Preparation of *cis*- and *trans*-Cyclodec-2- and -3-enones and Studies of Interconversions between Them

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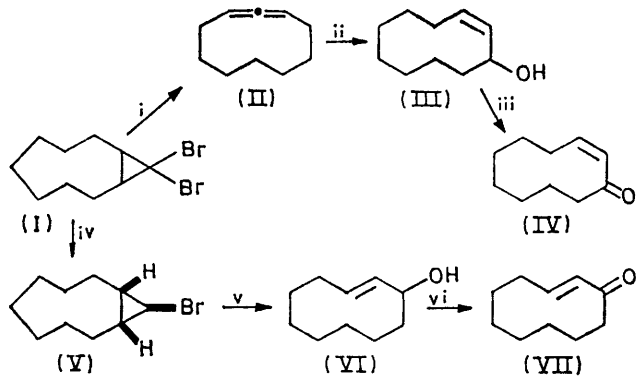
The *cis*- and *trans*-cyclodec-2- and -3-enones have been synthesised by stereospecific routes; a preparation of 3-hydroxycyclodecanone has also been developed. Under conditions of acid catalysis *cis*- and *trans*-cyclodec-2-enones are rapidly interconverted to give an equilibrium mixture containing 96% of the *cis*- and 4% of the *trans*-isomer. Efficient equilibration with the unconjugated isomers was not achieved. Deuteriation of the unsaturated ketones has given information on their relative ease of enolisation and the position of protonation (deuteriation) of the respective enols.

The acid-catalysed isomerisation of *trans*- to *cis*-cyclodec-2-en-1-ol has been studied by use of [1-^{2}H]-labelled substrates.

Some years ago we studied interconversions between cycloalk-2-enones and cycloalk-3-enones for rings of from five to nine members inclusive.[1] We did not at that time study the ten-membered ring because of the possible added complication from *cis–trans* isomerisation. In the mean time, methods have become available for the stereospecific synthesis of cyclic allylic [2] and homoallylic alcohols [3] which should be suitable precursors of the corresponding unsaturated ketones. We decided therefore to investigate the cyclodecenones, since the added dimension of *cis–trans* isomerisation might be expected to lead to some interesting features.

Synthetic Methods.—'Cyclodec-2-enone' has been reported on a number of occasions,[4] but in no case has its stereochemical integrity been assured. Similar doubts exist about cyclodec-2-en-1-ol [5] and cyclodec-3-en-1-one;[6] in fact the cyclodec-2-en-1-ol tentatively assigned a *trans*-geometry by Cope *et al.*[5a] has been shown in the present study to be the *cis*-isomer.

The methods used for the preparation of *cis*- and *trans*-cyclodec-2-enones are summarised in Scheme 1. In the preparation of *cis*-cyclodecenol (III) by mercuric sulphate-catalysed formolysis of cyclodeca-1,2-diene (II) followed by saponification, the stereochemistry of the product is not assignable on the basis of the reaction used. The reaction presumably involves the protonolysis of an initially formed formyloxymercurial, which could lead either to a *cis*- or to a *trans*-double bond (oxymercuration of acyclic allenes leads to both *cis*- and *trans*-adducts [7]). Furthermore formolysis of the kinetically favoured

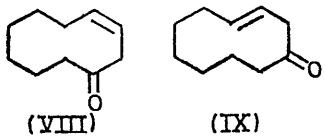


Scheme 1 Reagents: i, MeLi–Et_2O; ii, (a) $HgSO_4$–HCO_2H, (b) $Ba(OH)_2$–H_2O; iii, H_2CrO_4–Me_2CO, 20°; iv, $NaCH_2$·SOMe–Me_2SO; v, aq. dioxan–$NaHCO_3$, reflux; vi, H_2CrO_4–Me_2CO, −30°

[1] N. Heap and G. H. Whitham, *J. Chem. Soc.* (*B*), 1966, 164.
[2] *Cf.* C. H. De Puy, *Accounts Chem. Res.*, 1968, **1**, 33.
[3] C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, 1970, **92**, 4282.
[4] N. J. Leonard and F. H. Owens, *J. Amer. Chem. Soc.*, 1958, **80**, 6039; M. Bertrand, M. Santelli, and R. Maurin, *Bull. Soc. chim. France*, 1967, 998; R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, 1967, **32**, 1608.
[5] (*a*) A. C. Cope, M. Brown, and H. H. Lee, *J. Amer. Chem. Soc.*, 1958, **80**, 2855; (*b*) V. Prelog and K. Schenker, *Helv. Chim. Acta*, 1952, **35**, 2044.
[6] R. G. Carlson and J. H. Bateman, *Tetrahedron Letters*, 1967, **42**, 4151.
[7] W. S. Linn, W. L. Waters, and M. C. Caserio, *J. Amer. Chem. Soc.*, 1970, **92**, 4018.

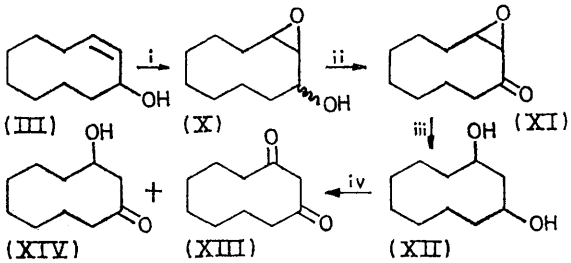
allylic formate(s) would probably lead to an equilibrium-controlled product. The stereochemistry of compound (III) is assigned on the basis: (*a*) of its oxidation to the ketone (IV), which in turn was reduced back to (III) with lithium aluminium hydride, and (*b*) that it is different from the *trans*-cyclodecenol (VI). *cis*-Cyclodec-2-enone (IV) was identified by its n.m.r. spectrum (see later). Preliminary attempts to prepare the *cis*-alcohol (III) by hydrolysis of *endo*-10-bromobicyclo-[7,1,0]decane, itself obtained by tri-n-butyltin hydride reduction [8] of the dibromide (I), were thwarted by the very low reactivity of the cyclopropyl halide even in aqueous acetone containing silver perchlorate.[9]

In contrast to the latter observations, hydrolysis of the *exo*-10-bromobicyclo[7,1,0]decane (V) proceeded smoothly in refluxing aqueous dioxan containing sodium hydrogen carbonate. Since the considerably more strained *trans*-cyclo-oct-2-en-1-ol is formed on analogous hydrolysis of *exo*-8-bromobicyclo[5,1,0]octane,[10] it follows *a fortiori* that the product (VI) has the *trans*-configuration. The much greater solvolytic reactivity of (V) than its *endo*-epimer is to be expected on the basis of extrapolation of the results of Schöllkopf, Schleyer, *et al.* on the solvolysis of bicyclic cyclopropyl tosylates.[11] Oxidation of the alcohol (VI) to the *trans*-cyclodec-2-enone (VII) was achieved with 8N-chromic acid in acetone at −30°. Some isomerisation to the *cis*-ketone (IV) occurred, and at higher temperature (25°) this was the major product.



(VIII) (IX)

The *cis*- and *trans*-cyclodec-3-enones (VIII) and (IX) were prepared by oxidation of the corresponding homoallylic alcohols.[3] A sample of 3-hydroxycyclodecanone (XIV) was prepared by the route summarised in Scheme 2.



SCHEME 2 Reagents: i, AcO_2H; ii, H_2CrO_4–Me_2CO, 0°; iii, Ca–liq.NH_3; iv, H_2CrO_4–Me_2CO

The diol (XII) appeared to be a single compound, since it had a sharp m.p. It is tentatively assigned the *trans*-stereochemistry on the basis of the sharp triplet (apparent splitting 4·1 Hz) observed in the n.m.r. spectrum for the methylene protons at C-2, which is compatible with absorption due to the A protons of an AA'XX' system. Direct oxymercuration–reduction [12] of cyclodecenol (III) to diol (XII) was not achieved, and attempts to reduce the epoxy-ketone (XI) to the hydroxy-ketone (XIV) with activated zinc in methanol or chromous acetate [13] were unavailing.

Spectroscopic Data.—The salient features of the u.v., i.r., and n.m.r. spectra of *cis*- and *trans*-cyclodec-2-enones are summarised in Table 1. The shorter wavelength, lower intensity u.v. absorption, and the higher frequency carbonyl stretching band in the i.r. both indicate that the *cis*-ketone is effectively less conjugated than the *trans*. This conclusion is verified by the n.m.r. data. For *cis*-cycloalk-2-enones of lower ring size the 3-proton always absorbs at lower field than the 2-proton,[1] presumably owing to conjugative deshielding of the former, although the chemical shift difference progressively diminishes with increasing ring size up to cyclonon-2-enone. As shown in Table 1, the 3-H resonance for *cis*-cyclodec-2-enone actually appears 0·57 p.p.m. to *higher* field than that due to the 2-H. Clearly this ketone is not notably conjugated. In contrast, for *trans*-cyclodec-2-enone the 3-H signal is at 0·32 p.p.m. to lower field than the 2-H; this difference is comparable to that for *cis*-cyclo-oct-2-enone.* The stereochemistry of the two ketones is established by the respective values for $J_{2,3}$.

TABLE 1

Spectroscopic data for *cis*- and *trans*-cyclodec-2-enones

	U.v. (EtOH)	I.r. (CCl_4)	N.m.r. ($CDCl_3$)			
					$J_{2,3}$	$J_{3,4}$
	$\lambda_{max.}$/nm (ε)	$\nu_{C=O}$/cm^{-1}	τ(2-H)	τ(3-H)	(Hz)	
cis-	224·5 (3760)	1690	3·67	4·24	12·0	8·6
trans-	230 (7200)	1690sh, 1675	3·68	3·36	16·3	7·6

Interconversions.—We attempted to interconvert the isomeric cyclodecenones under a variety of conditions. Different basic catalysts led either to no isomerisation or to destruction of starting material, presumably by condensation reactions. Toluene-*p*-sulphonic acid in benzene under reflux caused rapid interconversion between *cis*- and *trans*-cyclodec-2-enones giving an equilibrium mixture approachable from either side containing 96% of the *cis*- and 4% of the *trans*-isomer. On prolonged treatment, very slow and incomplete interconversion between *trans*-cyclodec-3-enone and the equilibrium mixture of *cis*- and *trans*-cyclodec-2-enones was observed. Under similar conditions, no isomerisation of *cis*-cyclodec-3-enone was observed.

On refluxing with aqueous N-sulphuric acid, the Δ^3-ketones were unaffected, but the conjugated ketones

* Further evidence for non-planarity of the *cis*-ketone is provided by the ^{13}C n.m.r. spectrum, which shows absorption due to C=O at −15·2 p.p.m. from CS_2 (*cf.* D. H. Marr and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 596).

[8] D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, 1963, **28**, 703.

[9] C. B. Reese and A. Shaw, *J. Amer. Chem. Soc.*, 1970, **92**, 2566.

[10] G. H. Whitham and M. Wright, *J. Chem. Soc.* (*C*), 1971, 883.

[11] U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Letters*, 1967, 3639.

[12] H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522; S. Moon and B. H. Waxman, *Chem. Comm.*, 1967, 1283.

[13] W. Cole and P. L. Julian, *J. Org. Chem.*, 1954, **19**, 131.

were converted into an equilibrium mixture, comprising again 96% of the *cis*- and 4% of the *trans*-isomer. It was suspected that 3-hydroxycyclodecanone was an intermediate in this equilibration, and a separate experiment showed that this β-hydroxy-ketone was indeed converted into the same mixture under the isomerisation conditions. Furthermore, treatment of *trans*-cyclodec-2-enone with N-sulphuric acid in 50% aqueous dioxan at 20° gave the β-hydroxy-ketone as major product.

We conclude that *cis*- and *trans*-cyclodec-2-enones are interconverted by way of an addition–elimination sequence, and that *cis*-cyclodec-2-enone is more stable than *trans*-cyclodec-2-enone, $\Delta G°$ being about 1·9 kcal mol^{-1} at 100°. Since *cis*-cyclodecene is more stable than *trans*-cyclodecene ($\Delta G°$ 1·86 kcal mol^{-1}) [14] and, as we have already argued, *trans*-cyclodec-2-enone is ' more conjugated ' than its *cis*-isomer, it is not at present clear why the *cis* preference at equilibrium is about the same for the αβ-unsaturated ketones as for the parent cycloolefins. Unfortunately we were unable to achieve satisfactory interconversion with the βγ-unsaturated ketones in order to examine the influence of the more remote carbonyl group.

Deuterium incorporation studies (in deuterium oxide–dioxan containing N-sulphuric acid) were also carried out. The results are given in Table 2.

TABLE 2

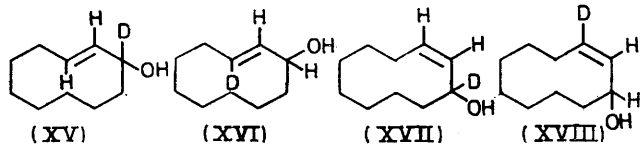
Deuteriation of cyclodecenones

Substrate	Product	Extent of deuteriation [a] at C-2	at C-10
cis-Δ^2	*cis*-Δ^2		70
trans-Δ^2	*cis*-Δ^2	45	72
cis-Δ^3	*cis*-Δ^3	94	71
trans-Δ^3	*trans*-Δ^3	29	Trace
β-Hydroxy-ketone	*cis*-Δ^2	61	76

[a] Total H (%) determined by integration of the relevant signals in the n.m.r. spectrum after isolation of product. The overall deuteriation figures were corroborated by mass spectrometry.

Clearly *trans*-cyclodec-3-enone does not enolise as readily as the *cis*-ketones, presumably because of the strain which would be involved in incorporation of a second double bond in the *trans*-cyclodecene skeleton. *cis*-Cyclodec-3-enone undergoes ready enolisation, but the resistance to isomerisation shown in the earlier results indicates that the probable intermediate, *cis,cis*-1-hydroxycyclodeca-1,3-diene, is protonated overwhelmingly at C-2. The deuteriation studies on *cis*- and *trans*-cyclodec-2-enones corroborate that the β-hydroxy-ketone is an intermediate, and indicate that the enol (1,3-dihydroxycyclodec-2-ene) is partitioned roughly equally between protonation (deuteriation) at C-2 to give eventually β-hydroxy-ketone and elimination of water from the relevant conjugate acid to give *cis*-Δ^2-ketone.

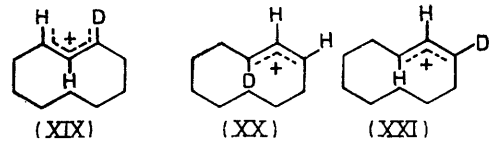
We also examined semiquantitatively the acid-catalysed isomerisation of *trans*-cyclodec-2-en-1-ol to *cis*-cyclodec-2-en-1-ol, by use of [1-^{2}H]-*trans*-cyclodecenol (XV) prepared by reduction of *trans*-cyclodec-2-enone with lithium aluminium deuteride. The results obtained under various conditions are summarised in Scheme 3. Control experiments showed that [1-^{2}H]-*cis*-cyclodec-2-en-1-ol (XVII) was unaffected under the specified conditions.



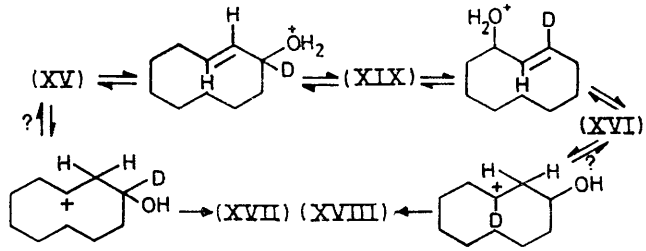
Conditions	(XV)	(XVI)	(XVII)	(XVIII)
2N-H_2SO_4, 20°, 12 h	0	0	70	30
	0	0	65	35
2N-H_2SO_4, 20°, 4 h	25	20	40	15
2N-H_2SO_4, dioxan–H_2O (1 : 1), 40°, 4 h	30	25	35	15

SCHEME 3 Figures quoted are percentages (rounded off to the nearest 5%) of the compounds indicated, obtained by integration of the n.m.r. spectra

We conclude first that there is a rapid allylic rearrangement leading to interconversion of the isotopically isomeric alcohols (XV) and (XVI), presumably involving the *trans,trans*-allylic cation (XIX). Second, the *trans*-alcohol (XV) is converted into the [1-^{2}H]-*cis*-alcohol (XVII) more rapidly than into the[3-^{2}H]-isomer-(XVIII). Formally, the second conclusion could be explained in two ways: either (i) there is a secondary α-deuterium isotope effect operating such that conversion of (XVI) into (XVII) *via* the *cis,trans*-allylic cation (XX) is much faster than the conversion of (XV) into (XVIII) *via* the *cis,trans*-cation (XXI), or (ii) there is a direct mechanism (*e.g.* protonation–deprotonation) for the isomerisation (XV) ⟶ (XVII) [and for (XVI) ⟶ (XVIII)] not involving allylic rearrangement.



Secondary α-deuterium isotope effects in solvolyses are usually small,[15] and we are therefore inclined to discount the former explanation in favour of the latter. Apparently the dissociation of protonated *trans*-cyclodec-2-en-1-ol



SCHEME 4

to an allylic cation is stereoelectronically controlled to give a *trans,trans*-cation [*cf.* (XIX)] in preference to a

[14] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, 1959, **81**, 3153.

[15] F. R. Thornton, ' Solvolysis Mechanisms,' Ronald Press, New York, 1964, p. 208.

cis,trans-cation [*cf.* (XX) and (XXI)]. The reaction scheme proposed for the isomerisation of (XV) is shown (Scheme 4).*

EXPERIMENTAL

Unless otherwise stated n.m.r. spectra are for solutions in [^{2}H]chloroform, obtained with a Perkin-Elmer R14 instrument at 100 MHz.

cis-*Cyclodec-2-en-1-ol.*—Cyclodeca-1,2-diene [16] (11 g) in formic acid (85%; 85 ml) containing mercuric sulphate (1 g) was stirred at 25° for 15 h. Water (300 ml) was added, followed by ether, and the aqueous phase was neutralised with potassium carbonate. Isolation of the product with ether followed by distillation gave the formate of *cis*-cyclodecenol (10 g, 68%), b.p. 62—63° at 0·2 mmHg, n_D^{20} 1·4880.

The formate was heated at 100° with barium hydroxide (hydrated; 8 g) in water (25 ml) for 1 h. Isolation of the product with ether followed by distillation gave the *alcohol* (5·8 g), b.p. 70° at 0·2 mmHg, m.p. 47—49°, (from light petroleum) (Found: C, 78·25; H, 11·75. $C_{10}H_{18}O$ requires C, 77·85; H, 11·75%). The p-*nitrobenzoate* had m.p. 152—153° (from ethanol) (Found: C, 67·55; H, 7·25; N, 4·8. $C_{17}H_{21}NO_4$ requires C, 67·3; H, 7·0; N, 4·6%) and the α-*naphthylurethane* m.p. 105° (from light petroleum) (Found: C, 78·1; H, 7·75; N, 4·4. $C_{21}H_{25}NO_2$ requires C, 78·0; H, 7·8; N, 4·35%).

cis-*Cyclodec-2-en-1-one.*—*cis*-Cyclodecenol (13 g) in ether (40 ml) was treated at 20—25° with stirring with a solution (50 ml) of sodium dichromate (hydrated; 10 g) in water containing sulphuric acid (7·5 ml). After 3 h the product was isolated with ether. Traces of unchanged alcohol were removed by chromatography on silica gel and distillation gave the *ketone* (10·5 g), b.p. 52—53° at 0·2 mmHg, n_D^{20} 1·5000 (Found: C, 78·55; H, 10·41. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). For spectroscopic data see Discussion section.

Reduction of 10,10-*Dibromobicyclo*[7,1,0]*decane with Sodium Methylsulphonylmethanide.*—A solution prepared from sodium hydride (5·6 g) and dimethyl sulphoxide (50 ml) was rapidly added dropwise to 10,10-dibromobicyclo-[7,1,0]decane [16] at 20° with stirring. After 5 min the mixture was poured on ice and the product was isolated with light petroleum. Distillation gave cyclodeca-1,2-diene (0·5 g), b.p. 40—45° at 0·2 mmHg; *exo*-10-bromobicyclo-[7,1,0]decane (15 g), b.p. 73—75° at 0·2 mmHg, n_D^{20} 1·5200; and unchanged 10,10-dibromobicyclo[7,1,0]decane (12 g), b.p. 90° at 0·2 mmHg. The monobromo-compound was contaminated with some allene as shown by i.r. spectrum and analysis (Found: C, 57·35; H, 8·0; Br, 35·0. Calc. for $C_{10}H_{17}Br$: C, 55·3; H, 7·9; Br, 36·8%), but was used as such for the next reaction.

trans-*Cyclodec-2-en-1-ol.*— *exo*-10-Bromobicyclo[7,1,0]-decane (3 g) in dioxan–water (2 : 1 v/v; 100 ml) containing sodium hydrogen carbonate (2 g) was heated under reflux for 48 h. Most of the dioxan was removed under reduced pressure and the product was isolated with ether. Distillation gave the alcohol (1·9 g, 89%), b.p. 80—82° at 0·5 mmHg, n_D^{20} 1·5080. The α-*naphthylurethane* had m.p. 124—125° (from light petroleum) (Found: C, 78·15; H, 7·75; N, 4·4%. $C_{21}H_{25}NO_2$ requires C, 78·0; H, 7·8; N, 4·35%).

trans-*Cyclodec-2-en-1-one.*—*trans*-Cyclodec-2-en-1-ol (3 g) in acetone (300 ml) was cooled to −30° and 8N-chromic acid (6·5 ml) was added in one portion to the stirred solution. After 5 min the solution was poured into ice–water (1·5 l) and the product was extracted with light petroleum. The organic phase was washed successively with aqueous sodium hydrogen carbonate and water. Evaporation of the dried extract followed by distillation gave material (1·6 g), b.p. 60° at 0·3 mmHg, n_D^{20} 1·5080, shown to contain *cis*-cyclodecenone and allylic alcohols by t.l.c. and i.r. spectrum.

The ketone (0·6 g) was purified by chromatography on silica gel; elution with light petroleum–ether (10 : 1) gave trans-*cyclodec-2-enone* (0·35 g) (Found: C, 78·8; H, 10·55. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The compound was sensitive to air, and was stored in sealed ampoules at 0°. For spectroscopic data see Discussion section.

trans-*Cyclodec-3-en-1-one.*—*trans*-Cyclodec-3-en-1-ol [3] (3 g) in acetone (100 ml) was oxidised at 20° with chromic acid (8N; 10 ml). Isolation of the product in the usual way gave trans-*cyclodec-3-en-1-one* (2 g), b.p. 64—65° at 0·3 mmHg, n_D^{20} 1·4950 (Found: C, 78·95; H, 10·65. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%), τ 4·2—4·5 (2H, m, 3-H and 4-H) and 7·0 (2H, d, *J* 6 Hz, 2-H).

cis-*Cyclodec-3-en-1-one.*—In a similar way *cis*-cyclodec-3-en-1-ol [3] (3 g) was oxidised to cis-*cyclodec-3-en-1-one* (2 g), b.p. 62—63° at 3 mmHg, n_D^{20} 1·4970 (Found: C, 79·3; H, 10·55. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%), τ 4·0—4·5 (2H, m, 3-H and 4-H), 6·85 (2H, d, *J* 7 Hz, 2-H), and 7·5 (2H, t, *J* 6 Hz, 10-H).

2,3-*Epoxycyclodecanol.*—To a stirred solution of *cis*-cyclodec-2-enol (15 g) in dichloromethane (100 ml) at 0° was added peroxyacetic acid [30 g, 30% containing sodium acetate (5 g)]. The mixture was stirred at 20° for 16 h, then aqueous sodium hydroxide (10%; 250 ml) was added. The organic layer was separated, and the aqueous phase was extracted with ether. The combined organic layers were washed with acidic ferrous sulphate solution, aqueous sodium hydrogen carbonate, and brine. Evaporation of the dried ($MgSO_4$) solution followed by distillation gave the epoxy-alcohol (15 g), probably as a mixture of stereoisomers, b.p. 98—99° at 1 mmHg, n_D^{20} 1·4980.

2,3-*Epoxycyclodecanone.*—The epoxy-alcohol (14 g) in acetone (300 ml) was oxidised with chromic acid (8N; 30 ml) at 0°. The product was isolated in the usual way and distilled to give 2,3-*epoxycyclodecanone* (13 g), b.p. 90—91° at 1 mmHg, n_D^{20} 1·4990 (Found: C, 71·6; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%), τ 6·13 (1H, d, *J* 4·5 Hz, 2-H), 6·6—7·0 (1H, m, 3-H), and 4·05—5·55 (2H, m, 10-H).

Cyclodecane-1,3-*diol.*—2,3-Epoxycyclodecanone (1 g) in tetrahydrofuran (10 ml) was added during 5 min to calcium (2 g) in liquid ammonia (350 ml). The mixture was stirred for 2 h, ethanol (10 ml) was added, and the ammonia was allowed to evaporate off. Water (20 ml) was added to the residue and the product was isolated with ether. Crystallisation from benzene gave the *diol* (0·8 g), m.p. 110—111° (Found: C, 69·85; H, 11·9. $C_{10}H_{20}O_2$ requires C, 69·7; H, 11·7%), τ 5·75 (2H, m, 1-H and 3-H), 7·65 (2H, OH), 8·05 (2H, t, 2-H), and 8·2—9 (14H).

Cyclodecane-1,3-*dione.*—Cyclodecane-1,3-diol (0·2 g) was oxidised with an excess of 8N-chromic acid in acetone to give the diketone (0·15 g), b.p. 80° at 0·1 mmHg, n_D^{20} 1·4910. The bis-2,4-dinitrophenylhydrazone had m.p. 236—237°

* *Note added in proof:* Spectroscopic data for *cis*-cyclodec-2-enone similar to those quoted here have been reported (M. Regitz and J. Rüter, *Chem. Ber.*, 1969, **102**, 3877).

[16] W. R. Moore and H. R. Ward, *J. Org. Chem.*, 1962, **27**, 4179.

(lit.,[17] 236—237°) (Found: C, 50·2; H, 4·65; N, 20·7. Calc. for $C_{22}H_{24}N_8O_8$: C, 50·0; H, 4·6; N, 20·2%).

3-*Hydroxycyclodecanone*.—Cyclodecane-1,3-diol (0·6 g) in acetone (30 ml) at −10° was treated with chromic acid (8N; 0·8 ml). The mixture was stirred for 15 min, and the product (0·5 g) was isolated with ether and shown by t.l.c. to contain starting material, cyclodecane-1,3-dione, and 3-hydroxycyclodecanone. Chromatography on silica gave the *hydroxy-ketone* (0·2 g), b.p. 90—92° at 0·1 mmHg, n_D^{20} 1·4980 (Found: C, 71·05; H, 10·45. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%).

Interconversions of Cyclodecenones.—Mixtures were analysed qualitatively by t.l.c. and quantitatively by g.l.c. [10 ft column of Carbowax 6000 (15%) in Embacel at 105°]. The following relative retention times were found (in parentheses are given response ratios for areas obtained by triangulation relative to cyclo-octanone as internal standard): *cis*-cyclodec-2-enone, 1·11 (1·14); *trans*-cyclodec-2-enone, 1·78 (1·05); *cis*-cyclodec-3-enone 1·04 (1·04); *trans*-cyclodec-3-enone 1·00 (0·92).

Typical conditions employed for isomerisation are as follows. (*a*) The ketone (50 mg) in dry benzene (20 ml) containing toluene-*p*-sulphonic acid (10 mg) was heated under reflux. Samples were withdrawn at intervals, washed with aqueous sodium carbonate, dried, and analysed by g.l.c. after addition of a known amount of benzene containing cyclo-octanone (internal standard).

(*b*) The ketone (50 mg) in aqueous sulphuric acid (1N; 10 ml) was heated under reflux and the product was isolated by extraction with ether after an appropriate interval. Under these conditions, the αβ-unsaturated ketones were interconverted to give a mixture comprising *cis*-isomer (96%) and *trans*-isomer (4%) within 1 h; the βγ-unsaturated ketones were unaffected.

Deuteriation.—The ketone (0·5 g) in dry dioxan (10 ml) containing deuterium oxide (5 ml) and sulphuric acid (3 drops) was heated under reflux for 2 h. After isolation with light petroleum the product was distilled, giving material (*ca.* 0·4 g) which was analysed by n.m.r. and mass spectrometry. Results are given in Table 2 (see Discussion section).

Other Interconversions.—(*a*) 3-Hydroxycyclodecanone (50 mg) was heated under reflux in aqueous sulphuric acid (2N; 10 ml) for 1 h. T.l.c. showed the product to comprise *cis*-cyclodec-2-enone, together with a trace of *trans*-cyclodec-2-enone.

(*b*) *trans*-Cyclodec-2-enone (20 mg) was added to a mixture of dioxan (1·5 ml) and sulphuric acid (2N; 0·5 ml). After 12 h at 20° water was added and the product was isolated with ether. T.l.c. showed the main component to be 3-hydroxycyclodecanone; a small amount of *cis*- and traces of *trans*-cyclodec-2-enone were also present.

Acid-catalysed Isomerisation of cis- *and* trans-[1-^{2}H]-*Cyclodec-2-en-1-ol*.—The deuteriated alcohols were prepared by reduction of the respective ketones with lithium aluminium deuteride in ether (1 h reflux). Isomerisations were studied under conditions specified in Scheme 3. Products were isolated with ether, and n.m.r. spectra were obtained after distillation. The approximate analyses quoted in the Scheme were derived on the basis of the following: for *cis*-cyclodec-2-en-1-ol, 1-H gives a multiplet at τ 5·0—5·3 and 83% of its total olefinic absorption is in the range 4·5—5·0; for *trans*-cyclodec-2-en-1-ol, 1-H gives a multiplet at τ 5·6—5·9 and 83% of its total olefinic absorption is in the range 4·0—4·5.

We thank the British Council for a fellowship (to M. Z.).

[1/2466 *Received*, 23*rd December*, 1971]

[17] K. Shank, B. Eistert, and J. H. Felzmann, *Chem. Ber.*, 1966, 1414.