repeated using equimolar quantities of the reactants and without neutralizing with ammonium chloride. In another experiment the ether solution of the reaction product was extracted with $2N$ hydrochloric acid; no trace of amine was obtained on filtering the resulting mixture and neutralizing the acid extract.

The hydrocarbon material V was soluble in ether but insoluble in ethanol. It readily decolorized bromine in carbon tetrachloride to produce dark gum, reacted slowly with maleic anhydride in ether to yield tarry material, but failed to take up hydrogen in ethyl acetate solution over Adams catalyst at 5 atm. during 24 hr., V being recovered. Treatment of ether solutions of V with $6N$ hydrochloric acid and with anhydrous aluminum chloride at room temperature produced polymeric material which precipitated immediately. This polymeric material had an average molecular weight of about 1100 (ebullioscopic). The infrared spectrum of this material was similar to that of V, with small differences. Hydrocarbon V did not react with butyllithium in ether.

Reaction of III *with lithium amide.* This reaction was carried out as described above for sodium amide employing 18.5 g. (0.05 mole) of salt III and 0.09 mole of lithium amide in 300 ml. of liquid ammonia. After replacing the ammonia with ether and filtering the resulting suspension, the ether filtrate was extracted with $2N$ hydrochloric acid, causing separation of much polymeric material. The mixture was filtered and the two layers of the filtrate were separated. The aqueous layer was made basic with sodium hydroxide and the liberated amine was extracted with ether. The ether was removed from this extract, leaving 0.35 g. (3%) of oil, presumably 3-benzyl-2-methylbenzyldimethylamine (VI). The infrared spectrum of this oil had strong peaks at 11.73 μ, characteristic of the benzyldimethylamino group,[5] at 12.85 μ, suggesting aromatic 1,2,3-trisubstitution,[7] and at 13.71 and 14.30 μ, suggesting aromatic monosubstitution.[16] The methiodide of this amine, prepared in dry acetone and recrystallized twice from this solvent, melted at 199–200.5°.

Anal. Calcd. for $C_{18}H_{24}IN$: C, 56.70; H, 6.30. Found: C, 56.33; H, 6.15.

Reaction of III *with disodiosuccinimide.* To a stirred suspension of 0.115 mole of disodiosuccinimide in 1200 ml. of liquid ammonia[8] was added 21.0 g. (0.057 mole) of salt III over a 5-hr. period. After 1 more hr., excess ammonium chloride was added, and the ammonia was replaced with ether. The resulting ether suspension was stirred with $3N$ sodium hydroxide to precipitate a gum insoluble in ether and water. On prolonged stirring with $2N$ hydrochloric acid this gum was changed to an ether soluble form. The resulting ether solution was concentrated to leave 4.7 g. of polymer (dried *in vacuo*).

Anal. Found: C, 88.02; H, 6.96; N, 1.50; mol. wt. (Rast) 763, 765.

This analysis suggests the xylylene IV and succinimide were involved in the molar ratio 4.4:1.

The infrared spectrum of this material was similar to that of V, but had additional strong peaks at 5.92 and 3.01 μ.

4-Benzylbenzyltrimethylammonium iodide (VII). Trimethylamine was bubbled through a solution of 32.3 g. (0.15 mole) of 4-benzylbenzyl chloride[17] for 30 min. After cooling, ether was added to precipitate 32.3 g. (79%) of 4-benzylbenzyltrimethylammonium chloride, which was highly hygroscopic.

A mixture of 31.8 g. (0.115 mole) of this chloride, 17.3 g. (0.115 mole) of sodium iodide, and 200 ml. each of ethanol and acetonitrile was rapidly stirred for a few minutes. The resulting mixture was filtered through a mat of Hyflow Supercel, and the filtrate was concentrated to about 200 ml. After another filtration to remove an additional small quantity of sodium chloride, 1500 ml. of ether was added to precipitate the iodide of VII. After recrystallization from acetonitrile, 31.0 g. (73%) of this salt was obtained, melting at 170–171°, and at 178–179° after another recrystallization.

Anal. Calcd. for $C_{17}H_{22}IN$: C, 55.63; H, 6.04; N, 3.82. Found: C, 55.80; H, 6.11; N, 3.88.

Reaction of VII *with sodium amide.* Essentially the same procedure was used as described above for VII. A dark green color developed. The product was an amorphous hydrocarbon almost identical in appearance to V.

Anal. Calcd. for $(C_{14}H_{12})_3$: C, 93.30; H, 6.70; mol. wt. 540. Found: C, 91.19; H, 7.32.

A sample of this material was dissolved in ether and precipitated with ethanol.

Anal. Found: C, 91.08; H, 6.60; mol. wt. (ebullioscopic) 558, 550, 481.

The reactions of this material with acid and with bromine were similar to those of V.

DURHAM, N. C.

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[16] Ref. 7, p. 76.

[17] C. Maquin and H. Gault, *Chem. Abstr.*, **49**, 13181i (1955); *Compt. rend.*, **234**, 629 (1952); *Bull. soc. chim. France*, C48 (1953).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. X. Oxidative Rearrangements with Certain β-Diketones

GEORGE B. PAYNE

Received June 27, 1961

The oxidation of several β-diketones by hydrogen peroxide in *tert*-butyl alcohol has been studied. In general, 2-acylcyclohexanones gave cyclopentanecarboxylic acids in 80–87% yields. 2-Acetylcyclopentanone, on the other hand, showed no comparable ring contraction to cyclobutanecarboxylic acid. Instead, α-methyladipic acid was secured in 93% yield. Other diketones investigated were 2-formylcyclohexanone, acetylacetone, and mono- and dimethylacetylacetone.

The reaction of β-diketones with peroxy acids has recently been studied.[1] As a general rule, hydroxy diketones (I) were obtained. Epoxidation of the enol form of the diketone was believed to be a reasonable path to account for the products observed.

Mannich[2] described the oxidation of a dispiro

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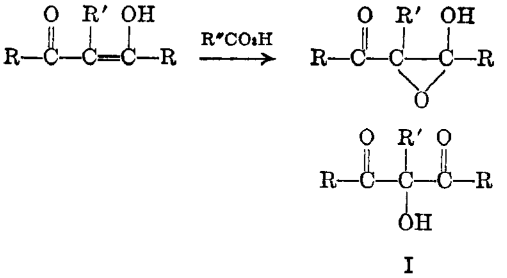
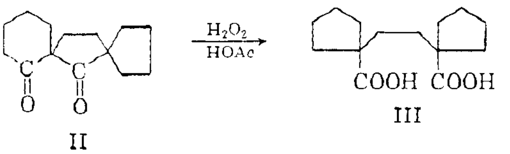
[1] H. O. House and W. F. Gannon, *J. Org. Chem.*, **23**, 879 (1958); see reference therein to earlier work on the peroxy acid oxidation of β-diketones.

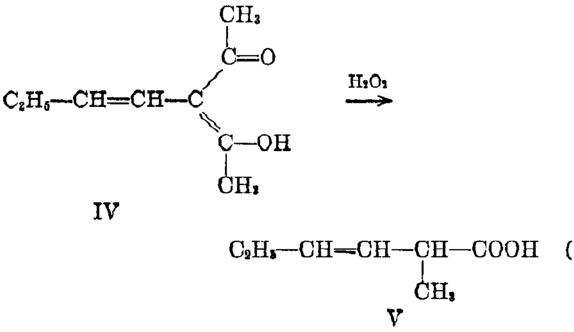
[2] C. Mannich, *Ber.*, **74**, 1007 (1941).


(1)

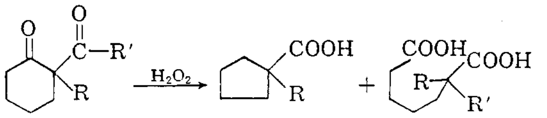
β-diketone (II) with hydrogen peroxide in acetic acid solution to give α,α,α′,α′-bis(tetramethylene)-adipic acid (III). It was not established whether the oxidizing agent was hydrogen peroxide or peroxyacetic acid; the latter, of course, might be expected from reaction of the peroxide with acetic acid.


(2)

The reaction of simpler saturated β-diketones with hydrogen peroxide has apparently not been reported. An unsaturated β-diketone (IV, enol form) was, however, recently observed to undergo an oxidative rearrangement on treatment with hydrogen peroxide.[3] The product, 2-methyl-3-hexenoic acid (V) was obtained in 70% yield when the reaction was carried out at a *p*H of about 6.


(3)

In the present study several 2-acylcyclohexanones (VI) were allowed to react with hydrogen peroxide in *tert*-butyl alcohol solution, usually at reflux. A trace of sulfuric acid catalyst was found to accelerate the reaction markedly.

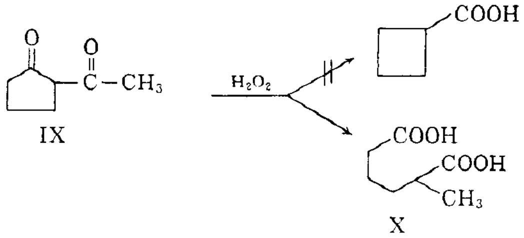

(4)

VIa. R = H, R′ = CH_3	VIIa. 87%	VIIIa. 1-2%
b. R = H, R′ = C_6H_5	b. 85%	b. —
c. R = CH_3, R′ = CH_3	c. 80%	c. —
d. R = H, R′ = H	d. 26%	d. 41%

2-Acetylcyclohexanone (VIa) and 2-benzoylcyclohexanone (VIb) gave cyclopentanecarboxylic acid in 87 and 85% yields, respectively. Similarly, 2-methyl-2-acetylcyclohexanone (VIc) gave 1-methylcyclopentanecarboxylic acid in 80% yield. 2-Formylcyclohexanone (VId) also afforded cyclopentanecarboxylic acid, but the major product was pimelic acid (VIIId), obtained in 41% yield.

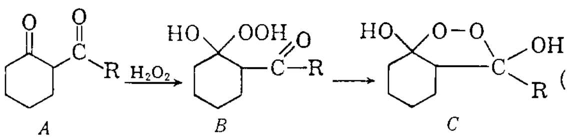
No attempt was made to secure yield figures on possible minor products VIIIb and VIIIc. In the case of 2-acetylcyclohexanone, however, recrystallization of a distillation residue did allow the recovery of a small amount of crystalline material. Carbon and hydrogen analysis indicated that it was probably α-methylpimelic acid, in spite of a melting point that was slightly lower than the literature value.

Having achieved a rather facile oxidative ring contraction of a six-membered ring to a five-,[4] it was of interest to determine whether ring contraction of a five-membered ring to a four- might also occur. To this end, 2-acetylcyclopentanone (IX) was oxidized in the usual manner. An uncatalyzed reaction was complete in sixteen hours at reflux (compared with a three-hour reaction time for 2-acetylcyclohexanone) to give α-methyladipic acid (X) in 93% yield. No evidence was obtained for the presence of even a trace of cyclobutanecarboxylic acid.


(5)

α-Methyladipic acid was identified by analysis and by mixed melting point with an authentic sample prepared from 2-methylcyclohexanol *via* nitric acid oxidation. Comparison of dianilide derivatives was also made by mixed melting point.

It is believed that the reactions described above probably proceed by way of intermediates *B* and *C*.[5] Certainly the enol form of the diketone appears not to be required, since the nonenolizable 2-methyl-2-acetylcyclohexanone (VIc) was oxidized successfully. The presence of a trace of mineral acid


(6)

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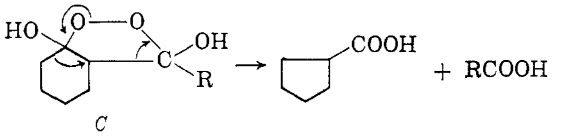
[3] G. B. Payne, *J. Org. Chem.*, 24, 1830 (1959).

[4] In view of the product Mannich obtained (III), it is suspected that his reaction (Equation 2) was a consequence of attack by hydrogen peroxide rather than peroxyacetic acid.

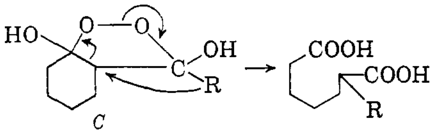
[5] See A. V. Tobolsky and R. B. Mesrobian, *Organic Peroxides*, Interscience, New York, 1954, pp. 41–51, for a discussion of peroxy derivatives of aldehydes and ketones.

undoubtedly facilitates *formation* of *C*, as well as its eventual collapse. In the case of 2-formylcyclohexanone it is possible, of course, that *C* (R = H) might be formed in an inverse manner: addition of hydrogen peroxide to the formyl group followed by cyclization with the ring carbonyl.

In order to account for the two types of products obtained, one may postulate a breakdown of intermediate *C* by either of two similar paths[6]:



(7)

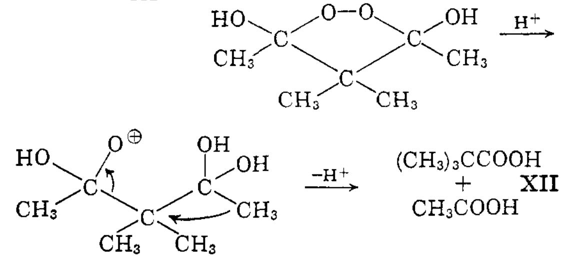


(8)

An attempt was made to isolate an intermediate peroxide from 2-acetylcyclohexanone by carrying out the reaction with anhydrous ethereal hydrogen peroxide. Disappearance of hydrogen peroxide and possible formation of organic peroxide was followed by differential titration with ceric sulfate (for hydrogen peroxide)[7] and acidified potassium iodide (for total peroxide). No evidence was obtained for buildup of an intermediate organic peroxide as 83% of the oxidant was consumed in four days at room temperature. Distillation gave cyclopentanecarboxylic acid in 61% yield based on diketone charged.

Since 2,4-pentanedione (acetylacetone) did not undergo an oxidative rearrangement under the present conditions,[8] it was of interest, from a mechanistic point of view, to determine whether a dialkyl analog might behave differently. 3,3-Dimethyl-2,4-pentanedione (XI) was prepared from acetylacetone by alkylation with methyl iodide. It reacted with hydrogen peroxide to give pivalic acid (XII) in 76% yield.

The success achieved with XI is believed to be a consequence of carbonium ion stabilization by the *gem*-dimethyl groups during breakdown of the cyclic peroxide[9]:



No isobutyric acid was identified as product from the oxidation of the monomethyl compound, 3-methyl-2,4-pentanedione. It was concluded, therefore, that one alkyl substituent does not provide sufficient carbonium ion stabilization to allow the rearrangement to proceed in the acyclic aliphatic series.

EXPERIMENTAL

Oxidation of 2-acetylcyclohexanone. A solution of 28 g. (0.20 mole) of 2-acetylcyclohexanone (Eastman White Label; redistilled, b.p. 83–84°/6 mm.) and 25.0 g. (0.22 mole) of 29.9% hydrogen peroxide in 100 ml. of *tert*-butyl alcohol was allowed to reflux for 3 hr. Iodometric titration indicated the presence of 0.02 mole of peroxide; 12 ml. of oxygen was collected in an inverted graduated cylinder.

A pinch of 10% palladium on charcoal was added to decompose the excess peroxide as the mixture was concentrated to low volume on the steam bath. Distillation then gave 19.9 g. (87% yield) of cyclopentanecarboxylic acid, b.p. 59–62° 1 mm., n_D^{25} 1.4507 (lit.,[10] b.p. 215–216°, n_D^{20} 1.4532).

The *amide* was prepared *via* the acid chloride; m.p. and mixed m.p. 176–177°.

In another experiment, carried out in methanol at 38–40° while maintaining a meter *p*H of 5.5–7.0, two molar equivalents of sodium hydroxide were added in 1.5 hr. Acidification, extraction, and distillation gave cyclopentanecarboxylic acid in 80% yield. A sample of the aqueous solution remaining after extraction was adjusted to *p*H 7 and treated with *p*-bromophenacyl bromide in ethanol. After 1.5 hr. of reflux, the mixture was processed to give *p*-bromophenacyl acetate, m.p. and mixed m.p. 82–84°.

In still another experiment using 25 g. of diketone, the residue remaining after distillation of cyclopentanecarboxylic acid was recrystallized four times from ether–petroleum ether (b.p. 30–60°) to give 0.3 g. of what appeared to be α-methylpimelic acid, m.p. 54–55° (reported,[11] m.p. 59°).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.2; H, 8.1. Found: C, 55.1, 55.2; H, 8.1, 8.1.

Oxidation of 2-benzoylcyclohexanone. A solution of 20.0 g. (0.100 mole) of 2-benzoylcyclohexanone[12] in 150 ml. of *tert*-butyl alcohol was treated with 0.120 mole of 29.9% hydrogen peroxide containing 1 drop of sulfuric acid. After 2 hr. on the steam bath, 0.022 mole of peroxide remained and 45 ml. of oxygen had been evolved.

Distillation from 0.1 g. of sodium acetate and a pinch of palladium on charcoal gave 11.4 g. of a mixture of cyclopentanecarboxylic and benzoic acids. Mass spectrophotometric analysis indicated the presence of 85% of the former and 12% of the latter. The yield of cyclopentanecarboxylic acid was calculated as 85%. Bottoms from the distillation were recrystallized from acetone-hexane to give 7.5 g. of benzoic acid, m.p. and mixed m.p. 119–121°.

Oxidation of 2-formylcyclohexanone. A solution of 25.2 g.

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[6] For simplicity, and because of several possible variations, ionic species have not been indicated.

[7] F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

[8] Acetylacetone appeared to form a stable, possibly cyclic, organic peroxide (differential titration with ceric sulfate and potassium iodide). No investigation of this material was made.

[9] The *gem*-dimethyls would also be expected to facilitate the *formation* of the cyclic peroxide. See G. S. Hammond in *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, pp. 460–470.

[10] S. S. Nametkin and A. K. Ruzhentzova, *J. Russ. Phys. Chem. Soc.*, **46**, 1540 (1914).

[11] I. Heilbron, *Dictionary of Organic Compounds*, Vol. III, Oxford University Press, New York, 1953, p. 490.

[12] C. R. Hauser, B. I. Ringler, F. W. Swamer, and D. F. Thompson, *J. Am. Chem. Soc.*, **69**, 2649 (1947).

(0.20 mole) of 2-formylcyclohexanone[13] and 28.6 g. (0.25 mole of 29.9% hydrogen peroxide in 150 ml. of *tert*-butyl alcohol was warmed to 50° and held at 50–55° by periodic cooling with an ice bath. When no longer exothermic, the mixture was allowed to stand at room temperature for 12 hr.

Palladium-on-charcoal catalyst was added, and the mixture was vacuum flashed into a Dry Ice trap at 10 mm. and 40° (bath temperature) to remove solvent and 0.055 equivalents of volatile acid. The latter was identified as formic by means of a *p*-phenylphenacyl ester derivative, m.p. and mixed m.p. 125–127° (preliminary softening *ca.* 115°).

Crystallization of the nonvolatile material from ether gave 10.0 g. (31% yield) of pimelic acid, m.p. 100–103°. Recrystallization from benzene afforded 9.4 g., m.p. and mixed m.p. 103–104°.

Distillation of the ether mother liquor allowed the recovery of 6.0 g. (26% yield) of cyclopentanecarboxylic acid, b.p. 70–75°/2 mm., n_D^{25} 1.4522. The 5.2-g. residue from this distillation gave, on recrystallization from chloroform, 3.1 g. (10% yield) of crude pimelic acid, m.p. 86–94°.

2-Methyl-2-acetylcyclohexanone. A solution of 70 g. (0.50 mole) of 2-acetylcyclohexanone and 107 g. (0.75 mole) of methyl iodide in 200 ml. of methanol was treated with a solution of 20 g. (0.50 mole) of sodium hydroxide in 100 ml. of water and allowed to stir overnight with tap water cooling.

After dilution with two volumes of water, extraction with two 250-ml. portions of chloroform was carried out. The combined chloroform was washed with 10% sodium hydroxide and water and dried over magnesium sulfate. Distillation gave 61 g. (79% yield) of 2-methyl-2-acetylcyclohexanone, b.p. 74–76°/3 mm., n_D^{25} 1.4657 (reported,[14] b.p. 190–222°).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 70.1; H, 9.2.

Infrared analysis showed carbonyl absorption at 5.90 μ with a strong shoulder at about 5.85 μ; a very small band at 6.23 μ may have been due to a small amount of enol ether impurity.

Oxidation of 2-methyl-2-acetylcyclohexanone. A 30.8-g. (0.20 mole) sample of diketone was oxidized by 0.25 mole of hydrogen peroxide in 100 ml. of *tert*-butyl alcohol. After 18 hr. at reflux, 0.04 mole of peroxide remained and 210 ml. oxygen had been collected (corresponding to about 0.02 mole of peroxide lost by decomposition).

Distillation gave 20.5 g. (80% yield) of 1-methylcyclopentanecarboxylic acid, b.p. 74–75°/1 mm.; n_D^{25} 1.4497 (reported,[15] b.p. 116–117°/16 mm.; n_D^{25} 1.4529).

When the reaction was carried out in the presence of 3 drops (0.11 g.) of sulfuric acid, only 1.5 hr. was required for completion. Distillation from 0.22 g. of sodium acetate and a pinch of palladium on charcoal gave 20.9 g. (82% yield) of product with the above boiling point and n_D^{25} 1.4502.

Redistillation of 39.6 g. of acid from the above experiments through a 0.7 × 50-cm. glass spiral-packed column gave 3.9 g. of material with b.p. 70–94°/3.5 mm. and 32.6 g. of purified product, b.p. 68–69°/1 mm.; n_D^{25} 1.4507.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.4.

Oxidation of 2-acetylcyclopentanone. The reaction was carried out in *tert*-butyl alcohol using 25.2 g. (0.20 mole) of 2-acetylcyclopentanone[16] and 0.25 mole of 29.9% hydrogen peroxide. After 16 hr. at reflux, 0.03 mole peroxide remained and 150 ml. of oxygen had been generated.

Distillation in the usual manner gave 29.9 g. (93% yield of product, b.p. 150–153°/< 1 mm.), which crystallized slowly in the receiver.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.6; neut. equiv., 160. Found: C, 52.4; H, 7.5; neut. equiv., 162.

Recrystallization of 5.3 g. from ether–petroleum ether (b.p. 30–60°) gave 4.3 g., m.p. 54–56°. Further crystallization from the same solvent pair or from a concentrated ether solution had no effect on this melting point. After standing for 3–4 weeks, however, the melting point was found to be 55–57°. A mixed melting point with an authentic sample of α-methyladipic acid (m.p. 53–56°) was not depressed (reported m.p.: 59°,[17] 59–60°,[18] 65°,[19]).

A *dianilide* was prepared *via* the acid chloride, m.p. and mixed m.p. 174–175° (reported[20] m.p. 174–175°) after recrystallization from acetone.

When the oxidation was carried out in methanol and the crude product was esterified using methanol–sulfuric acid, there was obtained a 68% yield of dimethyl α-methyladipate, b.p. 65–66°/1.5 mm.; n_D^{25} 1.4265.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6; sapon. equiv., 94. Found: C, 57.4; H, 8.6; sapon. equiv., 93.

Saponification afforded α-methyladipic acid with m.p. 51–55° after crystallization from chloroform–petroleum ether. Recrystallization of 3 g. from a concentrated water solution gave 0.5 g., m.p. 57–58°.

Authentic α-methyladipic acid. A solution of 1 g. of ammonium vanadate in 490 ml. of 70% nitric acid was stirred at 100° and treated with a few drops of 2-methylcyclohexanol (Eastman Yellow Label). After initiation of the reaction, the mixture was held at 55–60° as 203 g. of the alcohol was added over 2 hr. After a further hour at 60–70°, the solution was held at gentle reflux until nitrogen oxide evolution ceased (1.5 hr.).

After concentration to a volume of 300 ml. followed by thorough chilling, the precipitate (mainly adipic acid) was removed by filtration. Further concentration gave an oily residue weighing 95 g. It was esterified using methanol–sulfuric acid; the resulting ester mixture was distilled through a 10-tray Oldershaw column to give, after removal of 53 g. of lower boiling material, 26 g. of dimethyl α-methyladipate, b.p. 107–108°/10 mm.; n_D^{25} 1.4268.

Saponification of the dimethyl ester afforded an authentic sample of α-methyladipic acid, m.p. 53–56°. Attempts to raise this value by further recrystallizations were not successful.

A *dianilide*, prepared by way of the acid chloride, had a m.p. of 174–175° after recrystallization from acetone.

3,3-Dimethyl-2,4-pentanedione. A solution of 200 g. (2.0 moles) of 2,4-pentanedione (Eastman White Label; redistilled, b.p. 131–133°) in 800 ml. of methanol was treated with 368 g. (2.6 moles) of methyl iodide and then with a solution of 80 g. (2.0 moles) of sodium hydroxide in 400 ml. of water. The mixture was stirred with ice bath cooling to hold the temperature below 40°. When no longer exothermic, the mixture was allowed to stand at room temperature for 16 hr. Another 300 g. (2.1 moles) of methyl iodide was added followed by 80 g. of sodium hydroxide in 400 ml. of water. Cooling was again needed to hold the temperature below 40°.

After 16 hr. longer at room temperature, the bulk of the methanol was removed by vacuum distillation. The concentrate was diluted with two volumes of water and extracted with five 200-ml. portions of chloroform. The combined chloroform extract was washed, dried, and distilled to give 61 g. (24% yield) of 3,3-dimethyl-2,4-pentanedione, b.p.

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(13) P. A. Plattner, R. Treadwell, and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

(14) C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

(15) Reference 11, p. 355.

(16) R. M. Manyik, F. C. Frostick, J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 5030 (1953).

(17) R. I. Reed and M. B. Thornley, *J. Chem. Soc.*, 3714 (1957).

(18) E. Hansche, *Ber.*, **88**, 1048 (1955).

(19) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

(20) L. Bouveault and R. Locquin, *Bull. Soc. Chim.*, [4] **3**, 451 (1908).

71-72°/20 mm., n_D^{25} 1.4287 (reported,[21] b.p. 172°; n_D^{25} 1.4330).

After washing with cupric sulfate to remove traces of 3-methyl-2,4-pentanedione,[21] the material was redistilled. It showed exactly the same boiling point and refractive index.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.4.

Oxidation of 3,3-dimethyl-2,4-pentanedione. The reaction was carried out using 100 ml. of *tert*-butyl alcohol, 25.6 g. (0.20 mole) of diketone, 28.5 g. (0.25 mole) of 29.9% hydrogen peroxide, and 0.10 g. of sulfuric acid. At the end of 1 hr. on the steam bath, 0.04 mole of peroxide remained and 475 ml. of oxygen had been evolved (corresponding to about 0.04 mole of peroxide).

After the addition of 0.2 g. of sodium acetate and a pinch of palladium on charcoal, distillation was carried out using a 0.7 × 50-cm. glass spiral-packed column to give 15.5 g. (76% yield) of pivalic acid, b.p. 67-70°/15 mm., m.p. 26-30° (reported,[22] b.p. 75-78°/20 mm., m.p. 35°).

A *p-phenylphenacyl ester* derivative showed m.p. and mixed m.p. 113-114°.

3-Methyl-2,4-pentanedione. A solution of 54 g. (1.0 mole) of sodium methylate in 500 ml. of absolute ethanol was stirred at 25-30° as 100 g. (1.0 mole) of 2,4-pentanedione was added portionwise with cooling. The addition of 154 g. (1.1 moles) of methyl iodide initiated a mildly exothermic reaction. Slight cooling was used to hold the temperature at 50-55°. When no longer exothermic, the mixture was held at the same temperature for 0.5 hr. and finally at reflux for 0.5 hr.

After concentration of the water pump using a bath temperature of 40°, the residue was dissolved in 300 ml. of water and extracted with four 150-ml. portions of chloroform. The combined chloroform was washed, dried, and concentrated on the steam bath. Distillation through a 10-tray Oldershaw column afforded 70 g. (62% yield) of 3-methyl-2,4-pentanedione, b.p. 68-70°/20 mm., n_D^{25} 1.4428 (lit., b.p. 86°/60 mm., n_D^{20} 1.4455[23]; b.p. 170°, n_D^{24} 1.4515[24]).

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.3; H, 8.8.

Oxidation of 3-methyl-2,4-pentanedione. A solution of 45.6 g. (0.40 mole) of diketone, 0.60 mole of 30% hydrogen peroxide, and 1 ml. of sulfuric acid in 200 ml. of *tert*-butyl alcohol was allowed to reflux for about 3 hr. Gas evolution amounted to 2.2 l., and 0.02 mole of hydrogen peroxide remained.

Distillation through a 10-tray Oldershaw column was carried out at 50 mm. until a head temperature of 37° was reached. Bottoms from this operation were poured into 200 ml. of chloroform and extracted with a solution of 20 g. of potassium carbonate in 100 ml. of water. This solution, after springing with sulfuric acid and extraction with chloroform, gave on distillation 2.4 g. of material, b.p. 55-59°/10 mm., n_D^{25} 1.3954.

Anal. Calcd. for $C_5H_{10}O_2$: Neut. equiv., 102. Found: Neut. equiv., 98.

The *p-phenylphenacyl ester* derivative, after three crystallizations from ethanol, had a constant m.p. of 108-109°. A mixture with the derivative from pivalic acid melted at 111-112°.[25]

Neutral material remaining in the chloroform after extraction with carbonate was isolated by distillation, b.p. 67-70°/20 mm., n_D^{25} 1.4361. It weighed 11.7 g. (26% recovery) and had an infrared absorption spectrum essentially identical with that of the starting diketone.

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[25] Pivalic acid was undoubtedly produced from 3,3-dimethyl-2,4-pentanedione impurity in the starting material.

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

Preparation of Organolithium Compounds by the Transmetalation Reaction. III. Allyllithium and Methallyllithium[1,2a]

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The transmetalation reaction occurring between phenyllithium and allyltriphenyltin (1:1 molar ratio) or phenyllithium and tetraallyltin (4:1 molar ratio) in ether produces allyllithium in good yield. A similar reaction between *n*-butyllithium and tetraallyltin (2:1 molar ratio) in pentane gives solid allyllithium, which is only sparingly soluble in pentane. The use of allyllithium in the preparation of a number of previously known allyl compounds, as well as of the new $[B(CH_2CH{=}CH_2)(C_6H_5)_3]^-$ ion, is described.

In Part I of this series[2b] we reported the preparation of vinyllithium by the exchange reaction between vinyltin compounds and phenyl- or *n*-butyllithium. We have extended this general method to the synthesis of allyllithium and methallyllithium by reaction of allyl- or methallyltin compounds with organolithium reagents.

The preparation of allyl derivatives of active metals presents special problems. If the synthesis of the allylic metallic reagent is based on the reaction of an allyl halide with an active metal, a coupling reaction between the allylmetal compound and the allylic halide is a serious complicating factor. Conditions have been defined which allow the preparation of allylmagnesium halides in good

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