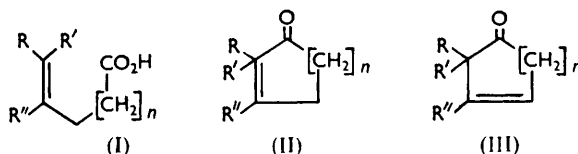


602. *Reduced Cyclic Compounds. Part IV.* The Intramolecular Acylation of Some Olefinic Acids.*

By M. F. ANSELL and S. S. BROWN.

Intramolecular acylation, in polyphosphoric acid, of the six alkenoic acids $R\cdot CH=CH\cdot CH_2\cdot [CH_2]_n\cdot CO_2H$ ($R = H$ or Me ; $n = 1, 2,$ or 3) has been shown to give (except where $R = H, n = 1$) mixtures of isomeric *cyclo*-pentenones and *cyclo*hexenones. Similar treatment of the three alkenoic acids $Me_2C=CH\cdot CH_2\cdot [CH_2]_n\cdot CO_2H$ ($n = 1, 2,$ or 3) gives 3-methylcyclohex-2-enone, a mixture of 2-isopropylcyclopent-2-enone and 2-isopropylidenecyclopentanone, and a mixture containing 2-isopropylcyclohex-2-enone and 2-isopropylidenecyclohexanone respectively.

INTRAMOLECULAR acylation of suitably constituted alkenoic acids^{1,2} (or the lactones of the related hydroxy-acids) and alkenoyl chlorides³ is known to yield *cyclo*alkenones. Attention has previously been chiefly directed⁴ to the ring closure of highly branched structures such as (I; $R = H, R'$ and $R'' =$ alkyl or aryl; $n = 1$ or 2) to the corresponding *cyclo*alkenones (II); if both R and R' are alkyl groups, the ketone (III) is formed. Hitherto the scope of the intramolecular acylation, particularly with respect to the relative



ease of formation of *cyclopentanone* and *cyclohexanone* derivatives, has not been defined. The preparation of *cycloheptanone* derivatives by this route is not recorded. We have, therefore, examined the intramolecular acylation of the acids [I; (a) $R = R' = R'' = H, n = 1, 2,$ or 3 ; (b) $R = Me, R' = R'' = H, n = 1, 2,$ or 3 ; and (c) $R = R' = Me, R'' = H, n = 1, 2,$ or 3], the preparation of which has been described elsewhere.⁵

Reaction of pent-4-enoyl chloride and *trans*-hex-4-enoyl chloride with aluminium

* Part III, *J.*, 1958, 1167.

¹ (a) Maschmeijer, *F.P.* 765,515/1934; (b) Plattner and St. Pfau, *Helv. Chim. Acta*, 1937, **20**, 1474; (c) Rai and Dev, *J. Indian Chem. Soc.*, 1957, **34**, 178, and references there cited.

² Burnop, Elliot, and Linstead, *J.*, 1940, 727.

³ Cook and Lawrence, *J.*, 1935, 1637; 1937, 817; Chuang, Tien, and Ma, *Ber.*, 1936, **69**, 1494.

⁴ *Inter al.*, Johnson, Johnson, and Peterson, *J. Amer. Chem. Soc.*, 1945, **67**, 1360; 1946, **68**, 1926; Johnson and Peterson, *ibid.*, 1945, **67**, 1366.

⁵ Ansell and Brown, *J.*, 1957, 1788.

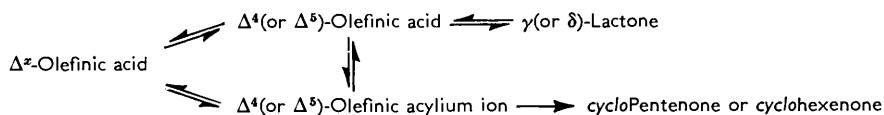
chloride in boiling carbon disulphide (cf. ref. 6) gave *cyclopent-2-enone* (30%) and 2-methyl-*cyclopent-2-enone* (50%) respectively. Hex-5-enoyl chloride, under these conditions, gave a small amount of *cyclohex-2-enone*, together with a chloro-ketone (possibly 3-chloro-*cyclohexanone*). Cyclisation of *trans*-hept-5-enoyl chloride gave a heterogeneous chlorine-containing ketone. In view of the difficulties in obtaining chlorine-free cyclization products from the alkenoyl chlorides, a study was made of the action of polyphosphoric acid on the free alkenoic acids.⁷

With the exception of pent-4-enoic acid, each of the six straight-chain acids (Ia and b) with polyphosphoric acid gave heterogeneous products from which ketonic and lactonic components were isolated, the proportions varying according to the reaction conditions (see Table I). No systematic attempts were made to identify the lactones in view of the paucity of reference compounds, but the ketones were identified.

Attempted cyclization of pent-4-enoic acid gave no detectable amount of ketone. γ -Valerolactone was the only volatile product. This is to be compared with the failure by Frank *et al.*⁸ to effect intramolecular acylation of γ -valerolactone by use of phosphoric oxide, and with Ferrier and Tedder's observation⁹ that treatment of the acid with trifluoroacetic anhydride gave only a trace of *cyclopent-2-enone* together with "a linear dimer." *trans*-Hex-4-enoic acid with an excess of hot polyphosphoric acid gave 2-methyl-*cyclopent-2-enone* (40%), which, together with a trace of *cyclohex-2-enone*, was also obtained from hex-5-enoic acid under the same conditions. Ferrier and Tedder,⁹ using trifluoroacetic anhydride, obtained *cyclohex-2-enone* from hex-5-enoic acid in 46% yield. Cyclisation of hept-6-enoic and *trans*-hept-5-enoic acid gave virtually identical mixtures of 2-methyl-*cyclohex-2-enone* and 2-ethyl-*cyclopent-2-enone*. Similarly, *trans*-oct-6-enoic acid gave a mixture of 2-ethyl-*cyclohex-2-enone* and 2-*n*-propyl-*cyclopent-2-enone*.

The three acids of class (Ic) behaved rather differently to the unsubstituted acids on treatment with polyphosphoric acid. 5-Methylhex-4-enoic acid gave only 3-methyl-*cyclohex-2-enone*; 6-methylhept-5-enoic acid gave a mixture of 2-*isopropylidenecyclopentanone* and 2-*isopropylcyclopent-2-enone*; 7-methyloct-6-enoic acid gave a mixture of unsaturated ketones from which derivatives of 2-*isopropylidenecyclohexanone* and 2-*isopropylcyclohex-2-enone* were isolated. No lactonic material was found.

These results, together with the known¹⁰ formation of mixtures of *cycloalkenones* from undec-10-enoic acid, 4-methyldec-9-enoic acid, and dec-9-enoic acid, may be rationalised by assuming that, under strongly acid conditions, the double bond of an alkenoic acid is highly labile, by virtue of carbonium-ion formation, and may migrate to a suitable position for electrophilic attack by the acylium ion¹⁰ derived from the carboxyl group of the same molecule. Concomitantly a lactone-enoic acid equilibrium^{11,12} must be set up. Since the experimental results indicate that only five- and/or six-membered rings may be formed by intramolecular acylation, the equilibria obtaining may be depicted as:



The absence of isolable amounts of *cyclopent-2-enone* and *cyclohex-2-enone* in the cyclisation products of pent-4-enoic and hex-5-enoic acid respectively, is undoubtedly due, not to the fact that intramolecular acylation does not occur, but to very ready polymerisation of these ketones under the reaction conditions. *cycloAlkenones* having α -alkyl

⁶ Gutsche and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 2239.

⁷ Cf. Dev, *Chem. and Ind.*, 1954, 1071; *J. Indian Chem. Soc.*, 1955, **32**, 255.

⁸ Frank, Armstrong, Kwiatek, and Price, *J. Amer. Chem. Soc.*, 1948, **70**, 1379.

⁹ Ferrier and Tedder, *J.*, 1957, 1435.

¹⁰ Baddeley, *Quart. Rev.*, 1954, **8**, 355.

¹¹ Linstead and Rydon, *J.*, 1934, 1995.

¹² Johnson and Hunt, *J. Amer. Chem. Soc.*, 1950, **72**, 935; Mathieson, *J.*, 1951, 177.

substituents are evidently less susceptible to cationic polymerisation, so that there is no difficulty in isolating such ketones in these cases. The higher straight-chain acids give mixtures of isomeric ketones (in conflict with a recent report¹³), which much reduces the preparative value of their intramolecular acylation.

TABLE I. Intramolecular acylations with polyphosphoric acid.

Acid	Conditions		Lactonic product		Ketonic product	
	Temp.	Time (min.)	B. p. mm.	Yield (%)	B. p. mm.	Yield (%)
Pent-4-enoic	100°	10	80—81°/12	22		0
<i>trans</i> -Hex-4-enoic	100	120	93—98°/12	48	51—52°/12	9
	120	7		24		38
	130	30		35		30
	140	15		30		24
Hex-5-enoic	80	100	102—104°/15	17	52—54°/15	7.2
	90	20		18		8.4
	100	10		40		9.6
	110	5		5.3		0
<i>trans</i> -Hept-5-enoic	85	60	112—117°/15	22	74—75°/24	51
	90	15		21		52
	95	40		13		55
	100	30		9.5		41
	105	30		2.1		16
Hept-6-enoic	90	30	115—120°/16	9	74—75°/24	37
	95	15		12		53
	100	15		17		57
	110	10		16		57
<i>trans</i> -Oct-6-enoic	90	25	120—127°/16	9.5	89—91°/24	57
	95	15		1.3		54
	100	10		2.0		47
5-Methylhex-4-enoic	90	30		0	94—95°/24	73
	110	15		0		77
6-Methylhept-5-enoic	80	10		0	80—84°/14	33
	100	5		0		38
7-Methyloct-6-enoic	95	15		0	48—50°/1	6
	85	5		0		9

Cyclisation of the three branched-chain acids (Ic) was accompanied by extensive polymerisation; a good yield of *cyclo*alkenone was indeed only obtained from 5-methylhex-4-enoic acid, which enters exceptionally readily¹¹ into the lactone-enoic equilibrium. Intramolecular acylation of this acid, which may be visualized as proceeding through the "isopropenyl isomer," 5-methylhex-5-enoic acid, finds precedents in the formation of substituted 3-methylcyclohex-2-enones from 4-methyl-4-isopropyl- γ -butyrolactone,⁸ dihydrolavandulic acid,¹⁴ and (2-methylallyl)succinic anhydride.¹⁵ In contrast, in the cyclization of 6-methylhept-5-enoic acid both steric and electronic factors are favourable to the formation of a *cyclopentanone* derivative. Although both 2-isopropylidene*cyclopentanone* and 2-isopropyl*cyclopent-2-enone* are actually formed, the former is probably the primary cyclization product¹⁶ since an authentic specimen was found to be largely isomerized to the endocyclic isomer by hot polyphosphoric acid. Similarly, it is likely that 2-isopropylidene*cyclohexanone* is the primary product of the intramolecular acylation of 7-methyloct-6-enoic acid; this reaction is analogous to the ring closure¹⁷ of citronellyl chloride to (\pm)-pulegone.

EXPERIMENTAL

Refractive indices are for the Na_D line at 20° unless otherwise stated. Fractional distillations marked (S) were effected with a spinning-band semimicro-fractionating column (E. Haage,

¹³ Dominquez, Diaz, and Slim, *Ciencia*, 1957, **16**, 151.

¹⁴ Kuhn and Schinz, *Helv. Chim. Acta*, 1953, **36**, 161.

¹⁵ Phillips and Johnson, *J. Org. Chem.*, 1956, **21**, 587.

¹⁶ Cf. Eschenmoser, Shinz, Fischer, and Colonge, *Helv. Chim. Acta*, 1951, **34**, 2329.

¹⁷ Bardhan and Bhattacharyya, *Chem. and Ind.*, 1951, 800.

Mulheim). Ultraviolet absorption spectra refer to 95% EtOH solutions. Hydrogenations were carried out at atmospheric pressure in ethanol solution over Adams catalyst. The acid chlorides were prepared with a 10% molar excess of thionyl chloride and a catalytic amount of pyridine in boiling ether and were distilled immediately before use.

Cyclisation of Pent-4-enoyl Chloride.—A stirred suspension of powdered aluminium chloride (33 g., 0.26 mole) in boiling carbon disulphide (130 ml.) was treated dropwise with pent-4-enoyl chloride (26 g., 0.22 mole) during 30 min. An exothermic reaction occurred and hydrogen chloride was evolved; after a further 1 hr. under reflux the mixture was poured on ice (150 g.), and sufficient concentrated hydrochloric acid (*ca.* 20 ml.) was added to dissolve the precipitate. The organic layer was separated and the aqueous layer extracted with carbon disulphide (2 × 80 ml.). The combined extracts were washed successively with 50 ml. portions of 5% hydrochloric acid, brine, saturated sodium hydrogen carbonate solution, and brine. Distillation of the dried (MgSO₄) extract gave *cyclopent-2-enone* (0.4 g.), b. p. 50–55°/25 mm. The aqueous residues from the above extraction were combined and continuously steam-distilled and ether-extracted (Vogel¹⁸). The residue obtained on evaporation of the dried (MgSO₄) extract was distilled, yielding *cyclopent-2-enone* (6.4 g.), b. p. 56–58°/24 mm. The redistilled cyclization product had *n* 1.4818, λ_{max} 218, $m\mu$ (log ϵ 3.86), and formed a semicarbazone (laths from aqueous ethanol), m. p. 212–213°, and a 2 : 4-dinitrophenylhydrazone (red needles from ethanol), m. p. 170–171°. The reported values for *cyclopent-2-enone* are: b. p. 42°/11 mm., *n* 1.4813 (ref. 19) λ_{max} 218 (log ϵ 3.99) (ref. 20), semicarbazone, m. p. 214–215° (refs. 21, 22) or 217–218° (ref. 23), 2 : 4-dinitrophenylhydrazone, m. p. 169–170° (ref. 23).

Cyclisation of trans-Hex-4-enoyl Chloride.—Cyclisation of this chloride (12 g., 0.091 mole) was effected as in the previous experiment. Evaporation of the carbon disulphide extract gave a chlorine-containing material which lost hydrogen chloride on distillation to give a ketonic product (4.1 g.), b. p. 60–64°/24 mm. A further 0.5 g. of ketone was obtained by continuous steam-distillation and ether-extraction (Vogel¹⁸) of the aqueous solutions. Redistillation of the combined material gave 2-methyl*cyclopent-2-enone*, b. p. 53–54°/15 mm., *n* 1.4780. The derived semicarbazone and 2 : 4-dinitrophenylhydrazone had m. p.s 218–220° (decomp.) and 221–222° respectively. For previously recorded constants see the cyclisation of *trans-hex-4-enoic acid* below.

Cyclisation of Hex-5-enoyl Chloride.—The cyclisation of this chloride (10 g., 0.075 mole) was effected as above. Evaporation of the carbon disulphide extract yielded a chlorine-containing material which was distilled at 1 mm., with very little decomposition, to yield fractions: (1) b. p. <40°, 0.5 g.; (2) b. p. 40–58°, *n* 1.4871, 0.6 g.; (3) b. p. 58–59°, *n* 1.4867, 1.6 g.; (4) b. p. 59–60°, *n* 1.4867–1.4861, 4.3 g. The 2 : 4-dinitrophenylhydrazones from fractions 1 and 2 were clearly heterogeneous but the former, after chromatography (in benzene–hexane on alumina), yielded the 2 : 4-dinitrophenylhydrazone of *cyclohex-2-enone* whose m. p., 162–163°, was not depressed in admixture with an authentic sample,²⁴ m. p. 165–167° (Rigby²⁵ records m. p. 164–165°).

Fraction (4) was redistilled (b. p. 59–60°/1 mm.; *n* 1.4867) (Found: C, 55.3; H, 6.6; Cl, 25.8. Calc. for C₆H₉OCl: C, 54.3; H, 6.8; Cl, 26.8%) and gave a semicarbazone (plates from water), m. p. 165–166° (Found: C, 44.7; H, 6.4; Cl, 18.0; N, 22.3. Calc. for C₇H₁₂ON₃Cl: C, 44.3; H, 6.4; Cl, 18.7; N, 22.1%), and a 2 : 4-dinitrophenylhydrazone (plates from ethanol–chloroform), m. p. 139–140° (Found: C, 46.1; H, 4.6; Cl, 11.3; N, 18.2. Calc. for C₁₂H₁₃O₄N₄Cl: C, 46.1; H, 4.2; Cl, 11.3; N, 17.9%). These data do not correspond with those for 2- or 4-chlorocyclohexanone;^{26a} derivatives of 3-chlorocyclohexanone^{26b} have not been reported.

¹⁸ Vogel, "Practical Organic Chemistry," Longmans Green, London, 1951, p. 223.

¹⁹ Alder and Flock, *Chem. Ber.*, 1956, **89**, 1732.

²⁰ Schubert and Sweeney, *J. Amer. Chem. Soc.*, 1955, **77**, 2297.

²¹ Godchot and Taboury, *Compt. rend.*, 1913, **156**, 333.

²² Nazarov, Bergelson, Torgov, and Ananchenko, *Bull. Acad. Sci. U.S.S.R.*, 1953, 889; *Chem. Abs.*, 1955, **49**, 1082.

²³ Mousseron, Jacquier, and Fontaine, *Bull. Soc. chim. France*, 1952, **19**, 767.

²⁴ Born, Pappo, and Szmuskovicz, *J.*, 1953, 1779.

²⁵ Rigby, *J.*, 1949, 1586.

²⁶ (a) Meyer, *Helv. Chim. Acta*, 1933, **16**, 1291; Ramirez and Kirby, *J. Amer. Chem. Soc.*, 1952, **74**, 4331; Campbell and McCall, *J.*, 1950, 2870; Sabatay and Palfray, *Bull. Soc. chim. France*, 1928, **43**, 906; Grewe, Lorenzen, and Vining, *Chem. Ber.*, 1954, **87**, 793; (b) Kotz and Grethe, *J. prakt. Chem.*, 1909, **80**, 503.

Cyclisation of trans-Hept-5-enoyl Chloride.—This chloride (18 g.) was cyclised as above. Evaporation of the carbon disulphide extract gave a chlorine-containing product (10 g.) which partially decomposed on distillation (b. p. 38—41°/0.5 mm.; n 1.4794) and was not obtained analytically pure. It gave heterogeneous derivatives, but by persistent recrystallisation, the 2 : 4-dinitrophenylhydrazone (yellow needles from benzene), m. p. 181—182° (Found: Cl, 10.4; N, 17.5. Calc. for $C_{13}H_{15}O_4N_4Cl$: Cl, 10.9; N, 17.1%), and the semicarbazone (plates from water), m. p. 182—183° (Found: N, 20.6; Cl, 17.5. Calc. for $C_8H_{14}ON_3Cl$: N, 20.6; Cl, 17.4%), possibly of 3-chloro-2-methylcyclohexanone, were obtained.

General Procedure for Cyclisation of the Olefinic Acids.—Polyphosphoric acid²⁷ (100 g.) was stirred gently (so as not to break the surface of the liquid) and heated to the required temperature. The alkenic acid (0.1 mole) was added in one portion and the mixture stirred and heated as before. The acid, at first having formed an upper layer, quickly dissolved and the mixture became first orange-red, then brown. After the requisite time, the mixture was cooled rapidly to 30° and ice (*ca.* 150 g.) added. The product was extracted with ether (3 × 70 ml.), either manually, or by the continuous steam distillation-ether extraction process (Vogel¹⁸). The extract was washed successively with saturated brine, saturated sodium hydrogen carbonate solution, and brine. After drying ($MgSO_4$), the solvent was removed through a short column and the residue separated by distillation into ketonic and lactonic fractions (see Table 1).

Cyclisation of Pent-4-enoic Acid.—No ketonic material was obtained and the lactonic material (n 1.4342) was identified as γ -valerolactone, the m. p. (66—67°) of the derived hydrazone not being depressed in admixture with an authentic specimen, m. p. 67—68°. The derived *S*-benzylthiuronium salt (rhombs from acetone) had m. p. 138—139° (Found: N, 9.8; S, 11.1. $C_{13}H_{20}O_3N_2S$ requires N, 9.85; S, 11.3%). Linstead and Rydon²⁸ record b. p. 88°/15 mm., n 1.4315. Reppe *et al.*²⁹ record a hydrazone, m. p. 67—68°.

Cyclisation of trans-Hex-4-enoic Acid.—Distillation of the combined ketonic material gave only 2-methylcyclopent-2-enone, b. p. 51—52°/13 mm., n 1.4798—1.4810, λ_{max} . 226, 309, λ_{min} . 268 $m\mu$ ($\log \epsilon$ 3.92, 14.7, 0.89) [oxime (needles from ethanol), m. p. 127—128°; semicarbazone (tablets from ethanol), m. p. 219—220° (decomp.); 2 : 4-dinitrophenylhydrazone (red tablets from chloroform), m. p. 221—222° (Found: N, 20.1. $C_{12}H_{12}O_4N_4$ requires N, 20.3%)]. Nazarov *et al.*²² record b. p. 52—53°/15 mm., oxime, m. p. 128°, and semicarbazone, m. p. 218° (decomp.). Hydrogenation gave 2-methylcyclopentanone³⁰ [semicarbazone (prisms from methanol), m. p. and mixed m. p. 177—178°; 2 : 4-dinitrophenylhydrazone (orange plates from ethanol-chloroform), m. p. and mixed m. p. 159—160°].

Cyclisation of Hex-5-enoic Acid.—Redistillation of the ketonic fraction gave material, b. p. 52—54°/15 mm., n 1.4773, λ_{max} . 226 and 310, λ_{min} . 269 $m\mu$ ($\log \epsilon$ 3.75, 1.33, 0.92), which yielded the semicarbazone, prisms, m. p. 220—221° (after three recrystallisations from aqueous ethanol), and the 2 : 4-dinitrophenylhydrazone, red tablets, m. p. 221—222° (after one recrystallisation from ethanol-chloroform), of 2-methylcyclopent-2-enone (see previous experiment for reported constants). Hand-sorting of the crystals obtained on evaporation of the mother-liquors from the 2 : 4-dinitrophenylhydrazone gave the 2 : 4-dinitrophenylhydrazone of cyclohex-2-enone (orange laths), whose m. p. (160—162°) was not depressed on admixture with an authentic sample²⁴ of m. p. 165—167°.

Cyclisation of trans-Hept-5-enoic Acid.—Distillation(S) of the combined ketonic material gave 11 fractions (each of 1.0 ml.), b. p. 74—75°/24 mm., n 1.4810—1.4780. The m. p.s of the derivatives (after two recrystallisations) of fractions (2), b. p. 74—74.5°/24 mm., n 1.4816, and (11), b. p. 74.5—75°/24 mm., n 1.4780, suggested that they were predominantly 2-methylcyclohex-2-enone and 2-ethylcyclopent-2-enone respectively. This was supported by mixed m. p. determinations with the derivatives of the original fractions and of the hydrogenated material (see Table 2.).

Cyclisation of Hept-5-enoic Acid.—Distillation (S) of the combined ketonic material gave 13 fractions (each of 0.6 ml.), b. p. 74—75.5°/24 mm., n 1.4823—1.4776. The derivatives of fractions (2), b. p. 74—74.5°/24 mm., n 1.4823, and (13), b. p. 74.5—75.5°/24 mm., n 1.4776 (after two recrystallisations), were respectively identical with those from fractions (2) and (11) from the cyclisation of *trans*-hept-5-enoic acid (see Table 2).

²⁷ Uhlig, *Angew. Chem.*, 1954, **66**, 435.

²⁸ Linstead and Rydon, *J.*, 1933, 580.

²⁹ Reppe, Kröper, Pistor, and Weissbarth, *Annalen*, 1953, **582**, 87.

³⁰ Cornubert and Borrel, *Bull. Soc. chim. France*, 1930, **47**, 301.

TABLE 2.

Ketone	2 : 4-Dinitrophenylhydrazone (m. p.)		Semicarbazone (m. p.)	
	Obtained	Authentic	Obtained	Authentic
2-Methylcyclohex-2-enone	191—192° ^a 189—192° ^b	206—207° ^c —	199—201° ^a 200—201° ^b	205—206° —
2-Methylcyclohexanone	127—129	133—134° ^d	167—170	185—186° ^d
2-Ethylcyclopent-2-enone	216—217° ^a 218—219° ^b	219—220° ^e —	196—198° ^a 198—200° ^b	— —
2-Ethylcyclopentanone	154—156	157—160° ^{f,g}	172—175	183—184° ^f

^a From cyclisation of *trans*-hept-5-enoic acid. ^b From cyclisation of hept-6-enoic acid (see below). ^c Ref. 24. ^d From commercial ketone. From the ketone obtained by reaction of 2-ethylcyclopentanone with sulphuryl chloride.³¹ The derivative formed crimson laths from ethanol-chloroform (Found: C, 53.7; H, 4.6. C₁₃H₁₄O₄N₄ requires C, 53.8; H, 4.9%). ^e From the ketone prepared by hydrolysis of ethyl 1-ethyl-2-oxocyclopentanecarboxylate.³² ^f Golden prisms from ethanol (Found: N, 18.8. C₁₃H₁₆O₄N₄ requires N, 19.2%).

Cyclisation of trans-Oct-5-enoic Acid.—Distillation (S) of the combined ketonic material gave 16 fractions (each of 0.7 ml.), b. p. 88—91°/24 mm., *n* 1.4783—1.4744. Fraction (4), b. p. 89—89.5°/24 mm., *n* 1.4826, gave a 2 : 4-dinitrophenylhydrazone, m. p. 233—234°, and semicarbazone, m. p. 181—182°, identical with those of 2-ethylcyclohex-2-ene prepared from the enol *isobutyl* ether of 2-ethylcyclohexane-1 : 3-dione by the method of Born *et al.*²⁴ (for previous constants see ref. 34). Fraction 11, b. p. 90—90.5°/24 mm., *n* 1.4778, was accepted as 2-*n*-propylcyclopent-2-enone on the basis of its analyses (Found: C, 77.1; H, 9.5. C₈H₁₂O requires 77.4; H, 9.7%) [2 : 4-dinitrophenylhydrazone, laths, m. p. 177—178°, from ethanol-chloroform (Found: C, 54.8; H, 5.2. C₁₄H₁₆O₄N₄ requires C, 55.25; H, 5.3%); semicarbazone, plates, m. p. 217—218°, from ethanol (Found: N, 23.0. C₉H₁₅ON₃ requires N, 23.2%), its ultraviolet spectrum [λ_{\max} . 228, 319, λ_{\min} . 278 m μ (log ϵ 4.03, 1.62, and 1.09)], and hydrogenation to 2-*n*-propylcyclopentanone³⁵ which was identified (mixed m. p.s) as 2 : 4-dinitrophenylhydrazone, m. p. 154—155°, and semicarbazone, m. p. 206—207°.

Cyclisation of 5-Methylhex-5-enoic Acid.—Distillation (S) of the combined ketonic material gave the following fractions, each of 0.7 ml.: (1, 2), b. p. 93—95°/24 mm., *n* 1.4890—1.4918; (3—14), b. p. 95—95.5°/24 mm., *n* 1.4930—1.4942. The ultraviolet spectra [λ_{\max} . 224 and 310, λ_{\min} . 227 m μ (log ϵ 4.13, 1.79, 1.33)] of fractions (3) and (13) were identical with each other and with that of an authentic specimen of 3-methylcyclohex-2-enone.³⁶ The m. p.s of the derived semicarbazone (m. p. 197—198°) and 2 : 4-dinitrophenylhydrazone (m. p. 178—179°) were not depressed in admixture with authentic derivatives.

Cyclisation of 6-Methylhept-5-enoic Acid.—Distillation of the combined ketonic material gave 5 fractions, each of 0.9 ml.: b. p. 80—84°/13 mm., *n* 1.4817—1.4878. The properties of

TABLE 3.

	Fraction (1)	A ^a	Fraction (5)	B ^d
B. p./mm.	80—81°/13	84.5—85°/24	83—84°/13	91.5—92°/24
<i>n</i>	1.4817	1.4722	1.4878	1.4855
λ_{\max} (m μ) (log ϵ)	229 (4.07)	225 (4.24)	243 (3.74)	255 (4.10)
Semicarbazone, m. p.	200—206°	204—206° ^b	210—213° ^c	216—217° ^e
2 : 4-Dinitrophenylhydrazone, m. p.	207—209° [*]	202—203° ^{*e}	216—218° [*]	226—227° ^{*e}

^{*} With decomp. ^a Prepared by isomerisation of 2-isopropylidenecyclopentanone with polyphosphoric acid at 100°. ^b Meerwein³⁸ reports m. p. 203—204°. ^c Red needles from ethanol-chloroform (Found: N, 18.2. C₁₄H₁₆O₄N₄ required N, 18.4%). ^d Reported³⁹ b. p. 92°/20 mm., *n*_D²⁰ 1.4968. ^e Maroon laths from ethanol-chloroform (Found: C, 55.5; H, 5.1. C₁₄H₁₆O₄N₄ requires C, 55.25; H, 5.3%).

fractions (1), b. p. 80—81°/13 mm., *n* 1.4817, and (5) b. p. 83—84°/13 mm., *n* 1.4878, and of their derivatives (after two recrystallisations), are compared in Table 3 with those of authentic 2-isopropylcyclopent-2-enone (A) and 2-isopropylidenecyclopentanone³⁷ (B).

³¹ Cf. Warnhoff and Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 94.

³² Case and Reid, *ibid.*, 1928, **50**, 3062.

³³ Stetter and Dierichs, *Chem. Ber.*, 1952, **85**, 61; Smith, *J.*, 1953, 803.

³⁴ Birch, *J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 245; Mousseron and Jacquier, *Bull. Soc. chim. France*, 1952, **19**, 767; Jaeger and Smith, *J.*, 1955, 160; Wallach and Mendelsohn-Bartholdy, *Annalen*, 1908, **360**, 48.

³⁵ Braude and Forbes, *J.*, 1951, 1755.

³⁶ Cronyn and Riesser, *J. Amer. Chem. Soc.*, 1953, **75**, 1664.

³⁷ Vavon and Apchié, *Bull. Soc. chim. France*, 1928, **43**, 667.

³⁸ Meerwein, *Annalen*, 1914, **405**, 129.

³⁹ Kon and Nutland, *J.*, 1926, 3101.

Fractional crystallisation (from ethanol-chloroform) of the 2:4-dinitrophenylhydrazone of fraction (1) yielded maroon laths, m. p. 222—223°, and crimson needles, m. p. 206—208° (decomp.), whose m. p.s were not depressed on admixture with the derivatives of authentic 2-isopropylidene-cyclopentanone and 2-isopropylcyclopent-2-enone respectively. Repeated recrystallisation of the derivatives of fraction (5) gave the semicarbazone, m. p. 214—216°, and the 2:4-dinitrophenylhydrazone, m. p. 218—220° (decomp.), of 2-isopropylidene-cyclopentanone (identified by mixed m. p.). Hydrogenation of fractions (1) and (5) gave the same homogeneous product whose semicarbazone, m. p. 191—192°, and 2:4-dinitrophenylhydrazone, m. p. 154—155°, were not depressed in m. p. on admixture with derivatives of authentic 2-isopropylcyclopentanone.

Cyclisation of 7-Methyloct-6-enoic Acid.—The ketonic material was combined and redistilled; its properties showed it to be a mixture of 2-isopropylcyclohex-2-enone (C) and 2-isopropylidene-cyclohexanone (D). It had b. p. 95—98°/13 mm., n 1.4873, and λ_{\max} . 235—255 (broad) ($\log \epsilon$ 1.74), λ_{inf} . 3.5 μ ($\log \epsilon$ 1.81). Its heterogeneous semicarbazone, on repeated crystallisation from methanol, afforded plates, m. p. 193—194° not depressed on admixture with the derivative of (D); but its 2:4-dinitrophenylhydrazone, on crystallisation, afforded red needles, m. p. 186—192°, not depressed on admixture with the derivative of (C). 2-isoPropylcyclohex-2-enone (Found: C, 77.6; H, 10.4. $C_9H_{14}O$ requires C, 78.2; H, 10.2%), prepared from 2-isopropylcyclohexane-1:3-dione [plates (from ethyl acetate), m. p. 153—154° (Found: C, 70.2; H, 9.1. $C_9H_{14}O_2$ requires C, 70.1; H, 9.25%)] via the enol isobutyl ether by the method of Born *et al.*,²⁴ had b. p. 92—92.5°/24 mm., n 1.4773, λ_{\max} . 235, 319 ($\log \epsilon$ 3.82, 1.44), and gave a semicarbazone, prisms (from methanol), m. p. 166—167° (Found: C, 60.5; H, 8.7; N, 22.4. $C_{10}H_{17}ON_3$ requires C, 61.5; H, 8.8; N, 21.5%), and a 2:4-dinitrophenylhydrazone, red needles (from ethanol-chloroform), m. p. 190—191° (Found: C, 56.0; H, 5.6; N, 18.2. $C_{15}H_{18}O_4N_4$ requires C, 56.6; H, 5.7; N, 17.6%). 2-isoPropylidene-cyclohexanone⁴⁰ had b. p. 103.5—104.5°/24 mm. (lit., 120—125°/20 mm.), n 1.4922, λ_{\max} . 254, λ_{inf} . 305 ($\log \epsilon$ 3.80, 1.84), and gave a semicarbazone, plates (from methanol), m. p. 196—197° (lit., 184°) (Found: N, 21.3%), and a 2:4-dinitrophenylhydrazone, maroon plates (from ethanol-chloroform), m. p. 182—183° (lit., 162—163°) (Found: C, 56.4; H, 5.8%).

The 2:4-dinitrophenylhydrazone of the cyclisation product gave also a derivative (? of 2-isobutylcyclopent-2-enone), scarlet laths, m. p. 217—218° (Found: N, 17.9%).

Catalytic hydrogenation of the cyclisation product gave a mixture of saturated ketones from which the only isolable homogeneous derivative was a 2:4-dinitrophenylhydrazone (orange needles) whose m. p., 135—137°, was not depressed on admixture with the 2:4-dinitrophenylhydrazone, m. p. 137—140°, of 2-isopropylcyclohexanone.⁴¹ Smith *et al.*⁴² record m. p. 134—136°.

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⁴⁰ Mukerji, Gandhi, and Vig, *J. Indian Chem. Soc.*, 1956, **33**, 853.

⁴¹ Kotz and Michels, *Annalen*, 1906, **350**, 213.

⁴² Smith, Norton, and Ballard, *J. Amer. Chem. Soc.*, 1953, **75**, 3316.