chloride on *m*-chlorobenzonitrile, 3′-chloro-2-phenylacetophenone, 76%, (m.p. 60.4–61.6°); and *m*-chlorobenzylmagnesium bromide on benzonitrile, 2-(*m*-chlorophenyl)acetophenone, 47%, (m.p. 41.8–42.8°).[8]

p-Chlorophenylphenylacetylene. A mixture of 10 g. of 4′-chloro-2-phenylacetophenone and 10 g. of phosphorus pentachloride was heated at 60° for 3 hr. and distilled to yield 8.0 g. of a solid, b.p. 180–185° at 5 mm. This solid was refluxed for 4 hr. in a solution of *t*-butyl alcohol in which 6.7 g. of sodium had been dissolved. About 60% of crude acetylene was obtained which, after several recrystallizations from alcohol, had a m.p. of 81.5–82.0°.

Anal.[9] Calcd. for $C_{14}H_9Cl$: C, 79.1; H, 4.3; Cl, 16.6. Found: C, 79.1; H, 4.5; Cl, 16.4.

o-Chlorophenyl-p-chlorophenylacetylene. A mixture of 5.3 g. of 4′-chloro-2-(*o*-chlorophenyl)acetophenone, 10 g. of phosphorus pentachloride, and 50 ml. of benzene was refluxed for 4 hr. and poured into ice water. The chlorinated products formed were refluxed in a solution of 75 ml. of absolute alcohol in which 3.4 g. of sodium had been dissolved. The crude acetylene thus formed in good but not exactly determined yield was recrystallized twice from aqueous alcohol to yield pure *o*-chlorophenyl-*p*-chlorophenylacetylene, m.p. 62.5–64.5°.

Anal. Calcd. for $C_{14}H_8Cl_2$: C, 68.0; H, 3.2; Cl, 28.7. Found: C, 67.9; H, 3.3; Cl, 28.5.

o-Chlorophenylphenylacetylene. 2-(*o*-Chlorophenyl)acetophenone (20 g.), selenium dioxide (15.4 g.), and acetic anhydride were heated to reflux for 4 hr. After filtration the reaction mixture was poured into water and the crude *o*-chlorobenzil isolated.[10] Alternatively, this diketone was obtained in similar yield by stirring a solution of 10 g. of ketone, 10 g. of potassium permanganate, 70 ml. of pyridine, and 70 ml. of water at room temperature for seven hours while controlling the *p*H near 7 by addition of carbon dioxide. By heating the diketone from the former oxidation with 6.4 g. of anhydrous hydrazine and 2 ml. of acetic acid in 250 ml. of alcohol for 18 hr. there was obtained 16.3 g. (69% over-all) of colorless dihydrazone. Recrystallization from acetonitrile yielded pure dihydrazone of *o*-chlorobenzil, m.p. 234–236° (dec.).

Anal. Calcd. for $C_{14}H_{13}N_4Cl$: C, 61.6; H, 4.8; N, 20.5; Cl, 13.0. Found: C, 61.6; H, 5.0; N, 20.4; Cl, 12.8.

To a stirred solution of 10 g. of dihydrazone in 200 ml. of *N*-methylpyrrolidone[11] at room temperature was added 50 g. of silver benzoate in three portions, each followed by the addition of 8 ml. of triethylamine. When the theoretical amount of nitrogen had been evolved (4 hr.) the mixture was filtered, poured into water, and worked up to yield a good but not exactly determined yield of acetylene. A pure 2.5 g. center cut of *o*-chlorophenylphenylacetylene, b.p. 146° at 3 mm. was taken for further work.

Anal. Calcd. for $C_{14}H_9Cl$: C, 79.1; H, 4.3; Cl, 16.7. Found: C, 78.9, 79.1; H, 4.4, 4.4; Cl, 16.5, 16.4.

m-Chlorophenylphenylacetylene. 3′-Chloro-2-phenylacetophenone was oxidized to *m*-chlorobenzil by the selenium dioxide and potassium permanganate methods described above. A pure sample melted at 88.8–89.8°.[12] The dihydrazone, m.p. 98–99°, was obtained in about 70% over-all yield. The pure dihydrazone, obtained by recrystallization from ethanol-water, melted at 98.4–99.0°.

To a stirred solution of 55 g. of silver trifluoroacetate in 150 ml. of alcohol was added 14.3 g. of *m*-chlorobenzil dihydrazone in 100 ml. of alcohol. During 45 min. five 5-ml. portions of triethylamine were made. After a total of 50 min., the theoretical volume of nitrogen had been evolved and the reaction mixture was poured into 150 ml. of concd. ammonium hydroxide. By ether extraction and distillation there was obtained 9.0 g. (80%) of *m*-chlorophenylphenylacetylene, b.p. 153–155° at 3 mm. A redistilled center cut was taken for the hydration studies.

Anal. Calcd. for $C_{14}H_9Cl$: C, 79.1; H, 4.3; Cl, 16.7. Found: C, 79.3; H, 4.4; Cl, 16.5.

Diphenylacetylene. To a stirred mixture of 15 g. of benzil dihydrazone,[13] m.p. 151–153°, 80 g. of silver trifluoroacetate, and 250 ml. of acetonitrile was added 70 ml. of triethylamine during 150 min. After 6 hr., 103% of the theoretical nitrogen had been evolved. After the mixture had been poured into 200 ml. of concd. ammonium hydroxide there was isolated 9.5 g. (85%) of diphenylacetylene, m.p. 58–60°.

Di-p-methoxyphenylacetylene. As in the case of diphenylacetylene di-*p*-methoxybenzil dihydrazone,[13] m.p. 115–118°, was oxidized to di-*p*-methoxyphenylacetylene,[14] m.p. 140–146°, in 85% yield. The pure acetylene melted at 145–146°, after two recrystallizations from 1:2 acetic acid-alcohol.

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(8) All of these ketones have been prepared previously; see reference 6 in this paper.

(9) Analyses by Galbraith Laboratories, Knoxville, Tenn.

(10) E. L. Shapiro and E. L. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

(11) We thank the General Aniline and Film Corp. for a generous gift of *N*-methylpyrrolidone.

(12) M. T. Clarke, E. C. Hendley, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 3280 (1955) report a m.p. of 86°.

(13) W. Schlenk and E. Bergmann, *Ann.*, **463**, 76 (1928).

(14) H. Wiechell, *Ann.*, **279**, 338 (1894) reported a m.p. of 142°.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of Dipivaloyl with Organometallic Reagents[1]

MELVIN S. NEWMAN AND GERALD R. KAHLE[2]

Received November 4, 1957

Dipivaloyl (I) reacts with ethoxyethynylmagnesium bromide and ethoxyethynyllithium to yield 3-*t*-butyl-5,5-dimethyl-1-ethoxy-3-hydroxy-4-keto-1-hexyne (II). On treatment with acid II rearranges stereospecifically to yield ethyl *cis* 3-*t*-butyl-5,5-dimethyl-4-keto-2-hexenoate (V). Reaction of I with ethyl bromoacetate yields a hydroxyester (III) which, after hydrolysis and dehydration yields IV, the acid corresponding to V. IV is shown to exist in about equal amounts in the acyclic and cyclic forms, IV and VI.

In the hope of preparing intermediates suitable for conversion into *o*-di-*t*-butylbenzene, 2,2,5,5-tetramethyl-3,4-hexanedione (I) (dipivaloyl) was treated with (*1*) ethoxyethynylmagnesium bro-

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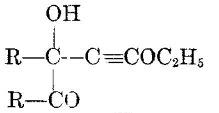
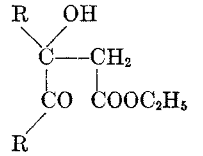
(1) Taken from the Ph.D. thesis of G. R. Kahle, Ohio State University, 1956.

(2) Holder of the Monsanto Chemical Co. Fellowship, 1954–1955.

mide, (*2*) ethoxyethynyllithium, and (*3*) ethyl bromoacetate and zinc. However, despite the use of excess reagent and long periods of heating only the condensation products 3-*t*-butyl-5,5-dimethyl-3-hydroxy-4-keto-1-ethoxy-1-hexyne (II) and ethyl 3-*t*-butyl-5,5-dimethyl-3-hydroxy-4-ketohexanoate (III) were obtained. This result was not entirely unexpected in view of the reported failure of dipivaloyl to react with *o*-phenylenediamine.[3]



II

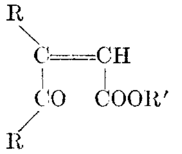


III

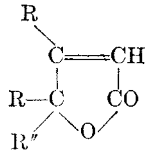
$R = (CH_3)_3C—$

Actually pure II was not isolated. The crude reaction mixtures containing II, as indicated by infrared absorption bands at 2.90 (m), 4.55 (s), and 5.86 μ (s) corresponding to hydroxyl, ethynyl, and carbonyl groups, were treated with ethanolic-hydrogen chloride to yield V ($R' = C_2H_5$) in over 50% yields.[4] The yields of V from the ethoxyethynyl carbinol reaction sequence were slightly better when the Grignard reagent was used rather than the lithium derivative. When we treated I with the solution formed by adding ethoxyacetylene to butyllithium we obtained 4-*t*-butyl-2,2-dimethyl-3-keto-4-octanol, the product to be expected by the addition of butyllithium, rather than ethoxyethynyllithium, to I.[5]

The hydroxy keto ester (III), formed in 39% yield in the Reformatsky reaction, was converted into 3-*t*-butyl-5,5-dimethyl-4-keto-2-hexenoic acid (IV) ($R' = H$) by alkaline hydrolysis followed by dehydration of the hydroxy acid with potassium acid sulfate. The structure, IV, was supported by the facts that oxidation afforded I and cyclic derivatives, VII and VIII, could be prepared from IV (see below).



IV $R' = H$
V $R' = C_2H_5$



VI $R'' = OH$
VII $R'' = Cl$
VIII $R'' = OC_2H_5$

The *cis* relationship of pivaloyl and carboxyl groups in IV and related compounds was established by the fact that normal and pseudo esters could be prepared from IV. When IV was treated with thionyl chloride the pseudo acid chloride VII was obtained in high yield. The cyclic structure for VII [and the other pseudo (cyclic) derivatives] was characterized by a single strong carbonyl absorption band at 5.65 μ. This acid chloride was recovered unchanged after refluxing for seven hours in absolute alcohol containing pyridine and thus appears to be an unusually unreactive cyclic acid chloride.[6] However, on refluxing VII with absolute ethanolic silver nitrate the pseudo ethyl ester (VIII) was obtained in high yield. On alkaline hydrolysis both V and VIII yielded the same acid, IV, and on treatment of IV with diazoethane V was formed.

By comparing the extinction coefficient at 300 mμ of a solution of IV in alcohol with those of the

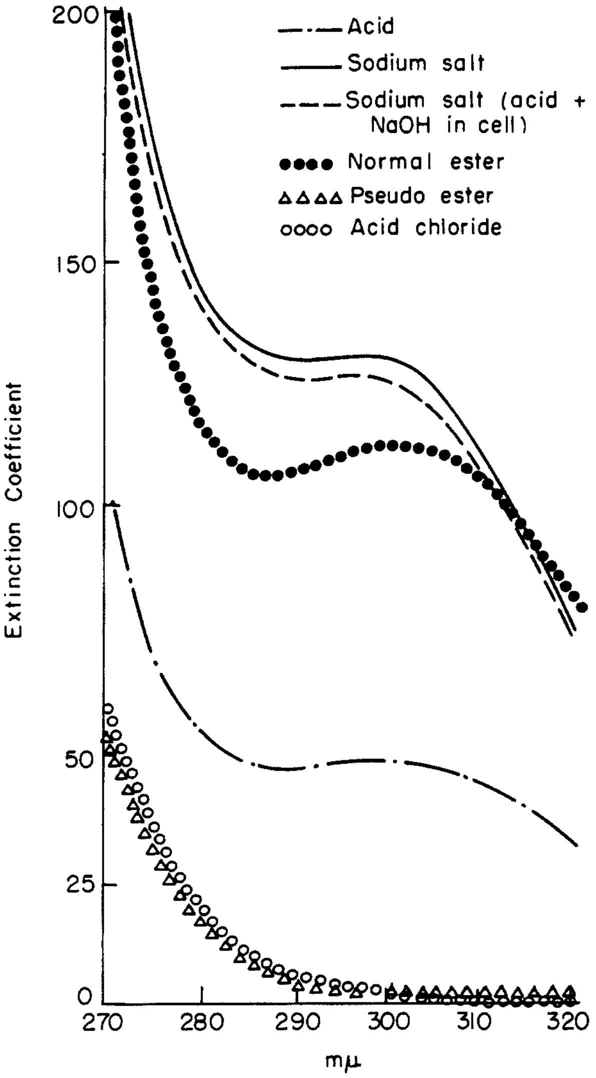


Fig. 1. Ultraviolet Absorption Spectra of IV and Derivatives of IV

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(3) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

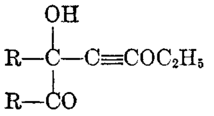
(4) I. Heilbron, E. R. H. Jones, M. Julia, and B. C. L. Weedon, *J. Chem. Soc.*, 1823 (1949), who discovered this synthesis of α,β-unsaturated esters, similarly proceeded without isolation of the ethoxyethynyl carbinols.

(5) Ethoxyethynyllithium may be formed by reaction of ethoxyacetylene with phenyllithium but not with butyllithium, private communication from Dr. D. A. van Dorp.

(6) R. E. Lutz, *J. Am. Chem. Soc.*, **52**, 3405 (1930) reports that certain pseudo acid chlorides are relatively stable towards alcoholysis. However, pseudo acid chlorides of *o*-benzoylbenzoic acids are usually reactive with alcohols, H. Meyer, *Monatsh.*, **25**, 475 (1904).

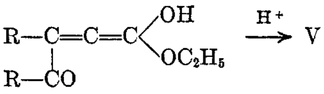
normal and pseudo ethyl esters, V and VIII, about 57% of IV was shown to be present in the cyclic form, VI.[7] The spectra are given in Fig. 1.

The fact that rearrangement of the ethynyl carbinol (II) yields V is of interest in that the hypothetical intermediate alleneol (IX) ketonizes stereospecifically to yield V. We were never able to isolate the trans isomer of V or the corresponding acid and hence assume that it was never formed. Examination of models did not indicate much difference in hindrance in *cis* and *trans* forms of IV or V. It should prove of interest to see if other analogs of II also rearrange stereospecifically.[8]



$\mathrm{R{-}\overset{OH}{\underset{R{-}CO}{C}}{-}C{\equiv}COC_2H_5}$

II



$\mathrm{R{-}\underset{R{-}CO}{C}{=}C{=}C{<}^{OH}_{OC_2H_5}} \xrightarrow{H^+} \mathrm{V}$

IX

The acid-catalyzed isomerization of II to V was accompanied by another reaction which produced in small yield an acid, $C_{12}H_{20}O_3$, isomeric with IV. Since this acid did not yield I on oxidation no further work to establish its structure was done.

The ethyl ester (V) was unreactive to ethoxyethynylmagnesium bromide and to attempts at catalytic reduction over various active platinic oxide catalysts or with Raney nickel and alkali.[9] However, reduction at 50–60° over a rhodium-on-alumina catalyst afforded ethyl 3-*t*-butyl-5,5-dimethyl-4-ketohexanoate (X). X was unreactive towards ethoxyethynylmagnesium bromide, ethoxyethynyllithium, and zinc and ethyl bromoacetate. In the latter case a vigorous reaction occurred and all of the bromoester was consumed. However, isolation of unchanged X in high yield from the reaction mixture and the formation of ethyl acetate (from ethyl bromoacetate) indicated that enolization had occurred.[10]

EXPERIMENTAL[11]

2,2,5,5-Tetramethyl-3,4-hexanedione, I, (*dipivaloyl*). Crude pivaloin, m.p. 69–79°, uncorr., prepared in 80–90% yields,[12] was sufficiently pure to be oxidized to I directly. A solution of 50 g. of chromic oxide in 80 ml. of water and 220 ml. of acetic acid was added dropwise to a solution of 103 g. of crude pivaloin in 250 ml. of acetic acid, the temperature being maintained near 15°. After stirring for 24 hr. at room temperature the product, isolated by conventional methods, was vacuum-distilled to yield 59.1 g. of I as a yellow oil, b.p. 66–72° at 20 mm., which showed no hydroxyl band by infrared analysis. The residues from several such oxidations could be combined and reoxidized to give high over-all conversions to I.

On refluxing a solution of 1 g. of I in 10 ml. of alcohol containing 0.9 g. of hydrazine hydrate and a drop of hydrochloric acid until the yellow color had gone (2 days) the monohydrazone of I was obtained as a colorless solid. Recrystallization from alcohol-water yielded pure hydrazone, m.p. 46.0–46.6°.

Anal. Calcd. for $C_{10}H_{20}N_2O$: C, 65.2; H, 10.9; N, 15.2. Found: C, 65.2; H, 10.9; N, 15.2.

In an attempt to react I with ethylenediamine in refluxing alcohol for 2 days no diminution of the yellow color of the solution was observed and I was recovered from the reaction mixture.

An attempt to oxidize pivaloin in acetic acid at 100° with bismuth trioxide[13] gave the diketone (I) in poor yield together with mostly unchanged pivaloin. Oxidation of pivaloin with neutral permanganate[14] was similarly unsuccessful.

Ethyl 3-t-butyl-5,5-dimethyl-4-keto-2-hexenoate (V). A solution of 18 g. of ethoxyacetylene[15] in 50 ml. of dry ether was added dropwise to 216 ml. of 1.15*M* ethylmagnesium bromide in ether cooled to 0–5°. The dark oily complex which separated dissolved on addition of 125 ml. of dry benzene. After refluxing this solution for 30 min. and cooling, a solution of 34 g. of I in 100 ml. of benzene was added dropwise. The reaction mixture was refluxed for 5 hr. (liquid temperature, 48°), then was cooled and treated with saturated ammonium chloride solution. The washed and dried solution was concentrated under reduced pressure to yield a dark oil which had strong absorption bands[11a] at 4.55 μ (C≡C) and 5.86 μ (C=O) and a medium band at 2.90 μ (OH). On adding alcohol containing hydrogen chloride a rise in temperature was noted, the extent of the rise depending on the size of the run and the amount of hydrogen chloride dissolved in the alcohol. Separation of the reaction products in a conventional way afforded 28.2 g. (58%) of colorless ester, V, b.p. 83–100° at 1 mm., n_D^{20} 1.4650, after a small forerun of I. A portion of redistilled V, b.p. 106° at 2 mm., n_D^{20} 1.4648, d^{20} 0.9672, was taken for analysis.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 70.0; H, 10.1; MR_D, 68.1. Found: C, 69.7; H, 10.3; MR_D, 68.8.

A sample of pure IV was converted into the ethyl ester (V), n_D^{20} 1.4640, with diazoethane.[16] This ester proved identical to the V originally prepared by rearrangement of II, as shown by an identical infrared spectrum.[11a]

Acidification of the alkaline extracts of the reaction

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(7) Compare with results in the *o*-benzoylbenzoic acid series, M. S. Newman and C. W. Muth, *J. Am. Chem. Soc.*, **73,** 4627 (1951), and in the β-aroylacrylic series, R. E. Lutz *et al.*, *J. Am. Chem. Soc.*, **75,** 5039 (1953); *J. Org. Chem.*, **18,** 1638 (1953). V had a maximum at 217 mμ (ϵ = 7.45 × 10^3).

(8) Stereospecific rearrangements of ethoxyethynyl carbinols formed by addition of ethoxyethynylmagnesium bromide to ketones have been observed previously but no emphasis was placed on the stereospecificity of the reaction. In most cases the stereochemistry of the product was not mentioned. Several references to such rearrangements follow. K. Brack and H. Schinz, *Helv. Chim. Acta*, **34,** 2009 (1951); H. Kappeler *et al.*, *Helv. Chim. Acta*, **36,** 1862 (1953); D. Magrath *et al.*, *J. Chem. Soc.*, 2393 (1950); P. A. Plattner *et al.*, *Helv. Chim. Acta*, **33,** 1088 (1950); R. Helg *et al.*, *Helv. Chim. Acta*, **39,** 1269 (1956); A. Caliezi and H. Schinz, *Helv. Chim. Acta* **33,** 1129 (1950); I. M. Heilbron *et al.*, *J. Chem. Soc.*, 1823 (1949).

(9) E. Schwenk, *et al.*, *J. Org. Chem.*, **9,** 175 (1944).

(10) M. S. Newman, *J. Am. Chem. Soc.*, **64,** 2131 (1942); A. S. Hussey and M. S. Newman, *J. Am. Chem. Soc.*, **70,** 3024 (1948).

(11) All melting points corrected except as noted. Analyses by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra marked *a* in chloroform, *b* in Nujol mull, *c* pure liquid.

(12) J. M. Snell and S. M. McElvain, *Org. Syntheses*, **Coll. Vol. II,** 114 (1943).

(13) W. Rigby, *J. Chem. Soc.*, 793 (1951).

(14) Compare N. A. Khan and M. S. Newman, *J. Org. Chem.*, **17,** 1063 (1952).

(15) G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

(16) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13,** 763 (1948).

products produced in the above-mentioned alcoholic hydrogen chloride treatment yielded 3.0 g. of an acid, m.p. 179–184° (uncorr.), which, on several recrystallizations from alcohol-water afforded an analytical sample, m.p. 189.4–190.2°. This acid did not yield I on oxidation.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.9; H, 9.5. Found: C, 67.6, 67.6; H, 9.4, 9.5.

Alternately, a solution of 5.1 g. of I in 20 ml. of benzene was added dropwise to the organolithium prepared by adding 5.6 g. of ethoxyacetylene in 30 ml. of benzene to a solution of phenyllithium made from 11.8 g. of bromobenzene and 1.12 g. of lithium in 60 ml. of ether. The mixture was stirred at room temperature for 15 hr. and was decomposed with 10 ml. of saturated ammonium chloride solution. The crude ethoxyethynyl carbinol (II) thus obtained was treated as described above for the Grignard reaction mixture to yield 3.8 g. (53%) of V.

In a similar experiment 9.0 g. of ethoxyacetylene was added to 104 ml. of a 1.16*M* solution of butyllithium[17] in ether cooled to −10°. Addition of 50 ml. of benzene failed to dissolve the white precipitate which formed. A solution of 5.1 g. of I in 25 ml. of ether-benzene (1:1) was added. After 2 hr. no reaction seemed to have occurred so 75 ml. of tetrahydrofuran was added, the ether was distilled, and the reaction mixture was refluxed (liquid temperature, 43°) for 2 hr. From the neutral fraction of the reaction mixture after basic and acidic hydrolysis there was isolated 3.6 g. of crude solids from which a moderate amount of pure 4-*t*-butyl-2,2-dimethyl-4-hydroxy-3-octanone, m.p. 81.6–82.0°, was obtained. Absorption bands[11a] at 2.80 (m) and 5.90 (s) μ were consistent with the structure which represents the addition of one equivalent of butyllithium to one carbonyl group of I.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.6; H, 12.3. Found: C, 73.1; H, 12.3.

3-t-Butyl-5,5-dimethyl-4-keto-2-hexenoic acid (IV). To a refluxing solution of 15 g. of ethyl bromoacetate and 5.0 g. of I in 35 ml. of dry ether and 100 ml. of benzene was added 10 g. of zinc granules. On distillation of the ether a vigorous reaction occurred. When this moderated 5 g. of bromoester and 4 g. of zinc were added and the mixture was refluxed for one hour. On distillation of the reaction products 1.2 g. of I was recovered in a forerun followed by 2.92 g. (39%) of ethyl 3-*t*-butyl-5,5-dimethyl-3-hydroxy-4-ketohexanoate (III), b.p. 89–93° at 1 mm. Redistillation afforded an analytical sample, n_D^{20} 1.4515, with absorption bands[11a] at 2.96 (s), 5.85 (s) and 5.93 μ (s, shoulder).

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 65.1; H, 10.1. Found: C, 65.1; H, 9.9.

The oily acid, obtained by alkaline hydrolysis of III, could not be crystallized. It was dehydrated to IV by mixing with 0.5 g. of freshly fused powdered potassium acid sulfate in a test tube and heating at 150–160° for 10 min. and at 200° for a very short time. Pure IV, m.p. 105.8–106.5°, formed colorless elongated prisms when recrystallized from Skellysolve B (petroleum ether, b.p. 60–70°). There was no depression of the melting point when mixed with a sample of IV obtained by alkaline hydrolysis of V and the infrared absorption curves[11b] were identical.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.9; H, 9.5; N.E., 212.3 Found: C, 67.8; H, 9.4; N.E., 213.1.

Oxidation of 200 mg. of IV by shaking in 10 ml. of acetic acid and 0.5 ml. of water containing 500 mg. of chromic oxide at room temperature for 5 hr. afforded a yellow oil which on refluxing for one day with 3 ml. of absolute alcohol, 3 ml. of pyridine, and 0.2 g. of hydroxylamine hydrochloride yielded 80 mg. of the monooxime of I, m.p. 121–122°, undepressed on mixing with an authentic sample.[18] Identical x-ray powder photographs were obtained from the two oximes. Similar oxidation of the acid, $C_{12}H_{20}O_3$, m.p. 189.4–190.2°, mentioned above yielded neither yellow (adjacent dicarbonyl) oil nor oxime, hence a rearranged carbon skeleton is indicated for this acid. No further work was done with it.

Treatment of 3.0 g. of IV with 12 ml. of thionyl chloride at reflux for 90 min. afforded a solid acid chloride, m.p. 78–79° (uncorr.), in quantitative yield. Recrystallization from Skellysolve B yielded colorless cubes of the acid chloride of IV, m.p. 82.2–83.0°. The infrared absorption[11a] (one carbonyl band at 5.65 μ) indicated that this acid chloride had the cyclic structure, VII.

Anal. Calcd. for $C_{12}H_{19}O_2Cl$: C, 62.5; H, 8.3; Cl, 15.4. Found: C, 62.4, 62.3; H, 8.8, 8.7; Cl, 15.1, 14.9.

Since a solution of 1.0 g. of VII and 0.85 g. of silver nitrate in 25 ml. of absolute alcohol and 2 ml. of pyridine at room temperature gave only a slight precipitation of silver chloride in 15 min., the mixture was refluxed. After 0.5 hr. the precipitation of silver chloride was complete. Filtration yielded 0.61 g. of silver chloride (0.62 g. theory) and from the filtrate 0.92 g. (89%) of colorless crystals, m.p. 72–76° (uncorr.), was obtained. Several recrystallizations from Skellysolve B afforded large colorless cubes of pure VIII, m.p. 82.5–83.2°, depressed on mixing with VII. VIII showed strong absorption[11a] at 5.70 μ and a band at 8.80 μ, characteristic of ether linkages, not possessed by VII.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 70.0; H, 10.1. Found: C, 70.2, 70.1; H, 9.9, 10.0.

When the acid chloride (VII) was allowed to stand for 2 days in a solution of absolute alcohol and pyridine at room temperature no reaction had occurred and VII was recovered after a work-up involving treatment with aqueous potassium carbonate. The acidified aqueous extracts did not even give a haziness when treated with silver nitrate.

Ethyl 3-t-butyl-5,5-dimethyl-4-ketohexanoate (X). In the best of several experiments a solution of 14.7 g. of V in 5.0 ml. of freshly distilled alcohol containing 1.5 g. of a 5% rhodium-on-alumina[19] catalyst was shaken under 50 p.s.i. of hydrogen in a bottle held at 50–60° by heating with heating tape. The reduction required 17 hr. until the theoretical amount of hydrogen had been absorbed. An additional 1.2 g. of catalyst was added in three portions during the reduction. Distillation yielded 14.5 g. (98%) of X as a colorless oil, b.p. 83.5–86.0° at 1 mm., n_D^{20} 1.4445. A redistilled center cut, n_D^{20} 1.4440, showed strong absorption bands[11c] at 5.75 and 5.86 μ but no band near 6.13 μ (due to the unsaturation in ester V).

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.4; H, 10.8. Found: C, 69.6; H, 11.0.

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[17] Prepared and standardized (85% yield) as described by H. Gilman and R. G. Jones, *Org. Reactions*, **6**, 352 (1951).

[18] L. Bouveault and R. Locquin, *Bull. soc. chim.*, (3) **35**, 657 (1906).

[19] Baker and Co., Newark, N. J.