# 37. *Reduced Cyclic Compounds. Part XI.* The Cyclisation of ω-Arylalkenoic Acids.*

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Cyclisations of 8-phenyl- and 8-*m*-methoxyphenyl-*trans*-oct-5-enoic acid and 7-phenylhept-4-enoic acid by various reagents are reported. Preparations of the two last-named acids are described.

It has been shown [1] that 8-phenyl-*trans*-oct-5-enoic acid (II; R = H) is converted into 1,2,3,7,8,9,10,10a-octahydro-7-oxocyclohepta[*de*]naphthalene (I) by the action of polyphosphoric acid and into 1,2,3,4,4a,9,10,10a-octahydro-1-oxophenanthrene (IV; R = H) by the action of aluminium chloride on the derived acid chloride. The use of alternative reagents in the latter reaction is now reported and the reaction has been applied to the cyclisation of 8-*m*-methoxyphenyl-*trans*-oct-5-enoic acid and 7-phenylhept-4-enoic acid. The latter has also been cyclised with polyphosphoric acid.

It was considered that the yield of ketone (IV; R = H) from the acid (II; R = H) would parallel the ease of formation of the derived acylium ion. Thus it is known, for

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* Part X, preceding paper.

[1] Ansell and Brown, *J.*, 1958, 3956.

example, that acetylium complexes are more ionic than benzoylium complexes and the former give the higher yields in acylation reactions.[2] Acylium ions are conveniently obtained from mixed anhydrides, the polarity of which ranges from the covalent acyl trifluoroacetates,[3] *via* the acyl perchlorates [4] which are largely ionised even in non-polar solvents, to the purely ionic tetrafluoroborates.[5] These mixed anhydrides are readily prepared by the action of the silver salt of the strong acid on an acyl halide. Thus those silver salts which have been used [6] to promote the intramolecular acylation of ω-arylalkanoyl chlorides, may be used to promote the intramolecular acylation of suitably constituted ω-arylalkenoyl chlorides. The accompanying Table shows the results obtained with 8-phenyl-*trans*-oct-5-enoic acid.

*Cyclisation of 8-phenyl-*trans*-oct-5-enoyl chloride.*

| Cyclising reagent | Solvent | Product (% yield) | | |
|---|---|---|---|---|
| | | (IV; R = H) | (III; R = H) | Lactone |
| $CF_3{\cdot}CO_2Ag$ | $Et_2O$ | | | 34 |
| $C_3F_7{\cdot}CO_2Ag$ | $Et_2O$ | | 10 | |
| $AgClO_4$ | $MeNO_2$ | 30 | | 28 |
| $AgBF_4$ | $Et_2O$ | | 10 | 18 |
| $AgBF_4$ | $MeNO_2$ | 36 | | 16 |
| $CH_3{\cdot}CO{\cdot}BF_4$ | $CHCl_3$ | 26 | | 17 |
| $CH_3{\cdot}COBF_4$ * | $CHCl_3$ | 45 | | 14 |
| $AlCl_3$ † | $CS_2$ | 17 | | |

* On the acid. † See ref. 1.

From the Table it can be seen that, of the silver salts, the perchlorate and tetrafluoroborate are the most effective. However, the nature of the solvent is important: thus, silver tetrafluoroborate in ether produces 2-phenethylcyclohex-2-enone (III; R = H) but in the more polar nitromethane " double cyclisation " to the octahydrophenanthrone (IV; R = H) occurs. Cyclisation of the free acid (II; R = H) with acetyl tetrafluoroborate gave better yields than those obtained with the acid chloride, although acetyl tetrafluoroborate is known [5b] to be an effective acetylating agent.

It is evident that the reaction:

$$\text{(II)}\quad R{\cdot}CO_2H + AcBF_4 \rightleftharpoons AcOH + R{\cdot}CO^+BF_4^- \longrightarrow \text{(IV)}$$

competes very favourable with the acetylation. A similar absence of acetylation is reported by Seel [5a] in the formation of triphenylmethyl tetrafluoroborate from triphenylmethyl chloride and acetyl tetrafluoroborate.

In the cyclisations in which the tricyclic ketone (IV) was formed the product was identical with that obtained by Ansell and Brown,[1] who assigned to it a *trans*-configuration on the basis of the known [7] preferential stability of the *trans*-configuration in the *as*-octahydrophenanthrene series. However, an apparently identical ketone, to which has been assigned a *cis*-configuration, has been obtained by reduction of the unsaturated ketone (V) with lithium in liquid ammonia.[8] Thus the stereochemistry of the ketone obtained in the present work is not, at present, certain.

The infrared spectrum of the lactonic material from these cyclisations showed absorption consistent with its having a six-membered lactone ring and a monosubstituted benzene ring, and was therefore considered to be the lactone of 5-hydroxy-8-phenyloctanoic acid.

[2] Seel and Bauer, *Z. Naturforsch.*, 1947, **2**b, 397; Smorganzkii, *J. Gen. Chem. U.S.S.R.*, 1951, **21**, 723; Cauquil, H. Barrera, and R. Barrera, *Bull. Soc. chim. France*, 1953, 1111.

[3] Bourne, Randles, Stacey, Tatlow, and Tedder, *J. Amer. Chem. Soc.*, 1954, **76**, 3206.

[4] Burton and Prail, *J.*, 1950, 2034.

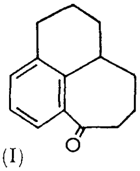
[5] (*a*) Seel, *Z. anorg. Chem.*, 1943, **250**, 331; (*b*) Olah and Kuhn, *Chem. Ber.*, 1956, **89**, 866; (*c*) Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 722.

[6] Burton and Munday, *J.*, 1957, 1718.

[7] Cook, McGinnis, and Mitchell, *J.*, 1944, 286.

[8] Dr. Herchel Smith, personal communication.

Cyclisation of 8-*m*-methoxyphenyl-*trans*-oct-5-enoic acid (II; R = MeO) was accomplished in a low yield by the action of silver perchlorate or tetrafluoroborate on the acid chloride. The product was pure *trans*-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-oxophenanthrene (IV; R = MeO), identical with that obtained[9] by reduction of the ketone (V; R = MeO) followed by epimerisation. The infrared spectrum of crude cyclisation product gave no indication of the presence of the *cis*-isomer, but showed the presence of a small amount of an αβ-unsaturated ketone, presumably 2-3′-methoxyphenethylcyclohex-2-enone (III; R = MeO). The infrared spectrum of the lactonic cyclisation product showed absorption consistent with a 6-membered lactone and a 1,3-disubstituted benzene ring.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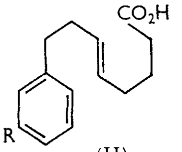
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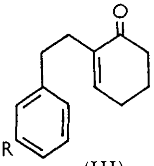
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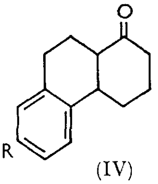
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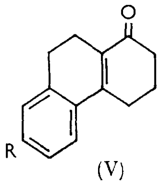
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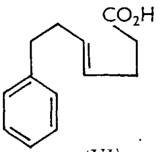
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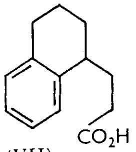
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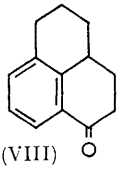
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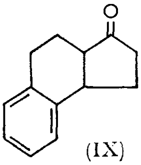
(IX)

Cyclisation of 7-phenylhept-4-enoic acid (VI) with polyphosphoric acid occurred, as expected, to yield 2,3,3a,4,5,6-hexahydroperinaphthen-1-one (VIII), presumably *via* the bicyclic acid (VII) which is known[10] to cyclise in this manner. When, however, the phenylheptenoyl chloride was cyclised with aluminium chloride, silver perchlorate, or silver tetrafluoroborate, the known[11] 1,2,3,3a,4,5-hexahydrobenz[*e*]indan-3-one (IX) was obtained in low yield, together with a trace of an αβ-unsaturated ketone, 2-phenethylcyclopent-2-enone. This constitutes the first example of the formation of a five-membered ring in a " double cyclisation," as Ansell and Brown[1] could not cyclise *trans*-7-1′ naphthylhept-4-enoic acid in this way. From the heterogeneous lactonic cyclisation product a solid was isolated whose infrared spectrum showed absorption characteristic of a 6-membered lactone and a monosubstituted benzene, and was therefore 5-hydroxy-7-phenylheptanoic lactone. The remaining liquid lactonic material showed, in addition to the characteristic absorption of the solid lactone, absorption characteristic of a five-membered lactone, and was therefore a mixture of the solid lactone and 4-hydroxy-6-phenylhexanoic lactone.

Of the acids described above, the preparation of 8-phenyl-*trans*-oct-5-enoic acid has been previously described.[1] The 8-*m*-methoxyphenyl-*trans*-oct-5-enoic acid was prepared in an analogous manner from 3′-methoxyphenethyl chloride. The report[12] that the preparation of this chloride by the action of thionyl chloride in the presence of pyridine on the parent alcohol gives inconsistent results has been confirmed and we have prepared the chloride by the action of lithium chloride on the corresponding toluene-*p*-sulphonate. An attempt to utilise 3′-methoxyphenethyl bromide was unsuccessful as this compound forms 1,4-di-(*m*-methoxyphenyl)butane to a considerable extent during the preparation of the

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[9] Birch, Smith, and Thornton, *J.*, 1957, 1339.
[10] W. S. Johnson, H. C. E. Johnson, and Peterson, *J. Amer. Chem. Soc.*, 1945, **67**, 1360.
[11] Mathieson, *J.*, 1953, 3248.
[12] Bergmann and Weizmann, *J. Org. Chem.*, 1939, **4**, 266.

derived Grignard reagent (cf. ref. 13). 7-Phenylhept-4-enoic acid was prepared from 6-phenylhex-3-en-1-ol [14] by carboxylation of the Grignard reagent derived from the corresponding chloride.

The preparation of 2-phenethylcyclohex-2-enone by the general method of Born, Pappo, and Szmuzkovicz [15] is described.

## EXPERIMENTAL

Refractive indices were taken at 20°.

1-*Chloro*-6-*phenylhex*-3-*ene*.—Thionyl chloride (36 g., 0·3 mole) was added in *ca.* 30 min. to a stirred, boiling solution of 6-phenylhex-3-en-1-ol [14] (51 g., 0·27 mole) and pyridine (0·5 ml.) in benzene (350 ml.). The mixture was then boiled until vigorous evolution of gas ceased, cooled, and poured on ice, and the organic layer was separated, washed with water, saturated sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated. Distillation gave 1-*chloro*-6-*phenylhex*-3-*ene* (42 g., 74%), b. p. 76—80°/0·1 mm., $n_D$ 1·5273 (Found: Cl, 18·4. $C_{12}H_{15}Cl$ requires Cl, 18·2%).

7-*Phenylhept*-4-*enoic Acid*.—This *acid* was prepared from the above chloride by the method described [1] for 8-phenyloct-5-enoic acid, a 75% yield being obtained on an 0·2-molar scale. The product had b. p. 100—110°/0·02 mm., $n_D$ 1·5216 (Found: C, 76·2; H, 8·0. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%). The derived acid chloride, prepared as for 8-phenyloct-5-enoyl chloride,[1] resinified on distillation and was not obtained analytically pure.

3′-*Methoxyphenethyl Chloride*.—3′-Methoxyphenethyl toluene-*p*-sulphonate [16] (1140 g., 3·7 moles) was added to a warm (60°) stirred solution of lithium chloride (210 g., 4·9 moles) in 2-ethoxyethanol (2 l.), and the mixture heated on a steam-bath for 4 hr. and then evaporated under reduced pressure. Enough water (*ca.* 1 l.) was added to dissolve the precipitated lithium salts. The organic layer was separated and the aqueous layer extracted with ether (2 × 300 ml.). Distillation of the dried ($MgSO_4$) combined organic material gave 3′-methoxyphenethyl chloride (514 g., 76%), b. p. 86—87°/0·4 mm., $n_D$ 1·5332 (Found: C, 63·7; H, 6·6; Cl, 20·6. Calc. for $C_9H_{11}ClO$: C, 63·4; H, 6·5; Cl, 20·7%) (lit.,[13] b. p. 85—87°/1·5 mm.).

cis- *and* trans-3-*Chlorotetrahydro*-2-3′-*methoxyphenethylpyran*.—This *compound*, b. p. 130—162°/0·4 mm., $n_D$ 1·5312—1·5350 (Found: Cl, 13·6. $C_{14}H_{19}ClO_2$ requires Cl, 13·9%), was prepared (94%) from 3′-methoxyphenethylmagnesium chloride (2·65 moles) and 2,3-dichlorotetrahydropyran (2·0 moles) as described [14] for 3-chlorotetrahydrophenethylpyran.

trans-7-3′-*Methoxyphenylhept*-4-*en*-1-*ol*.—This *alkenol*, b. p. 132—137°/0·2 mm., $n_D$ 1·5273 (Found: C, 76·1; H, 9·4. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·1%), was prepared (50% on a 2-molar scale) from the above chloro-ether as described [14] for *trans*-7-phenylhept-4-en-1-ol. The derived α-*naphthylurethane* [tablets from light petroleum (b. p. 60—80°)] had m. p. 72—73° (Found: N, 3·9. $C_{25}H_{27}O_3N$ requires N, 3·6%).

trans-1-*Chloro*-7-m-*methoxyphenylhept*-3-*ene*.—The above alcohol (110 g., 0·5 mole) was added dropwise to a stirred suspension of toluene-*p*-sulphonyl chloride (95 g., 0·5 mole) in pyridine (62 g.), kept at 20°. The mixture was then poured on ice (200 g.) and extracted with ether (2 × 75 ml.). The extracts were washed with 6N-sulphuric acid (2 × 50 ml.), water (2 × 50 ml.), saturated sodium hydrogen carbonate solution (2 × 50 ml.), and again water (50 ml.) and dried ($MgSO_4$). The crude toluene-*p*-sulphonate left on removal of the solvent was converted into trans-1-*chloro*-7-3′-*methoxyphenylhept*-3-*ene* (105 g., 88%), b. p. 132—136°/0·6 mm., $n_D$ 1·5234 (Found: C, 70·3; H, 7·9; Cl, 14·7. $C_{14}H_{19}ClO$ requires C, 70·4; H, 8·0; Cl, 14·9%), as described above for 3′-methoxyphenethyl chloride.

trans-8-m-*Methoxyphenyloct*-5-*enoic Acid*.—This *acid*, b. p. 174—177°/0·1 mm., $n_D$ 1·5195 (Found: C, 72·3; H, 7·9. $C_{15}H_{20}O_3$ requires C, 72·5; H, 8·0%), was prepared (15% on a 0·38-molar scale) as for 8-phenyl-*trans*-oct-5-enoic acid.[1] This acid was thermally unstable and only a small sample was distilled; the remainder was used in the crude state. The derived acid chloride, prepared as for 8-phenyl-*trans*-oct-5-enoyl chloride decomposed above 60° and was not distilled. The derived *amide* [plates from light petroleum (b. p. 40—60°)] had m. p. 73—74° (Found: C, 72·8; H, 8·7; N, 5·5. $C_{15}H_{21}NO_2$ requires C, 72·8; H, 8·6; N, 5·7%).

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[13] Johnson, Bannerjee, Schneider, Gutsche, Shelberg, and Chinn, *J. Amer. Chem. Soc.*, 1952, **74**, 2832.

[14] Ansell and Selleck, *J.*, 1956, 1238.

[15] Born, Pappo, and Szmuszkovicz, *J.*, 1953, 1779.

[16] Nelson and Wollensak, *J. Amer. Chem. Soc.*, 1958, **80**, 6626.

*General Cyclisation Procedure.*—A solution of the acid chloride (0·05 mole) in dry solvent (50 ml.) was added to one of the cyclising agent (0·05 mole) in the same solvent (50—60 ml.) at 0°. Silver chloride was immediately precipitated, and the mixture was shaken intermittently at room temperature for 30 min. and then filtered on to crushed ice. The silver chloride was washed with water (20 ml.) and solvent (20 ml.). The aqueous phase was separated and extracted with ether (50 ml.), and the combined organic solutions were washed with saturated sodium hydrogen carbonate solution (2 × 50 ml.), then with water, and dried ($MgSO_4$), and the solvent was removed. The crude product, Girard's reagent P (8 g.), glacial acetic acid (8 ml.), and ethanol (80 ml.) were boiled under reflux for 2 hr.; the mixture was then cooled, and a solution of sodium hydroxide (4·8 g.) in water (400 ml.) added. The mixture was extracted with ether (3 × 100 ml.) to remove non-ketonic material. Concentrated hydrochloric acid (50 ml.) was added to the aqueous phase, which was left at room temperature for 12 hr. and then extracted with ether (4 × 100 ml.). The latter solution was dried ($MgSO_4$) and distilled to yield the ketonic fraction.

*Cyclisation of 8-Phenyl-*trans*-oct-5-enoyl Chloride.*—(a) *With silver trifluoroacetate*[17] *in ether* (0·045-*molar scale*). The ketonic product (1·6 g., 19%), b. p. 115—125°/0·1 mm., formed a heterogeneous 2,4-dinitrophenylhydrazone (red crystals and yellow crystals) which could not be separated. The non-ketonic product (3·4 g., 34%), b. p. 136—137°/0·4 mm., $n_D$ 1·5155, was soluble in warm 2N-sodium hydroxide, and its infrared spectrum showed absorption at 5·85, 13·45 and 14·35 μ characteristic of a 6-membered lactone and a monosubstituted benzene. So the product was accepted as *5-hydroxy-8-phenyloctanoic lactone* (Found: C, 77·9; H, 8·5. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%). The lactonic material obtained in the other cyclisations was essentially similar.

(b) *With silver perfluorobutyrate in ether* (0·05-*molar scale*). The ketonic fraction (1 g., 10%), b. p. 108—110°/0·3 mm., $n_D$ 1·5582, was identified as 2-phenethylcyclohex-2-enone. The derived 2,4-dinitrophenylhydrazone had m. p. and mixed m. p. 155—157° (for authentic constants see below).

(c) *With silver perchlorate in nitromethane* (0·035-*molar scale*). The ketonic material (2·1 g., 30%), b. p. 116—118°/0·1 mm., $n_D$ 1·5581, partially solidified to yield 1,2,3,4,5a,9,10,10a-octahydro-1-oxophenanthrene, m. p. and mixed m. p. (with sample of Ansell and Brown's material) 76—77°. Smith[8] reports m. p. 74—77° for the *cis*-isomer. The infrared spectrum of the liquid product showed, in addition to the absorption due to the octahydro-1-oxo-phenanthrene, absorption at 5·95, 13·45, and 14·35 μ as in the spectra of a cyclohex-2-enone and a monosubstituted benzene (attributable to 2-phenethylcyclohex-2-enone). The 2,4-dinitrophenylhydrazone derived either from the liquid before solidification or from the solid product had (after two recrystallisations) m. p. and mixed m. p. 221—224° (lit.,[1] 221—224°). The derived semicarbazone had m. p. and mixed m. p. 218—220° (lit.,[1] 218—219°).

(d) *With silver tetrafluoroborate*[18] *in ether* (80 ml.) (0·046-*molar scale*). The ketonic fraction (0·9 g., 10%), b. p. 134—140°/0·4 mm., $n_D$ 1·5566, was essentially 2-phenethylcyclohex-2-enone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 115—117°).

(e) *With silver tetrafluoroborate in nitromethane* (50 *ml.*) (0·03-*molar scale*). The ketonic fraction (2·2 g., 36%), b. p. 120—126°/0·2 mm., partially solidified to yield 1,2,3,4,4a,9,10,10a-octahydro-1-oxophenanthrene, m. p. and mixed m. p. 76—77°. The presence of 2-phenethylcyclohex-2-enone in the residual liquid product was detected spectroscopically.

(f) *With acetyl tetrafluoroborate*[5a] *in chloroform* (0·04-*molar scale*) *initially at* −10°, *then* 10 *min. at room temperature.* The properties of the ketonic and the lactonic fraction were as in the previous experiment (see Table for yields).

(g) *With acetyl tetrafluoroborate and the free acid* (0·046-*molar scale*), *as in the previous experiment.* The properties of the ketonic and the lactonic material were as in the previous experiment (see Table for yields).

*Cyclisation of 8-*m*-Methoxyphenyl-*trans*-oct-4-enoic Acid.*—This acid (0·016 mole) was cyclised by the above general method, with silver perchlorate in nitromethane. The crude ketonic material (15%) was dissolved in 4 : 1 light petroleum (b. p. 60—80°)-benzene and adsorbed on fuller's earth. Elution with chloroform gave *trans*-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-oxophenanthrene, m. p. 109—110° after crystallisation from light petroleum (b. p. 60—80°) (lit.,[9] m. p. 111°). The derived 2,4-dinitrophenylhydrazone (yellow tablets

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[17] Crawford and Simons, *J. Amer. Chem. Soc.*, 1955, **77**, 2605.

[18] Sharpe, *J.*, 1952, 4538; Clifford and Kongpricha, *J. Inorg. Nuclear Chem.*, 1957, **5**, 76.

from ethanol–chloroform) had m. p. 208—209° (lit.,[19] m. p. 208—209°). The use of silver tetrafluoroborate gave essentially the same result.

The infrared spectrum of the crude material showed absorption at 5·95 μ characteristic of an αβ-unsaturated ketone (2-3′-methoxyphenethylcyclohexene) but no absorption at 11·6 μ characteristic [9] of the *cis*-octahydro-1-oxophenanthrene.

*Cyclisation of* 7-*Phenylhept*-4-*enoyl Chloride*.—(*a*) This was done with aluminium chloride on a 0·05-molar scale as described [1] for the comparable cyclisation of 8-phenyloct-5-enoic acid, followed by treatment with Girard's reagent P as described in the general cyclisation procedure. Distillation of the ketonic product gave essentially 1,2,3,3a,4,5-hexahydrobenz[*e*]indan-3-one (1·5 g., 17%), b. p. 100—107°/0·1 mm. The derived 2,4-dinitrophenylhydrazone (pale orange plates from chloroform–ethanol) had m. p. 214—215°, and the semicarbazone (needles from ethanol) had m. p. 230—231° (both m. p.s after two recrystallisations). Mathieson [11] records b. p. 135—140°/6 mm. and m. p.s 214—215° and 231—235° respectively. The infrared spectrum of the cyclisation product showed absorption at 5·7 and 13·3 μ as in the spectra of 5-membered cycloalkanones and 1,2-disubstituted benzene, together with absorption at 5·9, 13·45, and 14·3 μ as in the spectra of cyclopent-2-enones and monosubstituted benzenes, indicating the presence of 2-phenethylcyclopent-2-enone.

(*b*) Cyclisation with acetyl tetrafluoroborate on a 0·05-molar scale by the above general method gave a 3% yield of unidentified ketonic product, together with a 75% yield of lactonic material, from which a solid separated. The solid was identified as 5-*hydroxy*-7-*phenylheptanoic lactone* [needles from light petroleum (b. p. 40—60°)], m. p. 53—54° (Found: C, 76·4; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·9%). Its infrared spectrum showed absorption at 5·86, 13·45, and 14·3 μ, characteristic of a 6-membered lactone and a monosubstituted benzene. The residual liquid lactonic material (Found: C, 76·3; H, 7·8%) showed absorption at 5·78, 5·86, 13·45, and 14·3 μ indicative of a mixture of the γ- and δ-lactone. The ketonic material obtained on cyclisation with either silver perchlorate (12% on an 0·03-molar scale) or silver tetrafluoroborate (20% on an 0·025-molar scale) was essentially the same as that obtained with aluminium chloride. In the latter ($AgBF_4$) experiment a mixture of γ- and δ-lactones was also obtained.

*Cyclisation of* 7-*Phenylhept*-4-*enoic Acid with Polyphosphoric Acid*.—A stirred mixture of polyphosphoric acid (30 g.) and 7-phenylhept-4-enoic acid (3 g.) was heated at 60—70° for 20 min. and then rapidly cooled. Ice-water (60 ml.) was added and the mixture extracted with ether (2 × 60 ml.). The ethereal extract was washed with sodium hydrogen carbonate solution (60 ml.) and water (60 ml.), dried $MgSO_4$), and evaporated to yield crude 2,3,3*a*,4,5,6-hexahydroperinaphthen-1-one (1·9 g., 70%), m. p. 67—70°. One crystallisation (from ethanol) yielded the pure ketone (as laths), m. p. 71—72°. The derived semicarbazone (tablets from ethanol–pyridine) had m. p. 231—232°; the derived oxime (needles from ethanol) had m. p. 161—162°; and the derived 2,4-*dinitrophenylhydrazone* (crimson plates from ethanol–chloroform) had m. p. 255—256° (Found: C, 62·4; H, 5·0; N, 15·4. $C_{19}H_{18}N_4O_4$ requires C, 62·3; H, 4·9; N, 15·3%). The recorded constants are: ketone [13] m. p. 69·7—70°, oxime [20] m. p. 159—160°, semicarbazone [13] m. p. 230·5—231·7°.

2-*Phenethylcyclohex*-2-*enone*.—A solution of 2-phenethylcyclohexane-1,3-dione [21] (5·5 g.) and toluene-*p*-sulphonic acid monohydrate (0·5 g.) in isobutyl alcohol (10 ml.) and benzene (20 ml.) was heated under reflux for 6 hr., the water formed in the reaction being removed by a Dean and Stark separator. The cold mixture was washed with 5% sodium hydrogen carbonate solution (10 ml.), 5% sodium hydroxide solution (3 × 10 ml.), and water (10 ml.) and dried ($MgSO_4$), the solvent removed, and the residue distilled to yield 3-*isobutoxy*-2-*phenethylcyclohex*-2-*enone* (4·7 g., 80%), b. p. 131—136°/0·2 mm., m. p. 69—70° (unrecrystallised) (Found: C, 78·8; H, 8·8. $C_{18}H_{24}O_2$ requires C, 79·3; H, 8·8%). A solution of the latter (4·0 g.) in ether (10 ml.) was added to a stirred suspension of lithium aluminium hydride (0·3 g.) in ether at such a rate that steady refluxing was maintained. The mixture was stirred for a further 15 min., then cooled to 0°, and sufficient (*ca.* 25 ml.) of 10% sulphuric acid added to yield two clear phases. The aqueous phase was continuously extracted with ether for 20 hr. Distillation of the combined dried ($MgSO_4$) ethereal solutions gave 2-phenethylcyclohex-2-enone (1·3 g.), b. p. 102—105°/0·4 mm., $n_D^{20}$ 1·5570 (Found: C, 84·0; H, 7·9. Calc. for $C_{14}H_{16}O$: C, 84·0; H, 8·0%). The derived semicarbazone (needles from ethanol) had m. p. 188—189°, and the 2,4-*dinitrophenylhydrazone* (red

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[19] Robinson and Walker, *J.*, 1936, 747.

[20] von Braun and Reutter, *Ber.*, 1926, **59**, 1922.

[21] Birch and Smith, *J.*, 1951, 1882; Stetter and Dierichs, *Chem. Ber.*, 1952, **85**, 61.

laths from ethanol–chloroform) had m. p. 155—157° (Found: C, 62·6; H, 5·4; N, 15·3. $C_{20}H_{20}N_4O_4$ requires C, 63·1; H, 5·3; N, 14·8%). Cohen and Cook [22] record this compound as a highly refractive liquid, b. p. 125—130°/0·7 mm. [semicarbazone, m. p. 188—189°).

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[22] Cohen and Cook, *J.*, 1935, 1570.