435. *The Preparation of* cyclo*Pentenones from the Products of Stobbe Condensations with Aliphatic Ketones.*

By M. Elliott.

Condensation of alkyl methyl ketones with diethyl succinate in the presence of potassium *tert.*-butoxide or sodium hydride gave mixtures of 3-ethoxycarbonyl-4-methyl-alk-3-enoic (I) and -alk-4-enoic acids (II). The acid chlorides of these compounds, on treatment with stannic chloride, gave, respectively, ethyl 3-alkyl-2-methyl-4-oxo*cyclo*pent-2-enecarboxylates (VII) and branched-alkylidenesuccinic anhydrides (VI). Hydrobromic acid in aqueous acetic acid decarbethoxylated the *cyclo*pentenes and converted the anhydrides into paraconic acids; the last were decarboxylated to γ-lactone-acid mixtures which were cyclodehydrated to *cyclo*pent-2-enones. Some properties of the compounds synthesized, and analogous reactions with *cyclo*hexanone, are discussed.

2-Alkyl-3-methyl*cyclo*pent-2-enones (VIII) and the corresponding 4-alkoxycarbonyl compounds (VII) were required as intermediates in an investigation[1] of the relation between insecticidal activity and chemical structure in compounds related to the pyrethrins (for reviews of the chemistry of these insecticides, see Harper and Crombie[2]).

Such *cyclo*pentenones have been obtained (*a*) by the ring closure of 2 : 5-diketones in dilute aqueous alkali;[3] (*b*) by Dieckmann-type cyclizations of ethylenic diesters;[4] (*c*) by the

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[1] Elliott, Needham, and Potter, *Ann. Appl. Biol.*, 1950, **37**, 490.; Elliott, *Pyrethrum Post*, 1951, **2**, No. 3, p. 18; *J. Sci. Food Agric.*, 1954, **5**, 505.

[2] Harper, *Ann. Reports*, 1948, **45**, 152; Crombie, *Sci. J. Roy. Coll. Sci.*, 1953, **23**, 40.

[3] (*a*) Wilds, *J. Amer. Chem. Soc.*, 1942, **64**, 1421; (*b*) Hunsdiecker, *Ber.*, 1942, **75**, 455; (*c*) Harper, *J.*, 1946, 892; (*d*) Schechter, Green, and LaForge, *J. Amer. Chem. Soc.*, 1949, **71**, 1517, 3165; (*e*) Crombie and Harper, *J.*, 1950, 1152; (*f*) Crombie, Edgar, Harper, Lowe, and Thompson, *ibid.*, p. 3552; (*g*) Crombie, Harper, Stedman, and Thompson, *J.*, 1951, 2445; (*h*) Crombie, Harper, and Thompson, *ibid.*, p. 2906; (*i*) Crombie and Harper, *J.*, 1952, 869.

[4] Duden and Freydag, *Ber.*, 1903, **36**, 953; Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 245; Treff and Werner, *Ber.*, 1935, **68**, 640; Werner, *Fette u. Seifen*, 1938, **45**, 623.

action of a mixture of hot phosphoric and formic acids on allyl vinyl and divinyl ketones;[5] and (*d*) by cyclodehydration of γ-lactones.[6] The route investigated here is related to (*d*), but suitably substituted $\gamma\delta$-unsaturated acids (II) were synthesized and themselves subjected to direct or indirect cyclodehydration, instead of using the lactones derivable from these acids. The acids were made by Stobbe condensations with aliphatic ketones. Johnson and his co-workers[7] developed an analogous route with alicyclic and alicyclic-aromatic ketones.

Preparation of Half-esters.—Methyl pentyl and hexyl methyl ketone, on condensation with diethyl succinate in the presence of potassium *tert.*-butoxide or sodium hydride, gave 80—85% yields of mixtures of half-esters (I and II; R = Bu and C_5H_{11}, respectively). No lactones (IX; R′ = Et) or $\alpha\beta$-unsaturated esters (III) were found. The proportion of alkylidene (I) and alkenyl (II) compounds in the mixtures was estimated by comparing their intensities of ultraviolet-light absorption in the region 2150—2250 Å with that of *iso*propylidenesuccinic acid ($\lambda_{max.}$ 2210 Å, ε 9350, in EtOH); for diethyl *iso*propylidenesuccinate, a substituted acrylic ester, Overberger and Roberts[8] give $\lambda_{max.}$ 2195 Å, ε 9200 (in *cyclo*hexane) (cf. Braude[9] and others[10]). Since the alk-4-enoic acids (II) were relatively transparent to ultraviolet light, such determinations were sufficiently precise for interpretation of the results.

Acetone gave a half-ester which was mainly the *iso*propylidene compound (I; R = H). The proportion of Δ^4-acid (II) was greatest from heptan-2-one and fell with longer alkyl groups. Half-esters with the highest attainable proportions of Δ^4-acid (II) were required, but the varying reaction conditions tried made little difference to the relative proportions of the isomers (I) and (II) in the distilled half-esters.

In contrast, Stobbe[11] found with acetone that alteration in the ratio ketone : ester : sodium ethoxide could give a variation of from 55% of *iso*propylidenesuccinic acid to 47% of *iso*propenyl compound. Moreover, he deduced[12] that ketones with a methylene group flanking the carbonyl group (*e.g.*, alkyl methyl ketones) would give mixtures containing *diacids* (produced by hydrolysis of the intermediate half-esters) mainly derived from compounds of type (II) (see also Stobbe; Stobbe *et al.*; and Linstead and Mann[13]). Here, on the other hand, it was found that the *half-ester* mixtures contained much more nearly equal quantities of the two types of isomer.

Cyclization of the Half-esters.—Neither a refluxing solution of acetic acid and acetic anhydride containing a catalytic quantity of zinc chloride[14,7] nor distillation from phosphoric oxide[6] gave acceptable yields of *cyclo*pentenones from the half-esters. The best route was by the action of stannic chloride on the half-ester chlorides, prepared by the action of thionyl chloride in the presence of one molecular proportion of pyridine (cf. Cook and Lawrence[15] and others[16]) to avoid any risk of ring–chain tautomerism (cf. Chase and Hey[17]). Ethyl 4-oxo*cyclo*pentenecarboxylates (VII) were formed from the half-ester chlorides (V), and branched-alkylidenesuccinic anhydrides (VI) from the isomers (IV), after two hours at 0°, but longer periods did not reduce the yields. No precautions to

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[5] Many papers by Nazarov *et al.*; Hennion and Davis, *J. Org. Chem.*, 1951, **16**, 1289; Braude and Coles, *J.*, 1952, 1430; Braude and Forbes, *J.*, 1953, 2202; Islam and Raphael, *ibid.*, p. 2247.

[6] (*a*) Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 1474; LaForge and Barthel, *J. Org. Chem.*, 1945, **10**, 222; Frank, Armstrong, Kwiatek, and Price, *J. Amer. Chem. Soc.*, 1948, **70**, 1379; Bowles, U.S.P. 2,623,071; Rai and Dev, *Experientia*, 1955, **11**, 114; (*b*) Frank, Arvan, Richter, and Vanneman, *J. Amer. Chem. Soc.*, 1944, **66**, 4.

[7] Johnson and Daub, "Organic Reactions," John Wiley and Sons, Inc., New York, 1951, Vol. VI, p. 31.

[8] Overberger and Roberts, *J. Amer. Chem. Soc.*, 1949, **71**, 3618.

[9] Braude, *Ann. Reports*, 1945, **42**, 111.

[10] *E.g.*, Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564; Adams and Van Duuren, *ibid.*, 1953, **75**, 4631.

[11] Stobbe, *Ber.*, 1893, **26**, 2312.

[12] *Idem, Annalen*, 1902, **321**, 83.

[13] *Idem, ibid.*, 1894, **282**, 280; Stobbe, Strigel, and Meyer, *ibid.*, 1902, **321**, 105; Linstead and Mann, *J.*, 1930, 2064.

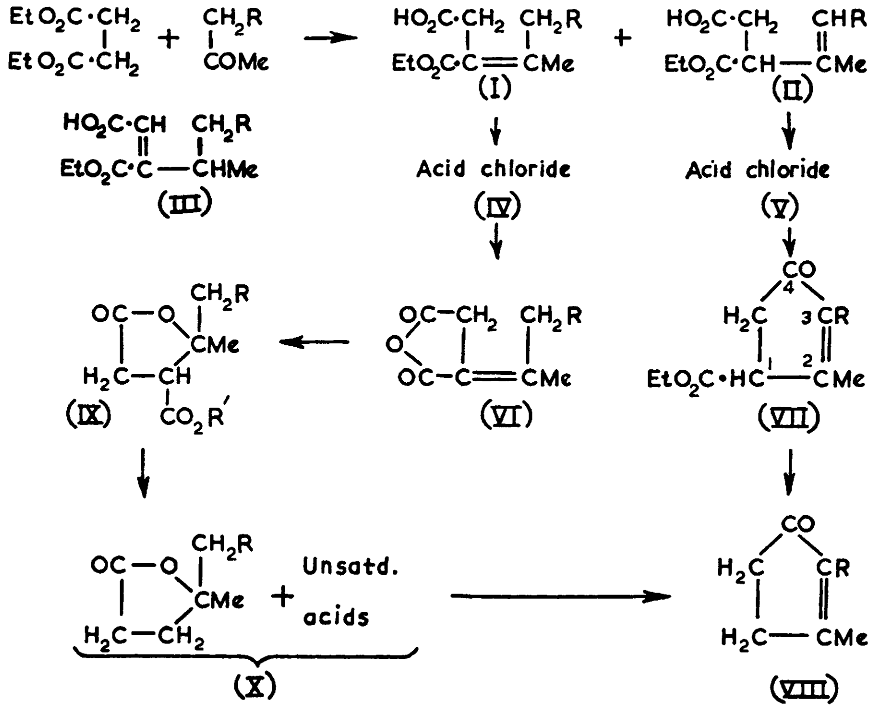
[14] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1028; Newman, *ibid.*, 1938, **60**, 1141.

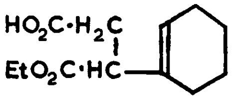
[15] Cook and Lawrence, *J.*, 1935, 1637.

[16] *E.g.*, Gerrard and Thrush, *J.*, 1953, 2117.

[17] Chase and Hey, *J.*, 1952, 553.

remove remnants of thionyl chloride, pyridine, etc., were necessary (cf. Johnson [18]). Both products (VI and VII) had maxima at 2350 Å (ε 10,000—12,000). *iso*Propylidenesuccinic anhydride (VI; R = H) showed $\lambda_{max.}$ 2350 Å (ε 12,000), although the acid had $\lambda_{max.}$ 2210 Å, and it was assumed that other anhydrides (VI; R = alkyl) would absorb similarly. One geometrical isomer of α-(1-methylheptylidene)succinic anhydride (VI; $R = C_5H_{11}$) was obtained crystalline and had the expected maximum at 2350 Å.

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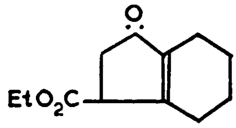
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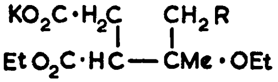
(XI)

The cyclized products gave 2 : 4-dinitrophenylhydrazones of the cyclic ketones (VII) in the yields to be expected from the relative proportions of the acids (I) and (II) if no interconversion of isomers took place on preparation and cyclization of the acid chlorides. It was desirable to prove that the higher-boiling fractions were alkylidenesuccinic anhydrides (VI) and not oxo*cyclo*pentene-acids which should also show maximum absorption at 2350 Å and produce 2 : 4-dinitrophenylhydrazones of the ethyl 4-oxo*cyclo*pentenecarboxylates on treatment with Brady's ethanolic reagent. The intense absorption at 2350 Å of the higher-boiling (anhydride) fractions and of *iso*propylidenesuccinic anhydride disappeared in the presence of alcoholic potassium hydroxide, whereas the spectra of the lower-boiling esters (VII) were substantially unchanged (but see below). It was assumed that half-ester potassium salts (XI; and/or isomers) were formed from the anhydrides in ethanolic potassium hydroxide, since Coulson and Kon [19] showed that the elements of ethyl alcohol were rapidly added to ethyl itaconate in sodium ethoxide solution.

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[18] Johnson, " The Formation of Cyclic Ketones by Intramolecular Acylation," " Organic Reactions," John Wiley and Sons, Inc., 1944, Vol. II, p. 130.

[19] Coulson and Kon, *J.*, 1932, 2568.

Cyclization of unsaturated acid chlorides by Friedel–Crafts-type reagents has been widely used since its introduction by Cook and Lawrence.[15] There are, however, few examples recorded of the preparation of monocyclic *cyclo*pentenones in this way (see Craig and Witt [20]; cf. Dahn [21]). Hydrogen chloride was either spontaneously eliminated in the reaction or else was split out under the mild conditions of isolation from the reaction mixture, whereas refluxing with a reagent such as dimethylaniline has frequently been carried out to produce the αβ-unsaturated ketone from the intermediate β-chloro-ketones (cf. Cook and Lawrence [15]). The anhydrides were also primary reaction products, since the mixture produced was almost completely insoluble in sodium hydrogen carbonate solution *before* distillation. Treatment of the half-esters themselves with stannic chloride in benzene gave only lactones, presumably (IX; R′ = Et), and no ketones; concentrated sulphuric acid at 0° merely lactonized the half-esters, and at higher temperatures considerable charring, with evolution of sulphur dioxide, took place.

Preparation of cyclo*Pentenones.*—When 2-alkyl-3-methyl*cyclo*pent-2-enones were required, the cyclization products were refluxed with a mixture of glacial acetic acid, constant-boiling hydrobromic acid, and water (3 : 2 : 1 by vol.) (cf. Johnson *et al.*[22]). The yield of dihydrocinerone (VIII; R = Bu) from heptan-2-one was 40% overall and of tetrahydropyrethrone (VIII; R = C_5H_{11}) 34% overall; these yields compare favourably with those obtained by other methods cited above. The slightly lower yield of *cyclo*pentenone from the half-esters derived from octan-2-one was related to the higher proportion of αβ-unsaturated ester (I; R = C_5H_{11}). The 2-octyl- and 2-decyl-*cyclo*pentenones (VIII) were similarly obtained in adequate yield from undecan-2-one and tridecan-2-one, respectively.

On treatment with the decarboxylation mixture, paraconic acids (IX; R′ = H) were produced from the alkylidenesuccinic anhydrides present. Fittig and his co-workers, and Fichter and Rudin,[23] showed that γγ-dialkylparaconic acids (IX; R′ = H) eliminate carbon dioxide when heated, producing mixtures of unsaturated acids and lactones. [Whereas the products of Stobbe condensations with arylalkyl ketones are decarboxylated by hot aqueous mineral acids,[24] the paraconic acid from *cyclo*hexanone [25] and compounds such as (IX; R′ = H) lose carbon dioxide only on pyrolysis.] The paraconic acids were decarboxylated in this way and the acid-lactone mixture (X) was cyclized by distillation from phosphoric oxide to *cyclo*pentenones (VIII) in yields as high as those obtained by using γ-lactones synthesized by Reformatski reactions with esters of lævulic acids.[6] In this way both isomeric half-esters were used to afford *cyclo*pentenones.

The preparation of paraconic acids directly from the half-ester mixtures was also examined, but difficulty in obtaining solid acidic material was experienced: a refluxing mixture of aqueous acetic and hydrobromic acid was the best reagent. This behaviour of the acids (I and II) was in marked contrast to the ease with which the paraconic acid was produced from the half-ester (XII) derived from *cyclo*hexanone; Johnson, Davis, Hunt, and Stork [26] showed that this acid was formed quantitatively when the ester was warmed at 100° for 15—30 min. with concentrated hydrochloric acid. The best specimens of paraconic acids were obtained from the alkylidenesuccinic anhydrides present in the mixture with *cyclo*pentene esters.

Experiments with cyclo*Hexanone and Acetone.*—With diethyl succinate and potassium *tert.*-butoxide [26] or sodium hydride, *cyclo*hexanone gave a half-ester that was exclusively the *cyclo*hexenyl (endocyclic) compound (XII) since it showed no intense absorption at 2100—2300 Å. The derived ester chloride gave a ketonic product on treatment with stannic chloride, 75% of which was tetrahydroindanone ester (XIII) and which furnished 4 : 5 : 6 : 7-tetrahydroindan-1-one in 50% yield (41% overall) on acidic decarboxylation

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[20] Craig and Witt, *J. Amer. Chem. Soc.*, 1950, **72**, 4925.
[21] Dahn, *Helv. Chim. Acta*, 1951, **34**, 1087.
[22] Johnson, Goldman, and Schneider, *J. Amer. Chem. Soc.*, 1945, **67**, 1357.
[23] Fittig, *Ber.*, 1887, **20**, 3179; Fittig *et al.*, *Annalen*, 1889, **255**, 1, 275; Fichter and Rudin, *Ber.*, 1904, **37**, 1610, 1615.
[24] Johnson and Heinz, *J. Amer. Chem. Soc.*, 1949, **71**, 2913.
[25] Johnson and Hunt, *ibid.*, 1950, **72**, 935.
[26] Johnson, Davis, Hunt, and Stork, *ibid.*, 1948, **70**, 3021.

(previous methods had given only a small yield of indanone[26]). Dehydrochlorination with collidine[27] after cyclization was not necessary.

Ethyl 4-oxo-2-methyl*cyclo*pent-2-enecarboxylate,[28] the five-membered ring analogue of Hagemann's *cyclo*hexene ester,[29] could not be obtained by the action of stannic chloride on the acid chloride of the half-ester from acetone: only *iso*propylidenesuccinic anhydride (VI; R = H) was isolated. This was expected since the ultraviolet absorption indicated that the half-ester contained 84% of the *iso*alkylidene compound (I; R = H).

*Ethyl 4-Oxo*cyclo*pentenecarboxylates: Properties and Derivatives.*—These compounds were isolated from mixtures with alkylidenesuccinic anhydrides by extraction of ethereal solutions with 5% aqueous sodium hydroxide. They were identified as semicarbazones, or, preferably, as 2 : 4-dinitrophenylhydrazones and were degraded by acid or alkali to *cyclo*pent-2-enones. They showed the expected maxima at 2350 Å (cf. Hagemann's ester,[28] $\lambda_{max.}$ 2300 Å, ε 12,150); the ethoxycarbonyl group therefore does not affect the position of maximum absorption of the αβ-unsaturated ketonic chromophore, whereas the maxima of 4-acyloxy-2-alkyl- and 4-acyloxy-2-alkenyl-3-methyl*cyclo*pent-2-enones at 2275 Å are *ca.* 75 Å nearer the vacuum-ultraviolet than those of the parent ketones.[3f] Both absorption bands of the 2 : 4-dinitrophenylhydrazones of the ketones (VII) and of those of the parent ketones (VIII) were at identical wavelengths. However, the main band of this derivative of the indanone ester (XIII) was at 3880 Å (in $CHCl_3$), whereas that of the parent ketone was at 3930 Å. Mathieson[27] reported a similar displacement and suggested that the 2 : 4-dinitrophenylhydrazone was derived, not from (XIII), but from the isomer containing the double bond adjacent to the ester group. Since the semicarbazone was derived from (XIII) (it showed a maximum at 2675 Å) and the 2 : 4-dinitrophenylhydrazone was orange-coloured, this relatively small hypsochromic effect is unlikely to be caused by the different position of the double bond. Mathieson's infrared evidence on this point must, strictly, be related only to the parent ketones on which it was obtained. In ethanol, the intensity at 2200 Å was not much greater for the 2 : 4-dinitrophenylhydrazone of (XIII) than for that of tetrahydroindanone; an αβ-unsaturated ester chromophore would have been expected to increase the intensity ε in this region by 5000—10,000. The sharp melting point of the derivative made the presence of a mixture of isomers unlikely.

The ethyl 3-alkyl-2-methyl-4-oxo*cyclo*pent-2-enecarboxylates did not react with lead tetra-acetate under conditions in which an acetoxy-group was introduced when the ester group was adjacent to the carbonyl group.[30]

The amides ($\lambda_{max.}$ 2370 Å) corresponding to the esters (VII) were obtained by the action of anhydrous ammonia in ethylene glycol (cf. Gordon, Miller, and Day[31]) on the mixture of anhydride (VI) and ester (VII). Anhydrous methanolic ammonia, alone and in the presence of sodium methoxide,[32] aniline, or other primary and secondary amines merely cleaved the anhydrides and did not react with the ester groups of the ketones (VII).

Ethyl 4 : 5 : 6 : 7-tetrahydro-3-oxoindane-1-carboxylate (XIII) [$\lambda_{max.}$ 2370 Å (ε 8600), neutral] was at least partly isomerized to the αβ-unsaturated ester ($\Delta^{1:9}$) [$\lambda_{max.}$ 2230 Å (ε 5720)] during three days in alcoholic potassium hydroxide. The keto-ester (XIII) itself was insoluble in sodium hydrogen carbonate, but had an equivalent of 544 on titration with alcoholic alkali; it was partly extracted from ether by 5% aqueous sodium hydroxide. These results are consistent with migration of the double bond and salt formation under the influence of alkali, and the lower extinction coefficient at 2370 Å indicated that the ester (XIII) itself may have contained some of its isomer. Mathieson[27] gives infrared evidence which supports this. Analogously, on treatment with potassium hydroxide in ethanol for 20 hours, the butyl derivative (VII; R = Bu) (neutral, ε 11,750 at 2350 Å) showed $\lambda_{max.}$ 2350 Å (ε 8170) and an inflexion at 2230 Å (ε 7570), due to the presence of some αβ-ethylenic ester.

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[27] Mathieson, *J.*, 1953, 3251.
[28] Acheson and Robinson, *J.*, 1952, 1127.
[29] Hagemann, *Ber.*, 1893, **26**, 876.
[30] LaForge and Soloway, *J. Amer. Chem. Soc.*, 1947, **69**, 2932.
[31] Gordon, Miller, and Day, *ibid.*, 1949, **71**, 1245.
[32] Russell, *ibid.*, 1950, **72**, 1853; Baltzly, Berger, and Rothstein, *ibid.*, p. 4149.

When the keto-esters and the derived amides were refluxed with aqueous alkali, the main products were alkali-soluble compounds that evolved carbon dioxide on being heated, to give the *cyclo*pent-2-enones. These acidic compounds were probably 3-alkyl-2-methyl-4-oxo*cyclo*pent-1-enecarboxylic acids; as αβ-unsaturated acids, they would be expected to be stable to heat and to lose carbon dioxide only on isomerization to βγ-ethylenic compounds, that, here, were the *cyclo*pent-2-enones (cf. Arnold, Elmer, and Dodson [33]).

Alkylation of the related Hagemann's ester probably proceeds *via* the salt of ethyl 2-methyl-4-oxo*cyclo*hex-1-enecarboxylate.[34, 35b] Its 3-alkyl derivatives [35] are six-membered ring analogues of the keto-esters (VII). The yellow colours of the 5% aqueous sodium hydroxide extracts of ethereal solutions of mixtures of the anhydride (VI) and ester (VII) were attributed to traces of the sodium salts of the isomeric esters; they were not produced during the hydrolysis of the anhydrides (VI), since none was obtained [36] from dimethylitaconic anhydride (VI; R = H) or from the γ-hexyl analogue (VI; R = C_5H_{11}) isolated in this work.

EXPERIMENTAL

M. p.s were determined on a Kofler block. Ultraviolet measurements (in EtOH, unless stated otherwise) were made on a Unicam SP 500 Quartz Photoelectric Spectrophotometer in 1 mm. silica cells. It is recognized [37] that at 2000—2300 Å scattered light is particularly likely to affect the values of $\lambda_{max.}$ and ε and may even produce spurious maxima; spectroscopic data quoted here are therefore considered of quantitative use only when compared with other determinations in the same solvent, under identical conditions with the same instrument.

Condensation of Ketones with Diethyl Succinate.—(a) *With potassium* tert.*-butoxide in* tert.*-butanol.* Potassium (4·73 g., 0·12 g.-atom) was added to *tert.*-butanol (120 ml.; dried over CaH_2) with stirring. When the metal had been melted by warming, it was powdered by rapid stirring and was dissolved during 30—60 min. by cautious heating. To this solution a mixture of octan-2-one (redistilled, b. p. 169—170°, n_D^{18} 1·4162; 14·10 g., 0·11 mol.) and diethyl succinate (n_D^{18} 1·4207; 30·2 g., 0·17 mol.) was transferred with *tert.*-butanol (10 ml.). After refluxing vigorously for 10 min., the solution was cooled to 0° and most of the alcohol was removed at reduced pressure. The residue was diluted with water, and ethyl succinoylsuccinate and starting materials were removed by extraction with ether. After acidification with hydrochloric acid, the liberated half-ester was taken up in ether and washed with water. Benzene was added and the solvents were removed at reduced pressure at 100° from the half-ester, which was thus dried azeotropically. The half-ester was diluted with benzene to 250 ml. in preparation for cyclization; distillation of 20 ml. of this solution gave a mixture of 3-ethoxycarbonyl-4-methyldec-3- and -4-enoic acid (1·806 g., 80%), b. p. 166—170°/2 mm., n_D^{20} 1·4616, $\lambda_{max.}$ 2220 Å (ε 4660) [Calc. proportion of (I; R = C_5H_{11}), 50%] (Found: equiv., 252·8. Calc. for $C_{14}H_{24}O_4$: 256·3). A similar preparation gave a fraction, b. p. 143—145°/1 mm., n_D^{18} 1·4644 (Found: C, 65·4; H, 9·5. Calc. for $C_{14}H_{24}O_4$: C, 65·6; H, 9·4%).

Extracting the ethereal washings of the condensation product before acidification with 5% sodium hydroxide solution, then drying and distilling the organic layer, led to recovery of diethyl succinate (7·8 g.). Acidification of the alkaline washings and extraction with ether gave ethyl succinoylsuccinate (0·9 g.; needles, m. p. 125·5—127°, from ethanol; blue fluorescence in solution; intense red colour with ferric chloride).

When the condensation product was isolated by addition of acid and removal of the alcohol, subsequent extraction of the half-ester with sodium hydrogen carbonate sometimes gave a lower-boiling fraction, b. p. 118—126°/0·05 mm., n_D^{20} 1·4323 (Found: C, 46·8; H, 7·6. Calc. for ethyl hydrogen succinate, n_D^{20} 1·4327, $C_6H_{10}O_4$: C, 46·2; H, 6·7%).

After a reaction period of 2 hr., the yield of crude half-esters from octan-2-one was 78%, and

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[33] Arnold, Elmer, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4359.

[34] Dieckmann, *Ber.*, 1912, **45**, 2697.

[35] (*a*) Bergmann and Weizmann, *J. Org. Chem.*, 1939, **4**, 266; Schwenk and Bloch, *J. Amer. Chem. Soc.*, 1942, **64**, 3050; Smith and Rauoult, *ibid.*, 1943, **65**, 631; Miescher and Wieland, *Helv. Chim. Acta*, 1950, **33**, 1847, 2215; Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1951, **73**, 3544; (*b*) Hogg, *ibid.*, 1948, **70**, 161.

[36] Stobbe, *Ber.*, 1908, **41**, 3720.

[37] Photoelectric Spectrometry Group Bulletin, No. 3, Oct., 1950; Bladon, Henbest, and Wood, *J.*, 1952, 2737; Eglington, Jones, and Whiting, *ibid.*, p. 2873; Bayliss and Brackenbridge, *Chem. and Ind.*, 1955, 477; Braude, Fawcett, and Timmons, *J.*, 1950, 1019.

after 4½ hours' refluxing and 16 hours at room temperature was 72%; with sodium ethoxide in boiling ethanol, only 7·8% of the required product was obtained after 10 min.

Similarly, heptan-2-one gave mixed 3-ethoxycarbonyl-4-methylnon-3- and -4-enoic acid (85%), b. p. 158—163°/2 mm., n_D^{20} 1·4589 (Found: C, 63·3; H, 9·1%; equiv., 230·5. Calc. for $C_{13}H_{22}O_4$: C, 64·4; H, 9·2%; equiv., 242·3), $\lambda_{max.}$ 2220 Å (ε 3790) [Calc. proportion of (I; R = Bu), 41%].

Tridecan-2-one, b. p. 136—140°/15 mm., gave mixed 3-ethoxycarbonyl-4-methylpentadec-3- and -4-enoic acid (74%), b. p. 189—190°/0·5 mm., n_D^{20} 1·4644 (used for cyclization without purification), $\lambda_{max.}$ 2250 Å (ε 5606) [Calc. proportion of (I; R = decyl), 60%].

*cyclo*Hexanone gave β-ethoxycarbonyl-β-*cyclo*hex-1′-enylpropionic acid, b. p. 140—143°/0·1 mm., n_D^{16} 1·4820 (Found: C, 63·7; H, 8·3%; equiv., 221·2. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 8·0%; equiv., 226·3), by the procedure of Johnson, Davis, Hunt, and Stork.[26] No max. in region 2070—3000 Å (ε_{2230}, 1140) and no difficulty in obtaining satisfactory analytical figures, as experienced by Mathieson,[27] was encountered.

Acetone gave a mixture of 3-ethoxycarbonyl-4-methylpent-3- and -4-enoic acid, b. p. 120—130°/2 mm., n_D^{15} 1·4693, which crystallized on cooling and scratching to give solid, m. p. 37—40° (soften 30°) [from light petroleum (b. p. 40—60°)] (Found: C, 57·9; H, 7·7. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·6%), $\lambda_{max.}$ 2220 Å (ε 7860) [Calc. proportion of (I; R = H), 84%]. Hydrolysis with aqueous sodium hydroxide gave *iso*propylidenesuccinic acid, m. p. 162—163° (from water); Stobbe[11] gives m. p. 161—162°. By distillation, or by the action of acetyl chloride, the anhydride, m. p. 42—43° (from carbon disulphide), was produced (lit.,[38] m. p. 44°) (Found: C, 60·7; H, 7·3. Calc. for $C_7H_8O_3$: C, 60·0; H, 7·3%).

(b) *With potassium* tert.*-butoxide in ether.* Potassium (20·6 g., 0·53 g.-atom) was dissolved in *tert.*-butanol; excess of solvent was removed by heating the mixture *in vacuo* and then adding, and distilling off, successive portions of benzene at reduced pressure. Heptan-2-one (29·3 g., 0·256 mol.) and diethyl succinate (67·0 g., 0·385 mol.) were added dropwise during 1 hr. to a suspension of the salt in dry ether (500 ml.) at 0°. After 41 hr. at room temperature, hydrochloric acid (50 ml.) in water (200 ml.) was added and the half-esters were extracted with saturated aqueous sodium hydrogen carbonate (13 × 100 ml.), liberated by acid, taken up in benzene, and dried azeotropically by removal of the solvent. They were then diluted to 250 ml. in preparation for cyclization. Distillation of 10 ml. of this solution at 0·3 mm. gave 1·948 g. (79%) of the half-esters (I and II; R = Bu), b. p. mainly 140—141°, n_D^{17} 1·4629, $\lambda_{max.}$ 2190 Å (ε 3690) [Calc. proportion of (I; R = Bu), 39%]. A portion redistilled for analysis had b. p. 145—147°/0·4 mm., n_D^{19} 1·4606 (Found: C, 64·3; H, 9·2%).

Similarly, octan-2-one gave 89% of a mixture of (I and II; R = C_5H_{11}), b. p. 142—148°/0·5 mm., n_D^{24} 1·4592, ($\lambda_{max.}$ 2220 Å) (ε 5190) [Calc. proportion of (I), 56%].

(c) *With sodium hydride.* To a stirred suspension of sodium hydride (8·0 g., 0·3 mol.) in benzene (200 ml.) was added a small quantity of a mixture of heptan-2-one (19·0 g., 0·167 mol.) and diethyl succinate (81·7 g., 0·5 mol.) and then a few drops of ethanol. When reaction had started, the rest of the ketone and ester was added at such a rate that the reaction did not become too vigorous. After 1½ hr. the evolution of hydrogen was very slow and the mixture was poured cautiously on ice and shaken. The benzene layer was separated and washed with water. All the aqueous phases were washed with ether and acidified; the liberated half-esters were taken up in benzene and dried azeotropically. The half-esters were diluted to 250 ml. with dry benzene in preparation for cyclization; distillation of 20 ml. of this solution gave 2·47 g. of a mixture of (I and II; R = Bu), b. p. 158—163°/0·5 mm., n_D^{20} 1·4589 (yield, 77%) (Found: C, 63·3; H, 9·1%).

Similarly, octan-2-one gave the acids (I and II; R = C_5H_{11}), b. p. 160°/0·5 mm., n_D^{18} 1·4690, in 86% yield.

Undecan-2-one (17·0 g., 0·1 mol.), diethyl succinate (52·3 g., 0·3 mol.), and sodium hydride (4·8 g., 0·2 mol.) gave 73% of a mixture of 3-ethoxycarbonyl-4-methyltridec-3- and -4-enoic acid, b. p. 176—178°/1·0 mm., n_D^{20} 1·4601, $\lambda_{max.}$ 2210 Å (ε 3813) [Calc. proportion of (I; R = octyl), 41%]. The crude ester was cyclized without purification.

From an attempted condensation of acetone with diethyl succinate in the presence of sodium hydride, only ethyl succinoylsuccinate was isolated.

Preparation of cyclo*Pentenones.*—The procedures described above furnished the benzene solutions of the half-esters which were cyclized as follows. The concentrations of the solutions were determined by distillation of small aliquot parts.

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[38] Fittig and Kfaft, *Annalen*, 1899, **304**, 195.

(a) 3-*Methyl*-2-*pentyl*cyclo*pent*-2-*enone*. The half-ester (13·3 g., from condensation of octan-2-one in the presence of potassium *tert.*-butoxide in ether) in benzene (100 ml.) was treated with pyridine (4·16 ml.) and then redistilled thionyl chloride (3·74 ml.) at 0° for 30 min. The benzene solution of the acid chloride was decanted from the solid cake, which was then pulverized and washed by decantation with benzene. The acid chloride solution and washings were treated with stannic chloride (6·1 ml.) for 15 hr. at 0°; the benzene solution was then poured on ice and concentrated hydrochloric acid (30 ml.) and shaken: the colour lightened from dark red to pale brown. The benzene layer was separated and the aqueous phase washed with ether. The combined ether and benzene phases were washed with saturated sodium hydrogen carbonate. (Fine solids sometimes made separation of the phases difficult; if necessary, they were removed by filtration.) The washings were extracted with ether, and the combined organic layers evaporated. The crude mixture of (V and VI; $R = C_5H_{11}$) was refluxed with glacial acetic acid (100 ml.), constant-boiling hydrobromic acid (66 ml.), and water (33 ml.) for 1 hr., during which carbon dioxide was evolved. The acidic mixture was cooled and poured carefully on sodium carbonate decahydrate (300 g.) in sufficient water to form a slurry. The ketone was extracted with ether after saturation of the aqueous layer with salt. After drying (Na_2SO_4) and evaporation of the solvent, distillation gave 3-methyl-2-pentyl-*cyclo*pent-2-enone (3·28 g.; overall yield, based on octan-2-one, 35%), b. p. 120—126°/16 mm., n_D^{21} 1·4767. Acidification of the sodium hydrogen carbonate washings gave 4·78 g. (37%, based on octan-2-one) of crude *paraconic acid* (IX; $R = C_5H_{11}$, $R' = H$), m. p. 137—141° (from aqueous ethanol) [Found: equiv. (*a*) cold, 225·2, (*b*) by addition of excess of alkali, heating at 100° for 1 hr., and back-titration, 115·3; C, 63·3; H, 9·0%. $C_{12}H_{20}O_4$ requires equiv., (*a*) 228, (*b*) 114; C, 63·1; H, 8·8%]. As shown below, the paraconic acid was pyrolysed to an acid–lactone mixture that was cyclized to the *cyclo*pentenone in an overall yield of 31%. Hence total yield of ketone was 66%. The *cyclo*pentenone was characterized as its semicarbazone, m. p. 176·5—177°, and 2 : 4-dinitrophenylhydrazone, m. p. 122°, both m. p.s being undepressed on admixture with authentic samples (cf. Crombie *et al.*[3f]).

(b) 2-Butyl-3-methyl*cyclo*pent-2-enone was obtained similarly in overall yield of 40% (without allowance for ketone from paraconic acid), b. p. 110—112°/15 mm., n_D^{20} 1·4799 [semicarbazone, m. p. 188·5—189°; 2 : 4-dinitrophenylhydrazone, m. p. 155—155·5°; m. p.s undepressed on admixture with authentic specimens (cf. Harper [3c])].

(c) 3-Methyl-2-octyl*cyclo*pent-2-enone (obtained in overall yield of 31% from undecan-2-one) had b. p. 150—160°/12 mm. and gave a semicarbazone, m. p. 158—159° (slight softening at 155°) (from ethyl acetate) (Hunsdiecker [3b] gives 159°) (Found: C, 68·4; H, 10·1; N, 16·5. Calc. for $C_{15}H_{27}ON_3$: C, 67·9; H, 10·3; N, 15·8%), and a 2 : 4-*dinitrophenylhydrazone*, m. p. 103—104° (from ethanol) (Found: C, 61·9; H, 7·0; N, 14·5. $C_{20}H_{28}O_4N_4$ requires C, 61·8; H, 7·3; N, 14·4%). The pure ketone regenerated from the semicarbazone with oxalic acid had b. p. 122—124°/1 mm., n_D^{20} 1·4782, $\lambda_{max.}$ 2350 Å (ε 13,900) (Found: C, 80·7; H, 11·4. Calc. for $C_{14}H_{24}O$: C, 80·7; H, 11·6%).

The paraconic acid obtained with the above ketone after decarboxylation of the cyclized half-esters was not completely extracted with sodium hydrogen carbonate from the ether solution of *cyclo*pentenone and paraconic acid. It was isolated as a small fraction, b. p. 190—220°/12 mm., on distillation of the *cyclo*pentenone, in addition to material obtained by acidification of the sodium hydrogen carbonate extracts.

(d) 2-Decyl-3-methyl*cyclo*pent-2-enone, obtained in 26% yield from tridecan-2-one, boiled mainly at 131—142°/0·09 mm. The paraconic acid (IX; R = decyl, $R' = H$) was not extracted from ether by saturated aqueous sodium hydrogen carbonate and was obtained as a high-boiling fraction, b. p. 180—190°/0·09 mm., on distillation of the ketone. An additional 18% of ketone was obtained from the paraconic acid (total yield of *cyclo*pentenone, 44%; all yields calc. on tridecan-2-one). Its *semicarbazone* (from ethanol) had m. p. 152—153°, softening at 120° (Found: C, 70·0; H, 10·8; N, 14·5. $C_{17}H_{31}ON_3$ requires C, 69·6; H, 10·7; N, 14·4%), and its 2 : 4-*dinitrophenylhydrazone*, orange-red crystals (from ethanol), had m. p. 100°, softening at 90° (Found: C, 62·9; H, 7·6; N, 13·6. $C_{22}H_{32}O_4N_4$ requires C, 63·4; H, 7·7; N, 13·5%). The pure ketone regenerated from the semicarbazone had b. p. 124—126°/0·5 mm., n_D^{21} 1·4770, $\lambda_{max.}$ 2350 Å (ε 13,900) (Found: C, 81·8; H, 12·0. $C_{16}H_{28}O$ requires C, 81·3; H, 11·9%).

(e) 4 : 5 : 6 : 7-*Tetrahydroindan*-1-*one*. The acid chloride of the half-ester from *cyclo*hexanone was treated with stannic chloride, by the usual procedure, but with reaction for only 75 min. at room temperature. The product was decarboxylated to 4 : 5 : 6 : 7-tetrahydroindan-1-one, b. p. 114—116°/10 mm., n_D^{16} 1·5199 (yield, 41% based on *cyclo*hexanone). Only a very small quantity of solid paraconic acid (Found: equiv., 201. Calc. for $C_{10}H_{14}O_4$: equiv., 198·2) was isolated from the sodium hydrogen carbonate extract. The ketone was identified as the 2 : 4-dinitrophenylhydrazone, m. p. 232—233° (Frank and Pierle [39] give n_D^{20} 1·5200, and 2 : 4-dinitrophenylhydrazone, m. p. 228° (Found : C, 57·0; H, 5·1; N, 17·7. Calc. for $C_{15}H_{16}O_4N_4$: C, 57·3; H, 5·1; N, 17·2%).

Products of Cyclization of the Half-ester Chlorides with Stannic Chloride.—(a) *Heptan-2-one.* The mixed half-esters from heptan-2-one (I and II; R = C_5H_{11}) (31·9 g.) in benzene (240 ml.) were converted into the acid chlorides with pyridine (10·7 ml.) and thionyl chloride (8·7 ml.), as previously described. The acid chlorides were cyclized with stannic chloride (15·5 ml.) for 65 min. (*A*, 50%), for 24 hr. (*B*, 25%), and for 48 hr. (*C*, 25%). The proportions indicated were removed and worked up as described for the preparation of *cyclo*pentenones after the above reaction periods. No material soluble in sodium hydrogen carbonate was found. Next morning the once distilled product from *A* (b. p. 123—145°/1 mm., n_D^{21} 1·4759—1·4802) had darkened slightly and smelt of hydrogen chloride. It was washed, in ether, with sodium hydrogen carbonate and distilled again as one fraction [$\lambda_{\text{max.}}$ 2350 Å ($E^{1\%}_{1\,\text{cm.}}$ 505) or 2350 Å ($E^{1\%}_{1\,\text{cm.}}$ 295) in 0·15% alcoholic potassium hydroxide]. Distillation gave fractions (the data being b. p./0·12 mm.; wt.; n_D^{19}; equiv. by titration in ethanol with 0·0832N-potassium hydroxide; analyses for C and H) : (*a*) 105—108°; 1·98 g.; 1·4772; 1362; 69·4; 8·7; (*b*) 108—110°; 2·64 g.; 1·4781; 795; 68·5; 8·3; (*c*) 110—115°; 1·08 g.; 1·4791; 467; (*d*) 115—118°; 2·59 g.; 1·4819; 237; 67·9; 8·4; (*e*) 118—120°; 2·10 g.; 1·4832; 199; (*f*) 120—125°; 0·83; 1·4823; 194; 67·4; 8·8 The fractions were mixtures of ethyl 3-butyl-2-methyl-4-oxo*cyclo*pent-2-enecarboxylate (Calc. for $C_{13}H_{20}O_3$: C, 69·6; H, 9·0%) and the two geometrical isomers of γ-methyl-γ-pentylitaconic anhydride (Calc. for $C_{11}H_{16}O_3$: C, 67·3; H, 8·2%). The *cyclo*pentenone was isolated by exhaustive extraction of the combined fractions (*a*—*f*, 9·8 g.) in ether, with aqueous sodium hydroxide. The colourless, neutral liquid obtained (4·34 g.) had b. p. 106—110°/0·5 mm., n_D^{19} 1·4758, $\lambda_{\text{max.}}$ 2350 (ε 11,750); and $\lambda_{\text{max.}}$ 2350 Å (ε 8170) [$\lambda_{\text{inf.}}$ 2200 Å (ε 7580)] after 20 hr. in alcoholic potassium hydroxide (Found : C, 70·0; H, 9·4%). Decarbethoxylation of this *cyclo*pentenone (2·43 g.) with boiling acetic acid (15 ml.), constant-boiling hydrobromic acid (10 ml.), and water (5 ml.) gave 1·44 g. (87%) of 2-butyl-3-methyl*cyclo*pent-2-enone, identical with the ketone described above.

Portions *B* and *C* gave fractions identical with those from *A*. $E^{1\%}_{1\,\text{cm.}}$ values at $\lambda_{\text{max.}}$ 2350 Å were determined for the following fractions from *B* in neutral (N) and alkaline (Alk) solution : (*a*) N, 484; Alk, 348; (*c*) N, 438; Alk, 304; (*e*) N, 432; Alk, no max. Decarboxylation of the *cyclo*pentenone–anhydride mixture (5·37 g.) from *B* in the usual way gave 1·44 g. of 2-butyl-3-methyl*cyclo*pent-2-enone, b. p. 108—112°/12 mm., corresponding to 40% of the keto-ester in the cyclized product. From *C* (5·89 g.) there was obtained the bright red *ethyl* 3-*butyl*-2-*methyl*-4-*oxo*cyclo*pent*-2-*enecarboxylate* 2 : 4-*dinitrophenylhydrazone* (3·25 g.), m. p. 82—83° (from ethanol) (Found : C, 55·6; H, 6·5; N, 13·9. $C_{19}H_{24}O_6N_4$ requires C, 56·4; H, 6·0; N, 13·9%). This yield indicated 30% of ketone in the mixture.

(b) *Octan-2-one.* Similarly, there was obtained from the half-esters (I and II; R = C_5H_{11}) derived from octan-2-one a mixture of *ethyl* 2-*methyl*-4-*oxo*-3-*pentyl*cyclo*pent*-2-*enecarboxylate* [b. p. 103—106°/0·03 mm., n_D^{20} 1·4745, $\lambda_{\text{max.}}$ 2350 Å (ε 10,950) (Found : C, 70·0; H, 9·2. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·4%)], and γ-hexyl-γ-methylitaconic anhydride (mixture of isomers) [b. p. 124—127°/0·02 mm., n_D^{20} 1·4859, $\lambda_{\text{max.}}$ 2350 Å (ε 11,940) (Found : C, 68·4; H, 8·9. Calc. for $C_{12}H_{18}O_3$: C, 68·5; H, 8·6%)]. The 2 : 4-*dinitrophenylhydrazone* of the keto-ester (prepared in ethanolic hydrogen chloride) had m. p. 98—99·5° (red needles) before recrystallization (Found : C, 57·3; H, 5·9; N, 13·6%). Recrystallization from ethanol gave orange needles, m. p. 122—123°, $\lambda_{\text{max.}}$ 2575, 3850 Å (ε 17,200, 28,360, respectively) (Found : C, 57·7; H, 6·3; N, 12·6. $C_{20}H_{26}O_6N_4$ requires C, 57·4; H, 6·2; N, 13·4%). [Tetrahydropyrethrone 2 : 4-dinitrophenylhydrazone, which contains the same chromophore, had $\lambda_{\text{max.}}$ 2575, 3850 Å (ε 19,600, 29,900, respectively)]. When the orange and the red form of the 2 : 4-dinitrophenylhydrazone were melted side by side, the red form melted at 95·5—98°, became orange and resolidified to melt at 120° with the orange crystals. Cooling, reheating to 100°, and cooling again produced a single mass of orange crystals only, m. p. 119·5—121·5°. The orange and the red crystals were therefore different forms of the same substance. The *semicarbazone* of the keto-ester separated after 3 days from alcohol–pyridine; it had m. p. 115—117° (Found : C, 60·5; H, 8·5; N, 14·1. $C_{15}H_{25}O_3N_3$ requires C, 61·0; H, 8·5; N, 14·2%), $\lambda_{\text{max.}}$ 2650 Å (ε 23,630); for other semicarbazones with the same chromophore, Crombie and Harper [3i] record $\lambda_{\text{max.}}$ 2650 Å (ε 20,000—25,700).

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[39] Frank and Pierle, *J. Amer. Chem. Soc.*, 1951, **73**, 724.

When the mixture of anhydrides was cooled, one isomer crystallized; this had m. p. 53·5° [from light petroleum (b. p. 40—60°)], $\lambda_{\text{max.}}$ 2350 Å (ε 12,640), no intense absorption in alcoholic potassium hydroxide (ε_{2350} 2545) (Found: C, 68·4; H, 8·8%). Acidification of the 5% aqueous sodium hydroxide extracts from an ethereal solution of an anhydride fraction, n_D^{18} 1·4851, gave a geometrical isomer, m. p. 119—123° (softening at 114°) (from benzene), $\lambda_{\text{max.}}$ 2250 Å (ε 8730) (Found: C, 63·1; H, 8·8%; equiv., 113·1. Calc. for γ-hexyl-γ-methylitaconic acid, $C_{12}H_{20}O_4$: C, 63·7; H, 8·6%; equiv., 114·1). The acid slowly decolourized bromine in carbon tetrachloride.

The same (m. p. and mixed m. p.) crystalline anhydride was obtained (*a*) by heating the mixture of acids obtained by alkaline hydrolysis of the half-esters (I and II; $R = C_5H_{11}$) to 250° and then distillation, and (*b*) by the action of acetyl chloride on this acid mixture. With ammonia in anhydrous methanol at 0° the anhydride gave *ammonium* 3-*carboxyamino*-4-*methyldec*-3-*enoate* (and/or isomers), m. p. 135·5° (softens at 115°), $\lambda_{\text{max.}}$ 2200 Å (ε 6950). (Found: C, 59·2; H, 9·4; N, 9·4. $C_{12}H_{24}O_3N_2$ requires C, 59·2; H, 9·9; N, 11·5%). When the anhydrides were mixed with aniline in a little methanol, heat was evolved and a solid separated. After being washed with benzene and dried (P_2O_5), it had m. p. 117° (softening at 90°), $\lambda_{\text{max.}}$ 2370 Å (ε 19,400) (Found: C, 71·2; H, 8·3; N, 4·6. $C_{18}H_{25}O_3N$ requires C, 71·3; H, 8·3; N, 4·6%); it was the *anilic acid* from γ-hexyl-γ-methylitaconic acid.

(c) cyclo*Hexanone*. The acid chloride, prepared in the usual way from the half-ester (11·47 g.), pyridine (4·1 ml.), and thionyl chloride (3·65 ml.), was cyclized for 75 min. at 20° with stannic chloride (6·0 ml.). Working up as usual gave a yellow liquid (8·60 g.), b. p. 116—140°/0·2 mm., n_D^{20} 1·5077 (Found: equiv., 544). *Ethyl* 4 : 5 : 6 : 7-*tetrahydro*-3-*oxoindane*-1-*carboxylate* (1·15 g., equivalent to 45% of the keto-ester in the cyclized material), b. p. 119—126°/0·2 mm., n_D^{15} 1·5042, was isolated from the neutral layer when the crude cyclized material (2·63 g.), in ether, was washed with 5% aqueous alkali (Found: C, 69·2; H, 8·2. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). This ester had $\lambda_{\text{max.}}$ 2370 Å (ε 8600), with a slight inflexion at 2190 Å ($\varepsilon_{\text{inf.}}$ 6370), and in alcoholic potassium hydroxide $\lambda_{\text{max.}}$ 2190 Å (ε 5720), with an inflexion at 2370 Å ($\varepsilon_{\text{inf.}}$ 2140) after 3 days at 20°. The 5% aqueous sodium hydroxide extracts were strongly acidified with hydrochloric acid and boiled for 1 hr. Addition of 2 : 4-dinitrophenylhydrazine precipitated the 2 : 4-dinitrophenyldrazone of tetrahydroindanone, identified by its m. p. and mixed m. p.

The once distilled cyclized material gave a 75% yield of the 2 : 4-dinitrophenylhydrazone of the keto-ester (prepared in ethanolic hydrogen chloride), m. p. 171—172° (orange needles from ethanol; Mathieson [27] gives m. p. 171—172°) (Found: C, 56·5; H, 5·2; N, 14·3. Calc. for $C_{18}H_{20}O_6N_4$: C, 55·6; H, 5·2; N, 14·9%), $\lambda_{\text{max.}}$ 2180, 2550, 3820 Å (ε 16,800, 18,600, 31,100 respectively), but 2600, 3880 Å (ε 17,500, 28,450, respectively) in $CHCl_3$. The 2 : 4-dinitrophenylhydrazone of 4 : 5 : 6 : 7-tetrahydroindan-1-one had $\lambda_{\text{max.}}$ 2210, 2550, 3875 Å (ε 12,900, 15,600, 24,000, respectively) but 2600, 3940 Å (ε 17,600, 27,400, respectively) in $CHCl_3$.

The semicarbazone of the keto-ester had m. p. 186—190° (needles from ethanol) (Found: C, 58·4; H, 7·1; N, 15·9. Calc. for $C_{13}H_{19}O_3N_3$: C, 58·8; H, 7·2; N, 15·8%), $\lambda_{\text{max.}}$ 2675 Å (ε 25,740) (Mathieson [27] gives m. p. 192—193° and $\lambda_{\text{max.}}$ 2670 Å, ε 25,500).

3-*Butyl*-2-*methyl*-4-*oxo*cyclo*pent*-2-*enecarboxyamide*.—A suspension of the once distilled, mixed cyclization products (VI and VII; R = Bu) from the half-esters derived from heptan-2-one (30·7 g), in redistilled ethylene glycol (100 ml.), was saturated with ammonia and set aside at 0° for 10 days. The *amide* (12·1 g.) was separated by filtration, washed with ether and water, and recrystallized from water as colourless needles, m. p. 133° (Found: C, 67·6; H, 8·6; N, 7·5. $C_{11}H_{17}O_2N$ requires C, 67·7; H, 8·8; N, 7·2%), $\lambda_{\text{max.}}$ 2385 Å (ε 10,900).

The amide (2·0 g.) was boiled with potassium hydroxide (4·0 g.) in water (40 ml.) for 8 hr. until there was no further evolution of ammonia; the yellow alkaline layer was saturated with salt and extracted with ether. The ethereal extracts, when washed with hydrochloric acid and water and dried, gave dihydrocinerone (VIII; R = Bu) (0·176 g.). The alkaline layer, on acidification, gave a yellow oil that was isolated with ether and on distillation gave more dihydrocinerone (1·072 g.), after evolution of gas had ceased. The total yield of ketone, identified as usual, was 80%.

2-*Methyl*-4-*oxo*-3-*pentyl*cyclo*pent*-2-*enecarboxyamide* was obtained similarly as colourless needles, m. p. 136·5° (from benzene), $\lambda_{\text{max.}}$ 2375 Å (ε 11,680) (Found: C, 68·4; H, 8·8; N, 6·7. $C_{12}H_{19}O_2N$ requires C, 68·8; H, 9·2; N, 6·7%).

Pyrolysis of Paraconic Acids.—γ-Hexyl-γ-methylparaconic acid (IX; $R = C_5H_{11}$, $R' = H$) (3·59 g.) was heated to 250—280° for 70 min. with a trace of potassium hydrogen sulphate. Distillation then gave a colourless mixture (81%) of γ-methyl-γ-decanolactone and related acids (partly soluble in aqueous sodium hydrogen carbonate) (2·31 g.), b. p. 103—107°/1·0 mm., n_D^{22} 1·4557 (Found: C, 70·8; H, 10·5. Calc. for $C_{11}H_{20}O_2$: C, 71·1; H, 10·9%). For γ-methyl-γ-decanolactone, Frank, Arvan, Richter, and Vanneman[6b] record b. p. 120—125°/4—5 mm., n_D^{20} 1·4487.

This mixture (1·49 g.) was heated slowly with phosphoric oxide (1·3 g., 1·1 mol.) until liquid (0·89 g.; b. p. 136—140°/25 mm., n_D^{19} 1·4779) had distilled. From this was obtained the 2:4-dinitrophenylhydrazone of tetrahydropyrethrone (VIII; R = C_5H_{11}) (1·11 g.; m. p. after recrystallization from EtOH, and mixed m. p., 122°), equivalent to an overall yield of ketone, based on paraconic acid, of 38%.

γ-Methyl-γ-undecylparaconic acid (IX; R = decyl, R′ = H) (5·64 g.) was heated with a trace of potassium hydrogen sulphate for 110 min. at 230—260°. Distillation of the residue gave a mixture of γ-methyl-γ-tetradecanolactone and related acids (4·91 g.; b. p. mainly 143—157°/0·09 mm.). Without further purification, this (3·34 g.) was heated slowly with phosphoric oxide (2·20 g.) until crude 2-decyl-3-methyl*cyclo*pent-2-enone (1·79 g; b. p. 140°/0·08 mm., n_D^{20} 1·4742) had distilled The ketone was purified *via* the semicarbazone described above; the yield was 1·21 g., and the m. p. and mixed m. p. were 152—153°.

Department of Insecticides and Fungicides, Rothamsted Experimental Station,
Harpenden, Herts.

[*Received, October* 17*th*, 1955.]