261. *Syntheses of Polycyclic Systems. Part III.* Some Hydroindanones and Hydrofluorenones. The Mechanism of the Nazarov Cyclisation Reaction.*

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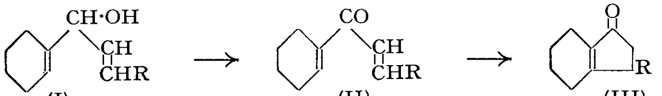
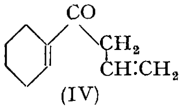
Oxidation of 1-*cyclo*hex-1′-enylalken-1-ols (I) (*J.*, 1950, 2014) with manganese dioxide affords the alkenyl *cyclo*hexenyl ketones (II) which undergo cyclisation with phosphoric acid to tetrahydro-indanones (III). Di*cyclo*hexenyl ketone (V) under similar conditions gives decahydrofluorenone (VI) (probably *cis*), which is catalytically hydrogenated to *syn*-perhydrofluorenone (probably *cis-cis*). The mechanism of the cyclisation reaction is discussed.

A VERSATILE route to hydroaromatic structures containing five-membered rings, which has been explored within recent years by Nazarov and his co-workers (cf. *Bull. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1946, 633; 1947, 205; *J. Gen. Chem. Russia*, 1950, **20**, 2009), consists in the cyclisation of substituted allyl vinyl ketones in the presence of moderately strong acids. For instance, allyl *cyclo*hexenyl ketone (IV) is converted into 4 : 5 : 6 : 7-tetrahydro-3-methylindanone (III; R = Me) on treatment with phosphoric and formic acids. Theoretical considerations, which are discussed below, suggested that the corresponding substituted divinyl ketones (*e.g.*, II) should similarly give the same products. Such ketones have recently become readily accessible by direct alkenylation with lithium alkenyls (Braude and Coles, *J.*, 1950, 2012, 2014), and, in the present paper, the cyclisation of three of them is described.



(I) (II) (III)



(IV)

*cyclo*Hexenyl vinyl and propenyl ketones (II; R = H and Me) were conveniently prepared by manganese dioxide oxidation (cf. Weedon and Woods, *J.*, 1951, 2687; Braude and Forbes, *ibid.*, p. 1755) of the corresponding carbinols (I; R = H and Me), previously obtained by the reaction of *cyclo*hexenyl-lithium with acraldehyde and crotonaldehyde respectively (Braude and Coles, *loc. cit.*). The ketones exhibited the expected ultra-violet light absorption properties (see Table) and were characterised by their 2 : 4-dinitrophenylhydrazones. A mixture of phosphoric and formic acids, under conditions identical with those employed by Nazarov and Pinkina (*loc. cit.*, 1947), converted them, in 50—70% yields, into the tetrahydroindanones (III; R = H and Me).

The position of the ethylenic bond in the tetrahydroindanones follows from their ultra-violet light absorption characteristics (see Table): the presence of maxima at 2370 and 3000 Å shows that the double bond is conjugated with the carbonyl group; the fact that the location of the high-intensity band is entirely unaffected by the introduction of a 3-methyl substituent excludes the 2 : 3-position (as in VIII, see below), and the fact that $\lambda_{max.}$ lies below 2400 Å excludes the 7 : 8-position (cf. Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 76); the 8 : 9-position is thus the only possible one. As in the case of other *cyclo*pentenones (cf. Gillam and West, *J.*, 1942, 486; Frank, Armstrong, Kwiatek, and Price, *J. Amer. Chem. Soc.*, 1948, **70**, 1379; Crombie and Harper, *J.*, in the press) the high-intensity bands of the indanones (III) lie at considerably *shorter* wave-lengths than those of the corresponding open-chain analogues; on the other hand, the positions of the characteristic maxima of the 2 : 4-dinitrophenylhydrazones are quite normal (Braude and Jones, *J.*, 1945, 498).

4 : 5 : 6 : 7-Tetrahydroindanone has previously been synthesised in low yield by cyclisation of β-*cyclo*hexenylpropionic acid (Nenitzescu and Przemetzky, *Ber.*, 1941, **74**, 676; Mathieson, *J.*, 1951, 177), as well as of the corresponding succinic half-ester (Johnson, Davis, Hunt, and Stork, *J. Amer. Chem. Soc.*, 1948, **70**, 3021). Since the completion of the present work, Nazarov and Pinkina's synthesis of 4 : 5 : 6 : 7-tetrahydro-3-methylindanone

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* Part II, *J.*, 1951, 3117.

has been re-examined by Hamlet, Henbest, and Jones (*J.*, 1951, 2653) who showed that extensive cyclisation of (IV) already takes place during its formation by the hydration of 4-*cyclo*hexenylbut-1-en-3-yne in the presence of mercuric oxide and sulphuric acid. These authors also determined the light-absorption properties of the ketones (III) with results similar to those obtained here. The identity of the tetrahydromethylindanones obtained by the two routes was confirmed by the mixed melting points of the 2 : 4-dinitrophenylhydrazones; we are indebted to Professor E. R. H. Jones and Dr. H. B. Henbest for kindly providing a sample.

Light absorption data.

	Dialkenyl ketone *		2 : 4-Dinitrophenylhydrazone †	
	$\lambda_{max.}$, Å	ε	$\lambda_{max.}$, Å	ε
(II; R = H)	2510	7 500	3850	21 500
	3300	30		
(II; R = Me)	2570	14 600	3860	29 400
	3280	80		
(V)	2420	16 500	3880	30 600
	3190	90		
	*cyclo*Pentenone *		2 : 4-Dinitrophenylhydrazone †	
(III; R=H)	2370	12 500	3900	27 500
	3000	50		
(III; R = Me)	2370	12 500	3920	26 400
	3020	60		
(VI)	2400	12 500	3980	25 500
	3040	70		

* In ethanol solution (the weak long-wave-length bands appear as inflections).
† In chloroform solution (main band only).

As a further example, di*cyclo*hexenyl ketone (V), obtained by the reaction of *cyclo*hexenyl-lithium with carbon dioxide (Braude and Coles, *loc. cit.*), has been cyclised to the decahydrofluorenone (VI), a low-melting solid. Catalytic dehydrogenation of the latter in the presence of palladised charcoal at 300° afforded fluorene but no trace of fluorenone; reduction of keto-groups accompanying dehydrogenation under similar conditions has been observed in a number of other cases (cf. Linstead and Michaelis, *J.*, 1940, 1134; Newman and Zahm, *J. Amer. Chem. Soc.*, 1943, **65**, 1097). Catalytic hydrogenation of (VI) in the presence of platinic oxide gave a liquid perhydrofluorenone. Its crystalline oxime was identical (mixed melting point) with that of the *syn*-perhydrofluorenone obtained by Davis, Doering, Levine, and Linstead (*J.*, 1950, 1423) by the pyrolysis of *syn*-perhydrodiphenic acids; we are indebted to Professor R. P. Linstead for kindly providing a sample.

Davis *et al.* (*loc. cit.*) were not able to decide the steric orientation of the 10- and the 13-hydrogen atom in their *syn*-perhydrofluorenone, but a tentative assignment can now be made. Catalytic hydrogenation of the 12 : 13-ethylenic bond in the decahydrofluorenone (VI) most probably involves *cis*-addition in the normal manner,* so that the 12 : 13-ring-junction in the *syn*-perhydrofluorenone will be *cis*. Furthermore, the fact that only *one* perhydrofluorenone appears to be formed indicates that the 10 : 11-ring junction in the antecedent decahydrofluorenone (the homogeneity of which is not in doubt) and, therefore, in the perhydrofluorenone, is also *cis*, as shown. *cis*-Decahydrofluorenone (VI) will be preferentially adsorbed owing to catalyst hindrance (Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985) in such a way that the two unsaturated rings are nearly flat, with the 10 : 11-hydrogen atoms directed towards, and the saturated ring directed away from, the catalyst surface; addition of hydrogen to the 12 : 13-bond will thus take place on the same side as the 10 : 11-hydrogen atoms, giving *cis-syn-cis*-perhydrofluorenone (VII). If, on the other hand, the ring junction in the decahydrofluorenone were *trans*, very little steric preference would be expected for either of the two possible modes of accommodation on the catalyst and a mixture of *syn-* and *anti*-perhydrofluorenones should result. It is interesting that the probable production of a *cis*-ring-junction in the cyclisation of (V) to (VI) is paralleled by the formation of *cis*-decalin derivatives in the somewhat related cyclisation of diolefins (Hibbit, Linstead, and Millidge, *J.*, 1936, 470, 476; Elliott and Linstead, *J.*, 1938, 662).

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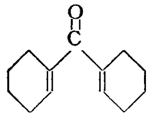
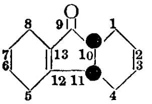
* *trans*-Addition in the hydrogenation of $\alpha\beta$-ethylenic ketones has been observed under special conditions (cf. Weidlich, *Chemie*, 1945, **58**, 30).

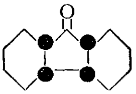
The present results provide some evidence concerning the mechanism of the cyclisation of diethylenic ketones. This reaction closely resembles the acid-catalysed cyclisation of diethylenic hydrocarbons (cf. Linstead *et al.*, *loc. cit.*, 1938; Stevens and Spalding, *J. Amer. Chem. Soc.*, 1949, **71**, 1687, and earlier references there cited), of benzenoid hydrocarbons

(V)



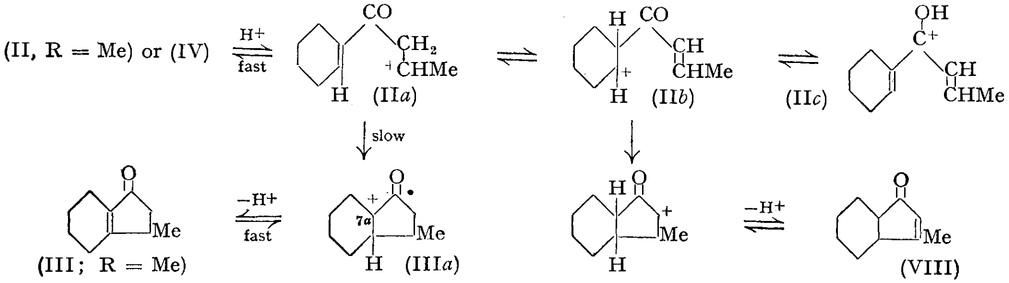


(VI)



(VII)

containing an ethylenic side chain (cf. Bogert *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 185; 1935, **57**, 151; *J. Org. Chem.*, 1936, **1**, 288; 1941, **6**, 105, and references there cited), and, more particularly, of ψ-ionone to α- and β-ionone (cf. Hibbert and Cannon, *J. Amer. Chem. Soc.*, 1924, **46**, 126), but it appears to take place somewhat less readily. There can be little doubt that the prime function of the acid medium in all these reactions is that of proton-donor, and that the ethylenic compound, acting as a weak base, is partly converted into a carbonium ion by reversible addition of one or more protons. The facts that the ketones (II) and (IV) give the same product and react with comparable rates are consistent with the formulation of the intermediate as (II*a*); the subsequent steps of the reaction consist of the formation of the new carbon–carbon link accompanied by the transference of the positive charge to $C_{(7a)}$ and the reversible loss of a proton from the new carbonium ion (III*a*). In the ethylenic ketones, the carbonyl group will compete as a basic centre with the ethylenic groups and deactivate the latter, but although the ion (II*c*) in which the proton is attached to the carbonyl group may predominate, (II*a*) will exist in equilibrium with it, as well as with the corresponding ion (II*b*) in which the proton is attached to the *cyclo*hexenyl group. The deactivating effect of the keto-group is clearly shown by the fact that the Nazarov cyclisation of dialkenyl ketones occurs less readily than the related reactions mentioned above, and also by the direction of cyclisation of ψ-ionone, which leads to the disappearance of the *unconjugated* double bond. Cyclisation of (II*b*) would lead to the ketone (VIII); since none of the latter is detected, the rate of cyclisation of (II*a*) must be rather faster than that of (II*b*), or, as appears more likely, the equilibrium proportion of (II*a*) must be considerably higher than that of (II*b*). This leads to the conclusion that the basicity of the propenyl group must be greater than that of the *cyclo*hexenyl group and, since (III; R = H) appears to be the sole product from the lower homologue, the same applies to the vinyl group.



EXPERIMENTAL

(M. p.s marked K were determined on a Kofler block and are corrected. For light absorption data, see Table.)

cyclo*Hex*-1-*enyl Vinyl Ketone*.—1-*cyclo*Hex-1′-enylprop-2-en-1-ol (10 g.; Braude and Coles, *J.*, 1950, 2014), light petroleum (b. p. 40—60°; 1 l.; distilled from sodium) and manganese dioxide (100 g.; vacuum-dried) were shaken together for 3 days in a brown, glass-stoppered bottle in an atmosphere of nitrogen. After filtration, the solvent was distilled off through an 8″ Fenske column, and the product was fractionated, giving the *ketone* (9 g.), b. p. 47—48°/0·1 mm., n_D^{23} 1·5100 (Found: C, 79·4; H, 9·3. $C_9H_{12}O$ requires C, 79·4; H, 8·9%). The 2 : 4-*dinitrophenylhydrazone*, after chromatography (alumina–benzene), crystallised from ethyl acetate–

ethanol in orange plates, m. p. 210—211° (Found: C, 56·8; H, 5·1; N, 17·5. $C_{15}H_{16}O_4N_4$ requires C, 56·95; H, 5·1; N, 17·7%).

4 : 5 : 6 : 7-*Tetrahydroindanone.*—A mixture of the above ketone (5 g.), phosphoric acid (2 g.), and formic acid (98%; 6 g.) was kept at 80—90° for 4 hours under nitrogen. After cooling, the mixture was carefully added to water (200 ml.), and the resulting solution was extracted with ether. The ethereal extract was washed with 10% aqueous sodium carbonate and water, dried (Na_2SO_4), and distilled, giving the indanone (2·5 g.), b. p. 126—128°/14 mm., n_D^{23} 1·5189 (Found: C, 78·8; H, 9·05. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·9%) (Nenitzescu and Przemetzky, *Ber.*, 1941, **74**, 685, give b. p. 124—125°/17 mm., n_D^{20} 1·5235). The 2 : 4-dinitrophenylhydrazone crystallised from benzene in orange plates, m. p. 235° (K) (Found: C, 56·6; H, 5·5; N, 17·6. Calc. for $C_{15}H_{16}O_4N_4$: C, 56·95; H, 5·1; N, 17·7%) (Johnson *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3022, and Mathieson, *J.*, 1951, 177, give m. p. 238°).

cyclo*Hex*-1-*enyl Propenyl Ketone.*—1-*cyclo*Hexen-1′-enylbut-2-en-1-ol (15 g.; Braude and Coles, *loc. cit.*), light petroleum (b. p. 40—60°; 1 l.) and manganese dioxide (100 g.) gave, as above, the *ketone* (12 g.), b. p. 64—65°/0·3 mm., n_D^{19} 1·5164 (Found: C, 80·4; H, 9·7. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%). The 2 : 4-*dinitrophenylhydrazone* was chromatographed (alumina–benzene) and crystallised from ethyl acetate in red prisms, m. p. 152° (Found: C, 58·4; H, 5·6; N, 16·85. $C_{16}H_{18}O_4N_4$ requires C, 58·1; H, 5·5; N, 16·95%).

Attempted oxidation of the carbinol with acetone and aluminium *tert.*-butoxide in benzene failed, mainly unchanged starting materials being obtained after 30 hours' refluxing.

4 : 5 : 6 : 7-*Tetrahydro*-3-*methyl-indanone.*—A mixture of the foregoing propenyl ketone (6 g.), phosphoric acid (2·5 g.), and formic acid (98%; 7 g.) was kept at 90° for 7 hours under nitrogen. The products were worked up as above, giving the indanone (4 g.) as a colourless liquid, b. p. 114°/15 mm., n_D^{19} 1·5106 (Nazarov and Pinkina, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1946, 633, give b. p. 104—106°/8 mm., n_D^{20} 1·5124). It formed a semicarbazone which separated from aqueous methanol in prisms, m. p. 214—217° (with decomp.) (Nazarov and Pinkina, *loc. cit.*, give m. p. 211°), and a 2 : 4-dinitrophenylhydrazone, which was chromatographed (alumina–benzene) and crystallised from chloroform in brilliant crimson prisms, m. p. 246—248° (K) (Found: N, 17·15. Calc. for $C_{16}H_{18}O_4N_4$: N, 17·0%). The m. p. was undepressed on admixture of the sample with the 2 : 4-dinitrophenylhydrazone since described by Hamlet, Henbest, and Jones (*J.*, 1951, 2658), who give m. p. 246°.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : (cis-?)10 : 11-*Decahydrofluorenone*—A mixture of di*cyclo*hex-1-enyl ketone (3·5 g.; Braude and Coles, *loc. cit.*), phosphoric acid (*d* 1·7; 4 g.) and formic acid (98%; 5 g.) was kept at 90° for 10 hours under nitrogen. Working up as above gave an oily product which was then dissolved in pentane. Cooling in carbon dioxide–methanol caused crystallisation of the *decahydrofluorenone* (1 g.), m. p. 26° which was not raised on recrystallisation from pentane (Found: C, 81·9; H, 9·6. $C_{13}H_{18}O$ requires C, 82·0; H, 9·5%). It formed an *oxime*, which separated from light petroleum (b. p. 100—120°) in cream-coloured prisms, m. p. 133—134° (Found: N, 6·5. $C_{13}H_{19}ON$ requires N, 6·8%), and a 2 : 4-*dinitrophenylhydrazone* which was chromatographed (alumina–benzene–chloroform) and crystallised from ethanol–ethyl acetate in dark red needles, m. p. 168—169° (Found: N, 15·0. $C_{19}H_{22}O_4N_4$ requires N, 15·1%).

Dehydrogenation.—A mixture of decahydrofluorenone (1 g.) and 25% palladised charcoal (0·2 g.) was heated at 300° for 28 hours in a stream of nitrogen. The crude product gave no precipitate with Brady's reagent and on extraction with hot light petroleum (b. p. 60—80°) afforded fluorene (0·4 g.), m. p. 112—113°, undepressed on admixture of the specimen with an authentic sample. A similar experiment with 10% palladised charcoal at 200° for 2 hours yielded mainly unchanged starting material.

cis-syn-cis(?)-*Perhydrofluorenone.*—A solution of decahydrofluorenone (2·3 g.) in methanol (30 ml.) was shaken with platinic oxide (20 mg.) in hydrogen until 295 ml. (1 mol.) at 18°/750 mm. had been absorbed. The product was converted into the oxime which was crystallised from ethanol and had m. p. 171—173° (K), undepressed on admixture of the sample with the specimen of *syn*-perhydrofluorenone oxime (m. p. 169—171°), described by Davis, Doering, Levine, and Linstead (*J.*, 1950, 1423; cf. Hückel, *Annalen*, 1934, **508**, 10) who give m. p. 172—174°.

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