and cyclopentenyl cases are consistent with the postulation that in these compounds there is little energetic difference to the attainment of coplanarity (assumed to be desirable for most facile adsorption)[4] onto the catalytic surface between the corresponding 1 and 2 isomers. Steric hindrance to attainment of coplanarity in the 2 isomers should be less than in the 1 isomers for the cyclohexenyl and cycloheptenyl pairs, however. The slower rate of hydrogenation of VIII as compared to IV (runs 15 and 19) seems to be ascribable to steric hindrance effects only (either greater hindrance to the attainment of coplanarity in VIII or hindrance to adsorption due to the sidewise projecting methyl group in this compound, or both).[24]

Syntheses of Jasmone and the Related Compounds.
I. Preparation of Dihydrojasmone and the Homologs from γ,γ-Dialkylparaconic Acids[1]

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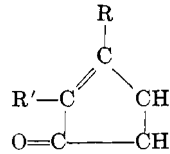
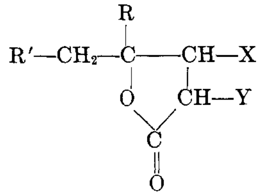
γ,γ-Dialkylparaconic acids (III) were synthesized by hydrolysis of γ,γ-dialkyl-α,β-dicarbethoxybutyrolactones (IV), or by means of lactonization of the Stobbe half-esters (IX). The butyrolactones (IV) were obtained by the condensation of ethyl β,β-dialkylglycidates (V) with sodiomalonate. Treatment of the paraconic acids (III) with polyphosphoric acid gave the corresponding 2,3-dialkyl-2-cyclopenten-1-ones (I), including dihydrojasmone. As by-products, unsaturated dibasic acids (VII) and acid anhydrides (VIII) were separated.

A new route to dihydrojasmone (I, R = CH_3 and R′ = C_5H_{11}) and its homologs from lactonic intermediates (III and IV) was studied. The cyclopentenones (I) previously have been obtained by dehydration of γ-butyrolactones (II),[2-8] but lactonic acids (III) or esters (IV), which can be prepared more readily than II, were found also to be converted into I in good yields. A number of cyclopentenones (I) were synthesized by this procedure.

The paraconic acids (III) were obtained in two ways. The first route involves the reaction of ethyl γ,γ-dialkylglycidates (V) with sodiomalonate.[9]

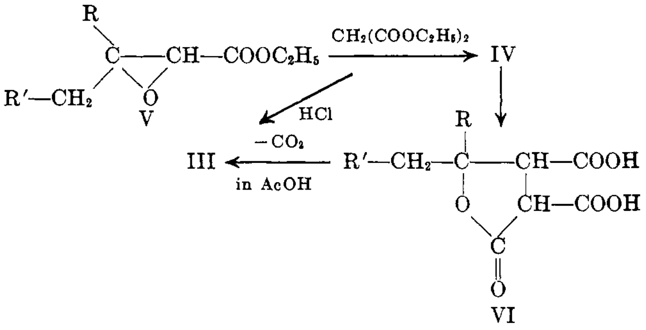


I



II, X = Y = H
III, X = COOH, Y = H
IV, X = Y = $COOC_2H_5$

In this reaction 70–80% yields of γ-methyl-γ-alkyl-α,β-dicarbethoxybutyrolactones (IV) were obtained. The new lactone diesters (IV) are listed in Table II. The lactone diesters (IV) were converted into the paraconic acids (III) by means of hydrolysis to VI followed by decarboxylation.[10] Pyridine[10] or 20% sulfuric acid,[11] when used as a decarboxylating agent, afforded the paraconic acids (III) in yields of 40–60%. Glacial acetic acid was found to give much better yields of 70–80%. The paraconic acids[12] (III) were obtained, however, in one step from the lactone diesters (IV) by the action of concentrated hydrochloric acid in 78% yield.



Hydrolysis of the lactone diesters (IV) in the presence of excess of 5 *N* sodium hydroxide followed by decarboxylation gave unsaturated dibasic acids (VII) through the fission of the lactone ring.

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[1] Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tôkyô, April, 1961.

[2] R. L. Frank, P. G. Arvan, J. W. Richter, and C. R. Vanneman, *J. Am. Chem. Soc.*, **66**, 4 (1944).

[3] F. B. LaForge and W. F. Barthel, *J. Org. Chem.*, **10**, 222 (1945).

[4] R. L. Frank, R. Armstrong, J. Kwiatek, and J. A. Price, *J. Am. Chem. Soc.*, **70**, 1379 (1948).

[5] M. Elliott, *J. Chem. Soc.*, 2231 (1956).

[6] C. Rai and S. Dev, *Experientia*, **11**, 114 (1955); *J. Indian Chem. Soc.*, **34**, 266 (1957).

[7] E. Demole, E. Lederer, and D. Mercier, *Helv. Chem. Acta*, **45**, 685 (1962).

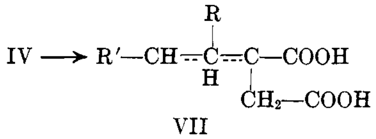
[8] L. Givaudan, German Patent 639,455 (1936); *Chem. Abstr.*, **31**, 1434 (1937).

[9] The reaction of β,β-dimethylglycidate with sodiomalonate has been recorded. See A. Haller and G. Blanc, *Compt. rend.*, **142**, 1471 (1906); G. V. Chelintsev and E. D. Osetrova, *J. Gen. Chem. USSR*, **7**, 2373 (1937); *Chem. Abstr.*, **32**, 2099 (1938). The reaction by the carbanion of malonate occurred at the α-position of glycidate. However, R. E. Parker, *Chem. Rev.*, **59**, 737 (1959), described that anions from amines combined with the β-carbon, while Y. Liwschitz, Y. Rabinsohn, and D. Perera, *J. Chem. Soc.*, 1116 (1962), showed the α-attack by ammonia. The present results of the reaction sequences confirmed the α-attack by malonate.

[10] W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubband, *J. Am. Chem. Soc.*, **83**, 606 (1961).

[11] S. F. Birch and J. F. Thorpe, *J. Chem. Soc.*, 1821 (1922).

[12] Infrared spectra of the neat paraconic acids (III) have a single carbonyl band at about 1735 cm.$^{-1}$. Absorption in chloroform showed two bands at 1780–1755 cm.$^{-1}$ for lactone carbonyl and at 1720–1700 cm.$^{-1}$ for carboxylic acid carbonyl, respectively. Ethyl γ-methyl-γ-hexylparaconate have a lactone carbonyl band at 1776 cm.$^{-1}$ and an ester carbonyl band at 1729 cm.$^{-1}$. The lowering of the lactone carbonyl frequency of neat γ,γ-dialkylparaconic acids (III) may be due to intermolecular hydrogen bonding. See C. Katsuta and N. Sugiyama, *Bull. Chem. Soc. Japan*, **35**, 1194 (1962).

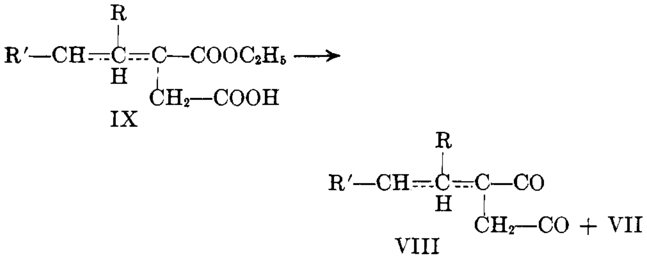


$$\mathrm{IV} \longrightarrow \mathrm{R'{-}\underset{H}{CH}{\cdots}\overset{R}{C}{\cdots}\underset{CH_2-COOH}{C}{-}COOH}$$

VII

The second route to the paraconic acids (III) is a lactonization of β,γ- or γ,δ-unsaturated acids (IX) which were readily prepared by the Stobbe condensation[5,13] of dialkyl ketones with diethyl succinate. This lactonization was effected by the action of hydrochloric acid[11] or hydrogen bromide in aqueous acetic acid.[14]

When the Stobbe half-esters (IX)[15] were distilled, corresponding acid anhydrides (VIII) were produced in varying amounts. Under more drastic conditions of distillation, the half-esters (IX, R = CH_3 and R′ = C_4H_9) were completely converted into a mixture of 64% of the acid anhydrides (VIII) and 35% of unsaturated dibasic acids (VII). VII and VIII also could be converted into the paraconic acids (III) by the action of concentrated hydrochloric acid or hydrogen bromide in acetic acid.



$$\mathrm{R'{-}\underset{H}{CH}{\cdots}\overset{R}{C}{\cdots}\underset{CH_2-COOH}{C}{-}COOC_2H_5} \longrightarrow \mathrm{R'{-}\underset{H}{CH}{\cdots}\overset{R}{C}{\cdots}\underset{CH_2-CO}{C}{-}CO} + \mathrm{VII}$$

IX VIII

Cyclopentenones (I) were obtained in high yields by the treatment of the paraconic acids (III) with polyphosphoric acid.[16] Reaction of γ-methyl-γ-hexylparaconic acid (III, R = CH_3 and R′ = C_6H_{11}) gave a mixture containing 65% of dihydrojasmone (I, R = CH_3 and R′ = C_5H_{11}),[5,6,13,17,18] 28% of dibasic acid (VII, R = CH_3 and R′ = C_5H_{11}), and 4% of acid anhydride (VIII, R = CH_3 and R′ = C_5H_{11}). Both recovered dibasic acid and acid anhydride were again lactonized to give γ-methyl-γ-hexylparaconic acid and subsequently subjected to cyclization. Such treatment, when repeated, gave after all 80% of dihydro jasmone.

It appeared that the decarboxylation preceded the cyclization. When the reaction was stopped at the early stage, γ-methyl-γ-decanolactone (II, R = CH_3 and R′ = C_5H_{11}) was isolated in fair yields along with the cyclopentenone (I).

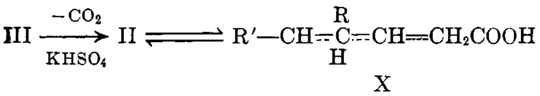
Other cyclopentenones (I) were prepared similarly. The physical constants together with yields of these compounds are listed in Table I.

Table I

2,3-Dialkyl-2-cyclopentenones (I)

R	R′	B.p., °C. (mm.)	Yield, %	$n^{20}D$
CH_3	CH_3	110 (35)	78.2	1.4830
CH_3	C_2H_5	96 (35)	63.1	1.4830
CH_3	C_3H_7	98 (14)	80.9	1.4811
CH_3	C_4H_9	123 (18)	78.7	1.4817
CH_3	C_5H_{11}	91 (2)	80.4	1.4807
CH_3	C_6H_{13}	143 (18)	81.2	1.4847
CH_3	i-C_3H_7	100 (26)	85.2	1.4812
CH_3	i-C_4H_9	112 (18)	85.2	1.4807
C_2H_5	CH_3	95 (16)	81.2	1.4850

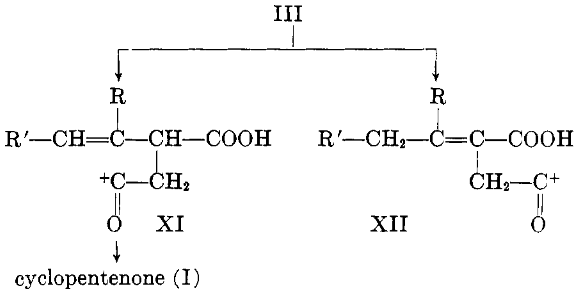
The decarboxylation of γ-methyl-γ-hexylparaconic acid (III, R = CH_3 and R′ = C_5H_{11}) to γ-methyl-γ-decanolactone (II, R = CH_3 and R′ = C_5H_{11}) and the lacto–enoic tautomerism[19] of the γ-butyrolactone and 4-methyldec-3(or 4)-enoic acid (X, R = CH_3 and R′ = C_5H_{11}) were observed also in this case.



$$\mathrm{III} \xrightarrow[\mathrm{KHSO_4}]{-\mathrm{CO_2}} \mathrm{II} \rightleftharpoons \mathrm{R'{-}\underset{H}{CH}{\cdots}\overset{R}{C}{\cdots}CH{=}CH_2COOH}$$

X

As to the mechanism for the cyclodehydration[20] of γ,γ-dialkylparaconic acid (III) with polyphosphoric acid, lactone ring opening and simultaneous elimination of water might be included as one of the possibilities. Thus the acyl cations (XI) undergo intramolecular condensation by a Friedel–Crafts type reaction to give cyclopentenone (I) with the elimination of carbon dioxide. As a side reaction, XI and XII gave unsaturated dibasic acids (VII), which could be separated from the cyclodehydration products by an alkali extraction.



XI XII

Experimental[21]

Ethyl β-Methyl-β-alkylglycidates (V).—Following Johnson's method,[22] a mixture of 22.8 g. (0.2 mole) of 2-heptanone, 24.5 g. (0.2 mole) of ethyl chloroacetate, and 22.4 g. of potassium t-butoxide in 160 ml. of dry t-butyl alcohol was stirred at 10–15° for 1 hr., and after addition of ice–water the reaction mixture was extracted with ether. The products obtained on evaporation of the ethereal solution were distilled under reduced pressure to give 30 g. (75%) of ethyl β-methyl-β-pentylglycidate (V, R = CH_3 and R′ = C_4H_9), b.p. 142° (28 mm.), $n^{23}D$ 1.4339; infrared: 1755 and 1730 cm.$^{-1}$ (ester C=O).

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.11; H, 10.19.

In a similar way, 75% (based on 5-methyl-2-pentanone) of ethyl β-methyl-β-isobutylglycidate was obtained, b.p. 119° (28 mm.), $n^{23}D$ 1.4302.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.71; H, 9.71.

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[13] W. S. Johnson and G. H. Daub, "Organic Reaction," Coll. Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 26. The product of the condensation is a mixture of the β,γ- and γ,δ-unsaturated acids (see ref. 5).

[14] J. H. Amin and S. C. Bhattacharyya, Indian Patent 64,959 (August 3, 1960); *Chem. Abstr.*, **55**, 2521 (1961).

[15] Ultraviolet spectra (ref. 5) of the Stobbe half-esters revealed that at the first step of the Stobbe condensation half-esters rich in the α,β-unsaturated type were produced, but during the distillation course their content decreased.

[16] R. F. Jameson, *J. Chem. Soc.*, 752 (1959).

[17] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIA, Elsevier Publishing Co., Amsterdam, 1953, pp. 96, 101.

[18] J. H. Amin, R. K. Razden, and S. C. Bhattachryya, *Perfum. Essent. Oil Record*, **49**, 502 (1958).

[19] W. S. Johnson and R. H. Hunt, *J. Am. Chem. Soc.*, **72**, 935 (1950).

[20] *Cf.* S. Dev, *Chem. Ind.* (London), 1071 (1954).

[21] Microelemental analyses were carried out by Miss Kenko Ogawa of this laboratory.

[22] W. S. Johnson, J. S. Belew, L. J. Chinn, and R. H. Hunt, *J. Am. Chem. Soc.*, **75**, 4995 (1953).

From 2-pentanone and 2-octanone the corresponding glycidates were obtained in 81% (lit.[23] 57%) and 76% (lit.[24] 41%) yields, respectively.

Reaction of Ethyl β-Methyl-β-pentylglycidate with Malonic Ester.—A mixture of 13.6 g. (0.2 mole) of sodium ethoxide, 37.5 g. (0.25 mole) of diethyl malonate in 120 ml. of anhydrous ethanol, and 20 g. (0.1 mole) of ethyl β-methyl-β-pentylglycidate (V, R = CH_3 and R′ = C_4H_9) was refluxed for 25 hr. The mixture was acidified and taken up in ether. The ether layer was washed with a saturated sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, and evaporated. Distillation of the residue yielded 12 g. (38% based on the glycidate) of γ-methyl-γ-pentyl-α,β-dicarbethoxybutyrolactone (IV, R = CH_3 and R′ = C_4H_9), b.p. 172° (2 mm.); infrared: 1785 cm.$^{-1}$ (lactone C═O), 1740 and 1725 cm.$^{-1}$. (ester C═O). Also yielded was the unchanged glycidate (11g.), which was treated again with the freshly prepared sodiomalonate solution. Thus in total, 23.3 g. (74%) of the lactone diesters were obtained.

Other lactone diesters (IV), obtained similarly, are given in Table II.

Table II

γ-Methyl-γ-alkyl-α,β-dicarbethoxybutyrolactones (IV) (R = CH_3)

R′	B.p., °C. (2 mm.)	$n^{21}D$	Yield,ᵃ %	Analyses, % Calcd. C	Calcd. H	Found C	Found H
C_2H_5	152	1.4534	81	58.73	7.75	58.84	7.76
i-C_3H_7	153	1.4520	66	59.98	8.05	60.33	8.12
C_4H_9	172	1.4531	72	61.16	8.35	61.47	8.44
C_5H_{11}	180	1.4542	70	62.17	8.59	62.57	8.77

ᵃ These yields are the total of the repeated reaction products.

Saponification of Lactone Diesters (IV) with 1 *N* Sodium Hydroxide. Paraconic Acids (III) *via* Lactonedicarboxylic Acids (VI).—A mixture of 100 ml. of a 1 *N* sodium hydroxide solution and 15.7 g. (0.05 mole) of γ-methyl-γ-pentyl-α,β-dicarbethoxybutylrolactone (IV, R = CH_3 and R′ = C_4H_9) was refluxed for 4–5 hr. and neutralized to pH 7–6.5 with dilute sulfuric acid. When the solvent was removed *in vacuo*, there was obtained in oily state the lactonedicarboxylic acid (VI), which could not be crystallized. A solution of this oil in 50 ml. of glacial acetic acid was boiled for 30 min. when vigorous evolution of carbon dioxide was observed. Acetic acid was removed and to the residue 150 ml. of water was added. The precipitated light brown material was recrystallized from a mixture of water and ethanol (9:1) to give 4.6 g. (43% based on the lactone diesters) of γ-methyl-γ-γ-pentylparaconic acid (III, R = CH_3 and R′ = C_4H_9), m.p. 177°.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.86; H, 8.53.

The evaporated residue of the mother liquor formed a tarry brown oil, which was hydrolyzed repeatedly with 1 *N* sodium hydroxide to afford 3.5 g. (33.5%) of the paraconic acid. In total, 8.1 g. (76.5%) of γ-methyl-γ-pentylparaconic acid was obtained.

Hydrolysis of Lactone Diesters (IV) with Concentrated Hydrochloric Acid. Paraconic Acids (III).—A mixture of 15.7 g. (0.05 mole) of γ-methyl-γ-pentyl-α,β-dicarbethoxybutyrolactone (IV, R = CH_3 and R′ = C_4H_9) and 70 ml. of concentrated hydrochloric acid was vigorously refluxed for 5 hr. Upon cooling to room temperature, the mixture solidified in a dark brown material, which, recrystallized from water–ethanol (9:1), gave 8.4 g. (78%) of α-methyl-γ-pentylparaconic acid (II, R = CH_3 and R′ = C_4H_9), m.p. and m.m.p. 177°. The infrared spectra also showed identity with the compound described in the preceding paragraph.

Hydrolysis of Lactone Diesters (IV) with an Excess Alkali. Unsaturated Dibasic Acids (VII).—A mixture of 100 ml. of 5 *N* sodium hydroxide and 15 g. (0.05 mole) of γ-methyl-γ-isobutyl-α,β-dicarbethoxybutyrolactone (IV, R = CH_3 and R′ = i-C_3H_7) was refluxed for 4–5 hr. and then acidified to pH 7–6.5 with dilute sulfuric acid. After most of the solvent was evaporated *in vacuo*, the residue was taken up in ether. Evaporation of the solvent left 7.3 g. of a pale yellow cake. The solid, dissolved in 50 ml. of pyridine, was refluxed for 2 hr. for the sake of decarboxylation, and the solution was evaporated. The residue was taken up in ether and washed with dilute hydrochloric acid and water. After removing the solvent *in vacuo*, the residue was recrystallized from water to give 4.4 g. [42% based on the lactone diesters (IV)] of 3-carboxyl-4,6-dimethyl-3(or 4)-hexenoic acid (VII, R = CH_3 and R′ = C_4H_9), m.p. 158°; infrared: 1680 cm.$^{-1}$ (C═O); 1610 cm.$^{-1}$ (C═C).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.21; H, 8.13.

Stobbe Half-Esters (IX).—These compounds were prepared by the condensation of dialkyl ketones with diethyl succinate in the presence of potassium *t*-butoxide as described in the literature.[13] From 11.4 g. of 2-heptanone and 26.1 g. of diethyl succinate, 21.8 g. (90%) of crude Stobbe half-esters (IX, R = CH_3 and R′ = C_4H_9) were obtained. Other half-esters were prepared similarly.

Distillation of the Half-Esters (IX).—Distillation of 8.0 g. of the half-esters (IX, R = CH_3 and R′ = C_4H_9) under 2.5 mm. at 145–155° gave 7.9 g. of a mixture of the half-esters (IX) and acid anhydrides (VIII). The mixture was dissolved in 50 ml. of ether and extracted with a 6% potassium carbonate solution. The ether layer was washed with water, dried, and evaporated. Distillation of the residue yielded 1.5 g. (18.7%) of acid anhydride (VIII, R = CH_3 and R′ = C_4H_9), b.p. 145° (2.5 mm.), $n^{21}D$ 1.4836; infrared: 1828 (m) and 1760 (s) cm.$^{-1}$ (C═O).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.52; H, 8.21.

The combined alkaline extracts were acidified. The half-esters were taken up in ether, dried over anhydrous sodium sulfate, and evaporated. Distillation of the residue afforded 6.4 g. (80%) of half-esters (IX, R = CH_3 and R′ = C_4H_9), b.p. 142° (0.8 mm.), $n^{21}D$ 1.4639. The infrared spectrum of this material was identical with that of an authentic sample.[5] The ultraviolet measurement[5] showed that the half-esters contained 77% of an alkylidene compound.

When the distillation was carried out at 210° under 70 mm. in the course of 2 hr., 8.0 g. of the half-esters gave 5.2 g. (64%) of acid anhydride (VIII), 58% of which consisted of an alkylidene compound. The residue gave, on recrystallization from a mixture of water and ethanol (1:5), an isomeric mixture of dibasic acids (VII, R = CH_3 and R′ = C_4H_9), m.p. 117°.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.71; H, 8.40.

Hydrolysis of the Half-Esters (IX) with an Aqueous Potassium Hydroxide Solution. Unsaturated Dibasic Acids (VII).—A mixture of 12.1 g. (0.05 mole) of half-esters (IX, R = CH_3 and R′ = C_4H_9) and 10 g. (0.18 mole) of potassium hydroxide in 300 ml. of water was heated for 3 hr. at 70–80°. White precipitates separated on acidification with hydrochloric acid were recrystallized from water to give 9.7 g. (90%) of dicarboxylic acids (VII, R = CH_3 and R′ = C_4H_9), m.p. 123°; infrared: 1700 and 1686 cm.$^{-1}$ (C═O); ultraviolet: λ_{max} 223 mμ (ε 8100) [lit.[5] for VII, R = CH_3 and R′ = H: λ_{max} 221 mμ (ε 9350) in ethanol]. The alkylidene and alkenyl type compounds were calculated[5] as to exist in a ratio of 86:14.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.80; H, 8.56.

Lactonization of the Stobbe Half-Esters (IX) into Paraconic Acids (III).—Refluxing of half-esters with concentrated hydrochloric acid[13] or with hydrobromic acid in aqueous acetic acid[14] gave the corresponding paraconic acids in good yields. New γ,γ-dialkylparaconic acids prepared in this way are shown in Table III.

Table III

γ,γ-Dialkylparaconic Acids (III) (R = CH_3)

R′	M.p., °C.	Yield, %	Analyses, % Calcd. C	Calcd. H	Found C	Found H
C_2H_5	144	66	58.05	7.58	58.23	7.55
C_3H_7	132	88	59.98	8.05	60.26	8.05
C_4H_9	177	84	61.66	8.47	61.86	8.53
C_5H_{11}[11]	167	85	...	...	...	...
C_6H_{13}	183	82	64.44	9.15	64.70	9.19
i-C_3H_7	170	95	59.98	8.05	60.22	8.09
i-C_4H_9	156.5	95	61.66	8.47	61.93	8.63

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[23] V. F. Martynov and Ua. A. Kastrom, *J. Gen. Chem. USSR*, **26**, 61 (1956); *Chem. Abstr.*, **49**, 9606 (1955).

[24] E. Fourneau and J. R. Billeter, *Bull. soc. chim. France*, [5]**6**, 1616 (1939).

Lactonization of the Acid Anhydrides (VIII) or the Dibasic Acids (VII) into the Paraconic Acids (III).—The refluxing of the acid anhydrides (VIII) or the dibasic acids (VII) with concentrated acid or with hydrobromic acid in aqueous acetic acid afforded the paraconic acids (III) in quantitative yield.

Ethyl γ-Methyl-γ-hexylparaconate.—Refluxing of 4.6 g. of γ-methyl-γ-hexylparaconic acid with 30 ml. of benzene and 10 ml. of ethanol in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate gave the ester in a quantitative yield, b.p. 148–149° (1.5 mm.), $n^{21}\mathrm{D}$ 1.4578.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.70; H, 9.49.

Decarboxylation of Paraconic Acids (III).—The decarboxylation was carried out following the procedure of Johnson and Hunt.[19] A mixture of 6 g. (0.028 mole) of γ-methyl-γ-pentylparaconic acid (III, R = CH_3 and R′ = C_4H_9) and 0.5 g. of potassium hydrogen sulfate was treated at 220–235° for 2 hr. and there were obtained 2.4 g. of γ-methyl-γ-nonanolactone (II, R = CH_3 and R′ = C_4H_9), b.p. 143° (18 mm.) [reported b.p.[25] 129–131° (13 mm.)], $n^{18}\mathrm{D}$ 1.4527, and 0.8 g. of 4-methyl-3(or 4)-nonenoic acid (X, R = CH_3 and R′ = C_4H_9), b.p. 145° (3 mm.), $n^{18}\mathrm{D}$ 1.4537; infrared: 1695 cm.$^{-1}$ (C=O) and 1625 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.61; H, 10.51.

The lacto–enoic tautomerism was observed with these compounds as in the literature.[19]

Cyclodehydration of γ-Methyl-γ-hexylparaconic Acid.—To 6 ml. of polyphosphoric acid warmed on an oil bath at 100–120° was added portionwise 11.4 g. (0.05 mole) of γ-methyl-γ-hexylparaconic acid (III, R = CH_3 and R′ = C_4H_9). After all of the solid had dissolved, the mixture was heated gradually for about 30 min. under reduced pressure to a final temperature of 150°. During this period vigorous evolution of carbon dioxide was observed. After the decomposition reaction subsided, the temperature was raised gradually during about 4 hr. to 190°, when crude cyclopentenone was distilled. From the ethereal solution of this crude cyclopentenone, acidic material was removed with a 5% potassium carbonate solution. The ether layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. On redistillation of the crude cyclopentenone 5.6 g. (67%) of 2-pentyl-3-methyl-2-cyclopentenone-1 (dihydrojasmone) (I, R = CH_3 and R′ = C_5H_{11}) was obtained, b.p. 90–91° (2 mm.) [reported[2] b.p. 91° (2 mm.)], $n^{20}\mathrm{D}$ 1.4855 (reported[5] $n^{20}\mathrm{D}$ 1.4851); semicarbazone, m.p. 173° (lit.[5] m.p. 174°); 2,4-dinitrophenylhydrazone, m.p. 121.5 (lit.[6] m.p. 123°). This ketone, semicarbazone, and 2,4-dinitrophenylhydrazone gave correct analyses. Infrared spectra of this ketone was identical with that of the authentic sample. The higher boiling fraction gave 4 g. of the acid anhydride, b.p. 143° (2 mm.), $n^{21}\mathrm{D}$ 1.4856 (lit.[5] $n^{20}\mathrm{D}$ 1.4851); infrared: 1830 (m) and 1780 (s) cm.$^{-1}$ (C=O).

The combined alkaline extracts were acidified with dilute hydrochloric acid, and the precipitated crystals were recrystallized from water–ethanol (5:1) to give 3.2 g. (28%) of dibasic acids (VII, R = CH_3 and R′ = C_5H_{11}), m.p. 153°; infrared: 1698 cm.$^{-1}$ (C=O); ultraviolet: $\lambda_{\max}$ 223 mμ (ϵ 3000). The alkylidene and alkenyl compounds were calculated[5] as to exist in a ratio of 30:70.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 61.66; H, 8.47. Found: C, 61.79; H, 8.56.

Both recovered dibasic acid and acid anhydride were repeatedly lactonized by means of hydrogen bromide in acetic acid to γ-methyl-γ-hexylparaconic acid which was subjected to cyclodehydration to give 1.1 g. of the cyclopentenone. After all, 6.7 g. (80%) of 2-pentyl-3-methyl-2-cyclopentenone-1 was obtained.

Other cyclopentenone derivatives are listed in Table II.

Similar treatment of 9.2 g. of γ-methyl-γ-decanolactone (II, R = CH_3, R′ = C_5H_{11}, X = H, and Y = H) with polyphosphoric acid[6] afforded 7.5 g. (90%) of dihydrojasmone. The corresponding ethyl paraconate and Stobbe half-esters gave inferior yields, *i.e.*, 43 and 29%, respectively.

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Formation of an Organotin–Nitrogen Bond. II.[1] Syntheses of Tris(trialkyltin)amines

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Tris(trialkyltin)amines, $(R_3Sn)_3N$, were prepared by the reaction of lithium amide or sodium amide with trialkyltin halide. Infrared absorption of these compounds at 728–712 cm.$^{-1}$ was assigned to an antisymmetric stretching vibration of an Sn–N–Sn linkage. The decomposition of these compounds in air revealed that tris(trimethyltin)amine was converted to trimethyltin hydroxide, while tris(triethyltin)- and tris(tri-*n*-propyltin)-amines were converted to trialkyltin carbonate *via* bis(trialkyltin) oxide. Except for bis(trimethyltin) oxide, bis(trialkyltin) oxides absorb atmospheric carbon dioxide to afford trialkyltin carbonates.

Bullard, *et al.*,[2] reported a product they assumed to be tris(trimethyltin)amine, $[(CH_3)_3Sn]_3N$, being produced by the reaction of (trimethylstannyl)sodium and bromobenzene in liquid ammonia, but they did not isolate nor characterize the compound.

Recently it has been noted in a short communication that tris(trimethyltin)amine was produced by treatment of trimethyl(dimethylamino)tin with ammonia, but experimental details were not described.[3]

These compounds have now been prepared by the reaction of the corresponding trialkyltin halide with lithium or sodium amide in liquid ammonia or ether and were isolated analytically pure by vacuum distillation in nitrogen atmosphere.

Lithium amide reacts with trialkyltin chloride in liquid ammonia, diethyl ether, and tetrahydrofuran, while sodium amide reacts only in liquid ammonia but not in diethyl ether, tetrahydrofuran, or pyridine at the respective refluxing temperatures.

It is known that the formation of a silicon compound having the structure of $(R_3Si)_3N$ type[3b] is very difficult owing to steric hindrance. In the case of tin compounds, however, owing presumably to the greater radius of the tin atom, the nitrogen atom could find a vacancy among the three tin atoms so that $(R_3Sn)_3N$ type compounds were obtained readily.

Evidence for the $(R_3Sn)_3N$ structure of these compounds is based upon, besides the coincidence of analyses and the absence of an infrared absorption of an N–H bond, the fact that these compounds liberate

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(1) Previous paper: K. Sisido and S. Kozima, *J. Org. Chem.*, **27**, 4051 (1962).

(2) R. H. Bullard and W. R. Robinson, *J. Am. Chem. Soc.*, **49**, 1368 (1927).

(3) (a) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1963); (b) NOTE ADDED IN PROOF.—A silicone compound of the $(R_3Si)_3N$ type was reported by U. Wannagat and O. Brandstätter, *Angew. Chem.*, **75**, 345 (1963); *Angew., Chem. Intern. Ed. Engl.*, **2**, 263 (1963).