson, *Bull. soc. chim.*, [2] **23**, 441 (1875).

(10) Müller and Freytag, *J. prakt. Chem.*, [2] **146**, 56–57 (1936).

Anal. Calcd. for $C_{18}H_{16}O_3N_2S$: N, 8.24; S, 9.41. Found: N, 8.00, 8.17; S, 9.36, 9.69.

Summary

1. Diethyl oxalo-phenoxyacetate, the hitherto uncharacterized intermediate in the Koelsch–Whitney synthesis of coumarone-2,3-dicarboxylic acid, has been isolated, purified and characterized.

2. Cleavage of this ester at the unsaturated linkage of its enolic form has been shown to occur under various conditions.

3. The analogous diethyl oxalo-(S-phenylmercapto)-acetate is so sensitive to this type of cleavage and also loses carbon monoxide so readily that extension of the Koelsch–Whitney method to the preparation of thianaphthene-2,3-dicarboxylic acid derivatives is impracticable.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Substitution Products of 5-Cyclopentyl-5-oxopentanoic Acid and 6-Cyclohexyl-6-oxohexanoic Acid[1]

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In the course of an investigation of methods applicable to the synthesis of compounds related in structure to those proposed by Kögl[3] for the plant growth hormones, auxin-a and auxin-b, we have had occasion to prepare and examine the two analogous hydroxy keto lactones, 5-(1-hydroxycyclopentyl)-5-oxo-4-hydroxypentanoic acid γ-lactone and 6-(1-hydroxycyclohexyl)-6-oxo-5-hydroxyhexanoic acid δ-lactone (XIV and XV, Fig. 1). As starting materials, 5-cyclopentyl-5-oxopentanoic acid and 6-cyclohexyl-6-oxohexanoic acid were utilized. These acids were first prepared by Wallach by hydrogenation and subsequent oxidation of cyclopentylidenecyclopentanone[4] and cyclohexenylcyclohexanone,[5] respectively. We have prepared these same keto acids also by an aluminum chloride condensation, as indicated in Fig. 1, obtaining products identical with those prepared by Wallach's method. The older method, however, is shorter and gives better yields. An analogous keto acid, 5-cyclohexyl-5-oxopentanoic acid, has also been synthesized by the aluminum chloride condensation, but has not been investigated further.

The keto acids, VII and X, reacted rapidly at room temperature with two moles of bromine, yielding in each case a crystalline dibromo keto acid which was readily hydrolyzed by dilute aqueous sodium hydroxide. The hydrolysis products were, respectively, the lactone, 5-(1-hydroxycyclopentyl)-5-oxo-4-hydroxypentanoic acid γ-lactone (XIV), and the acid, 6-(1-hydroxycyclohexyl)-6-oxo-5-hydroxyhexanoic acid (XIII). The latter was readily converted to a corresponding lactone (XV) by refluxing in benzene with a trace of iodine. The following considerations serve to establish the structures of these two lactones.

Bromination of keto acids of this type is to be expected only in the positions adjacent to the keto or carboxyl groups, and bromine atoms in these positions would be expected to be readily removed by hydrolysis. The two dibromo keto acids, XI and XII, in fact rapidly consumed three moles of alkali when titrated in hot 50% alcohol with dilute sodium hydroxide. A fleeting end-point corresponding to the consumption of one equivalent of alkali was observed in a cold solution with XII, but not with XI. The hydrolysis products, XIII, XIV and XV, readily reduced Fehling solution when heated, a behavior characteristic of α-ketols. None of the three compounds gave with ferric chloride the positive color test expected of an alpha hydroxy acid,[6] and a quantitative analysis for this group[7] confirmed the absence in any of the three compounds of an hydroxyl adjacent to a carboxyl group. This conclusion is further verified by the results of periodic acid titration of XIII, XIV and XV.

In a periodic acid titration[8] of the dihydroxy keto acid (XIII), two moles of periodate was consumed in eighteen hours at room temperature. On titration of the lactones XIV and XV, however, only one mole of periodate was consumed in twenty-four hours, and three days were required to consume a second mole. When the lactones were first converted to the sodium salts and titrated with periodic acid, two moles of periodate were consumed in twenty-four hours. The lactone rings in XIV and XV are therefore fairly stable to periodic acid (0.2 *N*). Treatment of XIV and XV with slightly less than one equivalent of periodic acid gave, on steam distillation, cyclopentanone and cyclohexanone, respectively, which were identified as the 2,4-dinitrophenylhydrazones.

Experimental[9]

Acid Chlorides of Methyl Hydrogen Glutarate and Ethyl Hydrogen Adipate.—Methyl hydrogen glutarate was prepared from glutaric anhydride and methanol in a

(1) From the theses submitted by G. W. Barber and L. J. Lapides to the faculty of the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Kögl and Erxleben, *Z. physiol. Chem.*, **235**, 181 (1935).

(4) Wallach, *Ann.*, **389**, 180 (1912).

(5) Wallach, *ibid.*, **381**, 95 (1911).

(6) Berg, *Bull. soc. chim.*, [3] **11**, 883 (1894).

(7) Mitchell, *et al.*, THIS JOURNAL, **62**, 1776 (1940).

(8) E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

(9) All melting points have been corrected.