Thermal Rearrangement of Halogenocarbene Adducts of Cyclic Olefins

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The thermal rearrangements of some 6-halogenobicyclo[3.1,0]hexane derivatives, and of 8,8-dibromobicyclo-[5,1,0]octane, are described. The effects of stereochemical and electronic factors and of ring-size on the rate of rearrangement are discussed.

Soon after they became readily accessible,¹ it was apparent that certain dihalogenocarbene adducts of cyclic olefins were thermally unstable. Parham et al. found² that the indene adduct (I) rearranged readily to give 2-chloronaphthalene (II). On the other hand, 8,8-dichlorobicyclo[5,1,0]octane (III) was reported ³ to



be very stable to heat. It has recently become clear that the ease of rearrangement of halogenocarbene adducts of cyclic olefins⁴ depends on stereochemical and electronic factors, and also on ring-size. We now report the results of a study of this synthetically important reaction with substrates derived mainly from the bicyclo[3,1,0]hexane ring system.

Stereochemical Considerations.⁵-Schweizer and Par-

ham found ⁶ that only one of the epimeric 7-chloro-2-oxabicyclo[4,1,0]heptanes (IV) and (V) was thermally unstable; when this compound [to which these authors 6 incorrectly 7 assigned the structure (V)] was heated in quinoline solution, it reacted readily to give 2,3-dihydrooxepin (VI). The other epimer was stable at its boiling



point. These observations suggested that the stereochemical disposition of the halogen (or halide) leaving group was a crucial factor in the rearrangement. In order to clarify this point we set out to prepare pure specimens of two epimeric monohalogenocarbene adducts, to establish their stereochemistry, and then to examine

⁴ W. E. Parham and E. E. Schweizer, Org. Reactions, 1963, 13, 55; W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1964, ch. 8.

¹ W. von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc., 1954, 76, 6162. ² W. E. Parham, H. E. Reiff, and P. Schwartzentruber, J.

Amer. Chem. Soc., 1956, 78, 1437.

³ E. Bergman, J. Org. Chem., 1963, 28, 2210.

⁵ For a preliminary account of this aspect of our work, see M. S. Baird and C. B. Reese, Tetrahedron Letters, 1967, 1379.
⁶ E. E. Schweizer and W. E. Parham, J. Amer. Chem. Soc.,

^{1960, 82, 4085.}

T. Ando, H. Yamanka, and W. Funasaka, Tetrahedron Letters, 1967, 2587.

the action of heat upon them. The 6-chlorobicyclo-[3,1,0]hexanes (VII) and (VIII) were chosen as the simplest pair of epimers to study. It seemed likely that they would both be stable enough to be isolable in a pure state, and that it would be possible to assign their structures on the basis of their n.m.r. spectra.



Treatment of cyclopentene with chlorocarbene, generated by the usual procedure,⁸ gave a 3:1 mixture (estimated by g.l.c.) of the adducts (VII) and (VIII) in 69% yield. The major component, which was isolated pure by preparative g.l.c., was identified as the endo-isomer (VII) by n.m.r. spectroscopy: the lowest field signal, a triplet (J 7 Hz) at τ 6.72, suggested ^{9,10} that H-6 was coupled with two *cis*-cyclopropyl protons. The minor component, which was isolated pure after distillation of the mixture from quinoline solution (see Experimental section), was identified as the *exo*-isomer (VIII): the lowest field signal in its n.m.r. spectrum, a triplet (11.5 Hz) at τ 7.38, suggested ^{9,10} that H-6 was coupled with two trans-cyclopropyl protons.

When the endo-isomer (VII) was heated at 126°, it was slowly converted into a single product, identified as 3-chlorocyclohexene (IX). This reaction was complete after 3 hr. (see Table). However, the exo-isomer (VIII) was markedly more stable to heat: it remained completely unchanged after 4 hr. at 250°. At 260°, it was slightly unstable (ca. 10% reaction after 4.5 hr.) and, at 300°, it was ca. 70% converted into benzene after 3 hr.

These experiments indicate that the endo-disposition of the leaving group is preferred in the thermal rearrangement of halogenocarbene adducts of cyclopentene. Jefford and his co-workers 11 have come to the same conclusion by studying the reaction between chlorocarbene and norbornene, but their evidence was more circumstantial in that they were able to isolate only one unrearranged adduct. However, since the preliminary publication of our work,⁵ Ghosez et al.¹² have prepared both the corresponding chlorocarbene adducts of 7-oxabicyclo[2,2,1]hept-2-ene, examined the action of heat upon them, and reached the same conclusion. The same

¹⁰ S. J. Cristol, K. M. Sequira, and C. H. De Luy, J. Amer.
 Chem. Soc., 1965, 87, 4007.
 ¹¹ C. W. Jefford and R. Medary, *Tetrahedron Letters*, 1966, 2069; C. W. Jefford, E. Huang Yeu, and R. Medary, *ibid.*, 1966, 6317; C. W. Jefford and W. Wojnarowski, *ibid.*, 1968, 193, 199.
 ¹² L. Ghosez, P. Laroche, and G. Slinckx, *Tetrahedron Letters*, 2007.

1967, 2767.

¹³ T. Ando, H. Yamanka, S. Terabe, A. Horike, and W. Funasaka, Tetrahedron Letters, 1967, 1123.

stereochemical preference has recently been demonstrated in the thermal rearrangement of the 7-halogenobicyclo[4,1,0]heptane system.¹³



It has been known for several years 14 that the solvolytic rearrangements of the 6-halogenobicyclo-[3,1,0]hexane and 7-halogenobicyclo[4,1,0]heptane systems are stereospecific, and it has been established more recently 10,15,16 that the endo-leaving group is preferred. A theoretical treatment of this problem ¹⁷ has led to the conclusion that the concerted rearrangement of a cyclopropyl to an allyl carbonium ion should proceed by a stereospecific disrotatory process such that the groups trans to the leaving group (X⁻) rotate outwards and those cis to it rotate inwards, as the C-X bond begins to break. The stereochemical consequences of this prediction for the solvolysis of halogenocarbene adducts of cycloalkenes (or the corresponding toluene-p-sulphonates) are illustrated in Scheme 1: (a) endo-derivatives lead to cis-, and (b) exo-derivatives lead to trans-substituted allyl carbonium ions. Therefore on grounds of ring-strain. exo-derivatives such as (VIII) and its homologue, exo-7-chlorobicyclo[4,1,0]heptane, or the corresponding toluene-p-sulphonates, would be expected to be parparticularly resistant to solvolysis. This has been verified.^{16,18} In view of these considerations, the remarkable stability of (VIII) to heat suggests that the thermal rearrangement reaction also involves a concerted heterolytic process, subject to the same stereochemical control.

Electronic Factors.--As the rate-determining step of the thermal rearrangement is likely to involve concerted heterolytic fission to give halide ion and an allylic carbonium ion, the rate of rearrangement would be expected to depend on the nature of the halide leaving group and on the stability of the resulting intermediate

14 P. S. Skell and S. R. Sandler, J. Amer. Chem. Soc., 1958, 80,

2024. ¹⁵ C. H. De Puy, L. G. Schnack, J. W. Hauser, and W. Wiede-mann, J. Amer. Chem. Soc., 1965, 87, 4006; P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, 1966, 88, 2868.

¹⁶ U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Letters*, 1967, 3639.

17 R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 1965, 87, 395; H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 1965, 87, 2045.

¹⁸ C. H. De Puy, Accounts Chem. Res., 1968, 1, 33.

⁸ G. L. Closs and L. E. Closs, J. Amer. Chem. Soc., 1958, 81, 4996; 1960, 82, 5723.

⁹ H. M. Hutton and T. Schaefer, Canad. J. Chem., 1962, 40, 875; J. D. Graham and M. T. Rogers, J. Amer. Chem. Soc., 1962, 84, 2249.

¹⁰ S. J. Cristol, R. M. Sequira, and C. H. De Puy, J. Amer.

carbonium ion. There is now much experimental evidence with which to substantiate these expectations.

(\mathbf{X}) (XI)a; X = CLb: X = Br

We had previously noted 19 that dibromocarbene adducts rearranged more readily than the corresponding dichlorocarbene adducts. This conclusion, which is important from the point of view of the synthetic applications of the ring-expansion reaction, can be clearly illustrated with bicyclo[3,1,0]hexane derivatives. Thus, while 6,6-dibromobicyclo[3,1,0]hexane²⁰ (Xb) was completely converted into 2,3-dibromocyclohexene (XIb) in 1 hr. at 120°, the corresponding dichlorocompound³ (Xa) required more drastic conditions (1.5 hr. at 170°, see Table) to complete its rearrangement into (XIa). Similarly, although 6,6-dichloro-2-oxabicyclo[3,1,0]hexane²¹ (XIIa) was stable enough to be isolable and required to be heated for 15 min. at 60° to effect complete isomerization, reaction between 2,3-dihydrofuran, bromoform, and potassium t-butoxide in t-butyl alcohol at 0° gave (XIII) as the sole heterocyclic product.²¹ Thus it seemed likely that (XIIb) was unstable even at 0° . In the same way, the isomeric 6,6-dibromo-3-oxabicyclo[3,1,0]hexane²² (XVb) (see later) was found to rearrange under milder conditions than the corresponding dichloro-compound ²² (XVa) (see Table).



The action of heat on the 6-fluorobicyclo[3,1,0]hexanes has not yet been investigated. However, studies with appropriate fluoro-derivatives of the tricyclo[3,2,1,0^{2,4}]octane²³ and bicyclo[4,1,0]heptane¹³ systems indicate that fluoride ion is a relatively poor leaving group in the present context. We therefore conclude that the rate of the thermal rearrangement reaction has the expected dependence ²⁴ on the leaving group, *i.e.* it decreases in the order Br⁻, Cl⁻, F⁻.

¹⁹ D. G. Lindsay and C. B. Reese, *Tetrahedron*, 1965, **21**, 1673. $\mathbf{20}$ J. Sonnenberg and S. Winstein, J. Org. Chem., 1962, 27, 748.

J. C. Anderson, D. G. Lindsav, and C. B. Reese, Tetrahedron, 1964, 20, 2091.

A number of electronic factors affect the stability of the intermediate allylic carbonium ions. The observation (see Table) that endo-6-chlorobicyclo[3,1,0]hexane (VII) undergoes thermal rearrangement more readily (3 hr. at 126°) than the corresponding dichlorocompound (Xa) (1.5 hr. at 170°), can be rationalized inasmuch as the negative inductive effect of the chlorogroup should cause the intermediate carbonium ion

Action of heat on 6-halogenobicyclo[3,1,0]hexane derivatives

R ¹ X CH ₂							
				Conditions		Yields	
			Formula		Time	% Re-	% Isol-
$R^{1}-R^{2}$	\mathbf{X}	Y	no.	Temp.	(min.)	action "	ated b
CHCH.	Cl	Cl	(Xa)	170°	90 c	100	90
CH ₂ -CH ₂	\mathbf{Br}	Br	(Xb)	120	60	100	85
$CH_2 - CH_2$	Cl	н	(VII)	126	180	100	
$CH_2 - CH_2$	\mathbf{H}	Cl	(VIII)	300	180	70	
D−ČH ₂	Cl	Cl	(XIIa) d	60	15	100	90
$H_2 - O$	Cl	Cl	(XVa)	235	160	95	69
$H_{2}-O$	\mathbf{Br}	\mathbf{Br}	(XVb)	184	135	55	33
CH=CH	Cl	Cl	(XIX)	55	25	100	48

" Represents % of reacted starting material, as indicated by g.l.c. b Represents % yield of isolated product (see Experimental section). c Bergman reported ³ that this reaction was complete in under 3 hr. at 153–188°. d See ref. 15.

(XIVa) to be of higher energy than (XIVb). Although there are few reported examples of this effect, dihalogenocarbene adducts of cyclic olefins generally seem to be thermally more stable than the corresponding monohalogeno-compounds with favourably disposed leaving groups.25



Two other cases where retardation in the rates of rearrangement can be ascribed to destabilization of the intermediate carbonium ions are those of 6,6-dichloro-3-oxabicyclo[3,1,0]hexane²² (XVa) and the corresponding dibromo-derivative 22 (XVb). The Table shows that both these compounds are considerably more stable to heat than their homocyclic analogues [(Xa)] and

²² J. C. Anderson and C. B. Reese, *Chem. and Ind.*, 1963, 575; J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 1964, 4874.

²³ L. Ghosez, G. Slinckx, M. Glineur, P. Hoct, and P. Laroche, Tetrahedron Letters, 1967, 2773; D. C. F. Law and S. W. Tobey,

J. Amer. Chem. Soc., 1968, 90, 2376.
 ²⁴ J. Hine, ' Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1962, p. 184.
 ²⁵ M. S. Baird and C. B. Reese, unpublished observations.

(Xb), respectively]. Owing to the negative inductive effect of the oxygen atom, the intermediate carbonium ions (XVIa) and (XVIb) would be expected to be of higher energy than (XIVa) and (XIVb), respectively. The rearrangement products (XVIIa) and (XVIIb) were isolated in the yields indicated in the Table.



There are also cases where increase in the rates of rearrangement (compared with those of the corresponding saturated homocyclic systems) may be ascribed to mesomeric stabilization of the intermediate carbonium ions. Thus the greater thermal lability of 6,6-dichloro-2-oxabicyclo[3,1,0]hexane (XIIa) compared with that of (Xa) (see Table) may be rationalized in terms of the mesomeric effect of an oxygen lone-pair in the intermediate cation (XVIII). It also seems likely that the high thermal lability [again compared with that of (Xa), see Table] of 6,6-dichlorobicyclo[3,1,0]hex-2-ene (XIX) is due at least partly to the mesomeric effect of the double bond.19

In 1961, ter Borg and Bickel²⁶ treated cyclopentadienyl sodium with chloroform and obtained chlorobenzene; they postulated (XIX) as an intermediate but did not isolate it. However, when ethyl trichloroacetate was added to a cooled suspension of sodium methoxide in a pentane solution of cyclopentadiene, (XIX) was obtained and could be isolated in 50%vield. The latter compound was completely converted into chlorobenzene in 25 min. at 55°.

There are also reported cases ^{19,27} of thermal rearrangements where mesomeric stabilization of the intermediate carbonium ions is provided by extra-annular electron-donating groups.

Ring-size Effects.-The report 28 that treatment of cyclobutene with dichlorocarbene at 0° gives 2,3-dichlorocyclopentene (XXI) directly suggests that 5,5-dichlorobicyclo[2,1,0] pentane (XX) is unstable at 0° . The comparative thermal stability of its next higher homologue³ (Xa) (see Table) indicates the important effect of ring strain on the rate of rearrangement. It is noteworthy that the stability of the dichlorocarbene adduct of norbornene 3,29 (XXII) lies between that of (XX) and that of (Xa).

Likewise the bicyclo [3,1,0] hexane system appears to be more strained than its next higher homologue. For example, 7,7-dibromobicyclo[4,1,0]heptane¹ (XXIII), which undergoes rearrangement when heated in quinoline solution at 200° or above,¹⁹ is appreciably more stable to heat than (Xb) (see Table). 8,8-Dibromobicyclo-

80, 1217. ²⁷ W. E. Parham, R. W. Soeder, and R. M. Dodson, J. Amer. Dec. Tatvahedron Letters, 1963. Chem. Soc., 1962, 84, 1755; M. Ohno, Tetrahedron Letters, 1963, 1754; F. Nerdel and J. Buddnis, *ibid.*, 1965, 3585. [5,1,0]octane³⁰ (XXIV) in turn rearranges less readily than (XXIII); it requires to be heated at 240° or above before it decomposes to give 1-bromocyclo-octene (XXV) as the major product. The relative reluctance of



(XXIV) to undergo rearrangement may be due to an unfavourable transition state rather than to lack of ring strain in the ground state. The formation of (XX) instead of 2,3-dibromocyclo-octane as the major product suggests that the reaction does not proceed by the usual pathway.

In conclusion, it seems clear from its stereospecificity that the thermal rearrangement of halogenocarbene adducts of cyclic olefins proceeds by a mechanism involving the concerted transformation of a cyclopropyl to an allylic cation. The effects of various electronic factors on the rates of rearrangement of 6-halogenobicyclo[3,1,0]hexane derivatives are in accordance with such an ionic mechanism. The latter effects and the effect of ring-size must be considered if this synthetically useful ring-expansion reaction is to be employed successfully.

EXPERIMENTAL

N.m.r. spectra were measured at 60 and 100 MHz with a Perkin-Elmer and a Varian HA 100 spectrometer, respectively. Tetramethylsilane was used as an internal standard. U.v. absorption spectra were measured with a Cary recording spectrophotometer, model 14M-50. I.r. spectra of liquids and solids were taken for films and potassium bromide discs, respectively, with Perkin-Elmer spectrometers (models 21 and 257). Mass spectra were obtained with an A.E.I. MS 9 spectrometer, by use of heated insertion. G.l.c. was carried out with an F. & M. model 720 chromatograph with hydrogen as carrier gas. Columns containing 10-15% of the following stationary phases on Celite were used: silicone gum rubber, polyphenyl ether, and LAC (ethylene glycol adipate, crosslinked with pentaerythritol).

6,6-Dichlorobicyclo[3,1,0]hex-2-ene (XIX).-Sodium methoxide (12 g., 0.22 mole) was added to a solution of freshly distilled cyclopentadiene (6.6 g., 0.10 mole) in pentane (100 ml.). Ethyl trichloroacetate (60 g., 0.31 mole) was added dropwise to the cooled, stirred suspension ³¹ at a rate

²⁶ A. P. ter Borg and A. F. Bickel, Rec. Trav. chim., 1961,

²⁸ E. Vogel, Angew. Chem. Internat. Edn., 1963, 2, 1.

²⁹ L. Ghosez and P. Laroche, *Proc. Chem. Soc.*, 1963, 90; W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, 1963, 28, 2200; R. C. DeSelms and C. M. Combs, *ibid.*, 1963, 28, 2206.

W. J. Bell and S. R. Landor, Proc. Chem. Soc., 1961, 143. ³¹ W. E. Parham and E. E. Schweizer, J. Org. Chem., 1959, 24, 1733.

such that the temperature of the reactants did not rise above 30°. After the cooled mixture had been stirred for a further 2 hr., it was filtered, and the filtrate was concentrated under reduced pressure below 20°. Distillation of the residual liquid gave 6,6-dichlorobicyclo[3,1,0]hex-2-ene (7·3 g., 50%) as a discoloured oil, b.p. 25—27°/0·08 mm. (collected in a trap cooled by acetone-solid carbon dioxide). This material displayed only end absorption in the u.v.; ν_{max} (strong bands) 1376, 1266, 1028, 858, and 736 cm.⁻¹, τ (neat liquid) 4·29 (2H, s, H-2 and H-3), 7·44 (3H, m, H-1 and H-4), and 7·74 (1H, m, H-5).

Action of Heat on 6,6-Dichlorobicyclo[3,1,0]hex-2-ene (XIX).—A vessel containing 6,6-dichlorobicyclo[3,1,0]hex-2-ene (5 g.) under nitrogen was immersed in a heating bath maintained at 55°. G.l.c. of the mixture revealed the formation of a material with a retention time corresponding to chlorobenzene. After 25 min. the reaction was complete, and the products were distilled to give chlorobenzene (1.8 g., 48%), b.p. 132°, $\tau 2.7$ (s).

Action of Heat on 6,6-Dichlorobicyclo[3,1,0]hexane (Xa).— A stoppered vessel containing 6,6-dichlorobicyclo[3,1,0]hexane ³ (2 g.) was immersed in a heating bath maintained at 170°. G.l.c. of the mixture revealed the gradual formation of a material with a longer retention time than (Xa). After 90 min., when all the starting material had been consumed, the products were distilled to give 2,3-dichlorocyclohexene ³ (1·8 g., 90%), b.p. 76–78°/14 mm. (lit.,³ 81–83°/15 mm.), τ (CCl₄) 4·05 (1H, t, H-1), 5·57 (1H, m, H-3), 7·86 (4H, m, H-4 and H-6), and 8·21 (2H, m, H-5).

Action of Heat on 6,6-Dibromobicyclo[3,1,0]hexane (Xb).— A stoppered vessel containing 6,6-dibromobicyclo[3,1,0]hexane ²⁰ (2 g.) was immersed in a heating bath maintained at 120°. G.l.c. revealed the gradual formation of a material with a longer retention time. After 60 min., when all the starting material had been consumed, the products were distilled to give 2,3-dibromocyclohexene (1·7 g., 85%), b.p. 56—59°/1 mm. (lit.,²⁰ 105—106°/9·5 mm.), τ (CCl₄) 3·8 (1H, t, H-1), 5·3 (1H, s, H-3), 7·8 (4H, m, H-4 and H-6), and 8·2 (2H, m, H-5).

endo- and exo-6-Chlorobicyclo[3,1,0] hexanes.--Ethereal methyl-lithium (0.475 mole; 500 ml. of 0.95M-solution) was added dropwise, over a period of 5 hr., to a stirred solution of cyclopentene (69 g., 1.01 mole) and dichloromethane (69 g., 0.81 mole) at 20°. The products were set aside overnight, then extracted with water, and the dried $(MgSO_4)$ organic layer was evaporated to leave a crude mixture of endo- and exo-6-chlorobicyclo[3,1,0]hexanes * (38 g., 69%) based on MeLi). A pure specimen of the major component (75%) was isolated by preparative g.l.c. and identified as endo-6-chlorobicyclo[3,1,0]hexane [Found: C, 61.4; H, 7.8; Cl, 30.9. C₆H₉Cl requires C, 61.5; H, 7.8; Cl, 30.6%), τ (CCl₄) 6.72 (1H, t, J 7 Hz, H-6) and 7.8—8.4 (8H, m, all other protons), v_{max} 3050m, 2950s, 2890m, 1480m, 1450m, 1330m, 1280s, 985m, and 758s cm.⁻¹, m/e 116 and 118 (M^+) ; base peak 79.

G.l.c. of the products obtained by heating a solution of the isomeric mixture (38 g.) and quinoline (35 g.) for 2 hr. (bath temperature 140°) revealed no *endo*-isomer, but a major component with a much lower retention time. The products were separated by fractional distillation [Nester-Faust steel spinning-band column (18 in.)] to give cyclohexa-1,3-diene (10.6 g., 28% based on MeLi) and exo-6-chloro-

 $bicyclo[3,1,0]hexane~(3.5~{\rm g.},~6\%~based~on~MeLi),~b.p.~135^{\circ}/$ 760 mm. (Found: C, 61.8; H, 7.6; Cl, 30.3%), τ (CCl₄) 7.38 (1H, t, J 1.5 Hz, H-6) and 7.9—8.4 (8H, m, all other protons), $\nu_{\rm max.}$ 3040m, 2950s, 2850s, 1480m, 1450m, 1295s, 1240m, 1220m, 1162m, 1045m, 1000s, 982m, 898m, 850m, 830m, 820m, and 742s cm.⁻¹, m/e 116 and 118 (M^+) ; base peak 67.

Action of Heat on endo-6-Chlorobicyclo[3,1,0]hexane (VII). —(a) A sealed tube containing (VII) was immersed in an oil-bath maintained at 126°. After 3 hr., g.l.c. revealed no starting material and a single product with a slightly greater retention time, isolated in a pure state by preparative g.l.c.; its retention time and i.r., n.m.r., and mass spectra were identical to those of authentic 3-chlorocyclohexene ³² (IX).

(b) No reaction was detected when 6-chlorobicyclo-[3,1,0]hexane was heated at 95° for 4 hr.; however, when it was heated at 103° for 3.5 hr., it was ca. 30% converted into 3-chlorocyclohexene.

Action of Heat on exo-6-Chlorobicyclo[3,1,0]hexane (VIII). —(a) After this compound had been heated as in the preceding experiment for 3 hr. at 300°, it was ca. 70% converted into a material of lower g.l.c. retention time, identified as benzene by comparison of its retention time and n.m.r. and mass spectra with those of authentic material.

(b) Only ca. 10% conversion of (VIII) into benzene occurred in 4.5 hr. at 260° .

(c) No reaction was observed after 4 hr. at 250° .

Action of Heat on 6,6-Dichloro-3-oxabicyclo[3,1,0]hexane (XVa).—A sealed tube containing a mixture (20·6 g.) of 2-dichloromethyl-2,5-dihydrofuran (1 part w/w) and 6,6-dichloro-3-oxabicyclo[3,1,0]hexane (1·86 parts) ²² was heated at 235°. After 160 min. g.l.c. revealed the presence of a product of longer retention time and only ca. 5% of unchanged (XVa). Distillation of the products (nitrogen atmosphere) gave 4,5-dichloro-5,6-dihydro-2H-pyran [9·3 g., 69% based on (XVa)] (Found: C, 39·7; H, 4·0; Cl, 46·7. C₅H₆Cl₂O requires C, 39·3; H, 3·9; Cl, 46·4%), b.p. 99—100°/19 mm., v_{max} (strong bands) 2880, 1740, 1650, 1455, 1360, 1328, 1300, 1270, 1240, 1140, 1088, 1060, 1000, 943, 938, 833, 824, and 697 cm.⁻¹, τ (CCl₄) 3·97 (1H, t, J 3 Hz, H-3), 5·78 (3H, m, H-2 and H-5), and 6·01 (2H, d, J 3·5 Hz, H-6).

4-Chloro-5,6-dihydro-2H-pyran.—A solution of 4,5-dichloro-5,6-dihydro-2H-pyran (XVIIa) (2.0 g.) in anhydrous ether (10 ml.) was treated with a suspension of lithium aluminium hydride (1.0 g.) in ether (10 ml.) at a rate which maintained the solvent under gentle reflux. The mixture was then heated externally for a further 40 min. before methyl formate (5 ml.) was added. The products were acidified with dil. sulphuric acid; the organic layer was separated, dried (MgSO₄), and distilled to give 4-chloro-5,6-dihydro-2H-pyran (0.74 g., 50%) (Found: C, 50.4; H, 6.0; Cl, 29.1. C₅H₇ClO requires C, 50.6; H, 6.0; Cl, 29.9%), b.p. 44—46°/17 mm., v_{max} 2945, 1678, 1663, 1598, 1196, 1117, 1065, 1026, 962, 920, 795, and 729 cm.⁻¹, τ 4.20 (1H, m, 3-H), 5.92 (2H, m, H-2), 6.23 (2H, t, J 5.5 Hz, H-6), and 7.64 (2H, m, H-5).

Action of Heat on 6,6-Dibromo-3-oxabicyclo[3,1,0]hexane (XVb).—A mixture (25.5 g.) of 2-dibromomethyl-2,5-dihydrofuran (1 part w/w) and 6,6-dibromo-3-oxabicyclo-[3,1,0]hexane (1.5 parts) ²² was heated (nitrogen atmosphere) under reflux (184°) for 135 min. G.l.c. showed that <50%of the latter component remained, and also that a material

³³ F. Hoffmann and P. Damm, Mitt. schlesischen Kohlenforsch. Kaiser-Wilhelm Ges., 1925, 2, 97 (Chem. Abs., 1928, 22, 1250).

^{*} This mixture contained a third component (ca. 2%), identified as *exo*-6-bromobicyclo[3,1,0]hexane.

with a longer retention time had been produced. Distillation of the products gave two fractions: (a) 16 g., b.p. 62—69°/0·4 mm., and (b) 5 g. [33% based on (XVb)], b.p. 69—70°/0·4 mm. Fraction (b), which was homogeneous on g.l.c., solidified. Recrystallisation from light petroleum gave 4,5-*dibromo*-5,6-*dihydro*-2H-*pyran* as colourless crystals, m.p. 28—30° (Found: C, 24·8; H, 2·3; Br, 66·8. $C_5H_6Br_2O$ requires C, 24·8; H, 2·5; Br, 66·1%), τ (CCl₄) 3·81 (1H t, J 4 Hz, 3-H) and 5·4—6·0 (5H, m, all other protons).

4-Bromo-5,6-dihydro-2H-pyran.—A solution of 4,5-dibromo-5,6-dihydro-2H-pyran (XVIIb) (6·4 g.) in anhydrous ether (10 ml.) was treated with lithium aluminium hydride (0·6 g.) and the products were worked up as in the preparation of 4-chloro-5,6-dihydro-2H-pyran. 4-Bromo-5,6-dihydro-2H-pyran (2·0 g., 46%) (Found: C, 37·1; H, 4·3. C₅H₇BrO requires C, 36·9; H, 4·3%), b.p. 86—87°/ 60 mm., was obtained by distillation of the products, τ (CCl₄) 3·96 (1H, m, H-3), 5·94 (2H, m, H-2), 6·22 (2H, t, J 6 Hz, H-6), and 7·50 (2H, m, H-5).

 a flask fitted with a Dean-Stark head, was heated under reflux (internal temperature of reaction vessel fell gradually from 260 to 240°). The distillate, collected in the Dean-Stark head over a period of 30 min., was returned to the flask and redistilled over a further period of 30 min. G.l.c. then indicated that the products (1.9 g.) consisted of a major component (*ca.* 80%) with a slightly shorter retention time than the starting material, and two more volatile minor components.

The major component had an i.r. spectrum identical with that of 1-bromocyclo-octene: ³³ $\nu_{max.}$ 2930s, 2850s, 1642m, 1463s, 1448m, 1212m, and 1110m cm.⁻¹, τ (CCl₄) 4·10 (1H, t, J 8·5 Hz, 2-H), 7·45 (2H, m, H-8), 7·94 (2H, m, H-3), and 8·48 (8H, m, all other protons), *m/e* 188 and 190 (*M*⁺); base peak, 67.

The minor components were identified (n.m.r. and mass spectra) as ethylbenzene and o-xylene.

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³³ G. Wittig and H. L. Dorsch, Annalen, 1968, 711, 46.