

Preparation of Medium-sized Ring *trans*-Cycloalkene Derivatives from Halogenocyclopropane Intermediates by Silver Perchlorate-promoted Solvolysis

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8,8-Dibromobicyclo[5.1.0]octane (8c), 9,9-dibromobicyclo[6.1.0]nonane (9c), and 9,9-dibromobicyclo[6.1.0]-non-4-ene (19a) readily undergo ring expansion in the presence of high concentrations of silver perchlorate to give, in methanol solution, the corresponding *trans*-cycloalkenyl ethers [(11a), (13a), and (20a), respectively] and, in aqueous acetone solution, the corresponding *trans*-cycloalkenols [(11b), (13b), and (20b), respectively] in high yields. The dichloro-compounds (8d), (9d), and (19b) undergo silver perchlorate-promoted methanolysis and hydrolysis in the same way. Compounds (8c), (8d), (19a), and (19b) all undergo stereospecific solvolysis to give only one of two possible diastereoisomers. *exo*-8-Bromobicyclo[5.1.0]octane (8a) and *exo*-9-bromobicyclo[6.1.0]nonane (9a) rapidly undergo silver perchlorate-promoted methanolysis and hydrolysis to give the respective *trans*-cycloalkenyl ethers [(6b) and (7b)] and *trans*-cycloalkenols [(6c) and (7c)] in high yields; their *endo*-isomers are solvolyzed much less readily to give the corresponding *cis*-isomers in lower yields. The silver perchlorate-promoted solvolysis of 10,10-dibromo-, *exo*-10-bromo-, and *endo*-10-bromo-bicyclo[7.1.0]decanes [(10c), (10a), and (10b), respectively] are also described. The main products of silver perchlorate-promoted solvolysis of 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]decane (21) are *trans,trans*-cyclodeca-1,6-diene derivatives. The interconversion of the diastereoisomers of the above 3-substituted *trans*-cyclo-octene, -cyclononene, and -cyclodecene derivatives is discussed.

ALTHOUGH several methods are available for the synthesis of strained medium-sized ring *trans*-cycloalkenes,¹ the ring expansion of the readily accessible halogenocarbene adducts of *cis*-cycloalkenes appeared to us to be a particularly attractive approach. This route was suggested by the application of the principle of the conservation of

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¹ For preparation of *trans*-cyclo-octene, see K. Ziegler and H. Wilms, *Annalen*, 1950, **567**, 1; A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, 1953, **75**, 3212; E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, 1965, **87**, 934; E. Vedejs and P. L. Fuchs, *ibid.*, 1971, **93**, 4070; E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, 1973, **38**, 1178; J. N. Hines, M. J. Peagram, E. J. Thomas, and G. H. Whitham, *J.C.S. Perkin I*, 1973, 2332; M. Jones, P. Temple, E. J. Thomas, and G. H. Whitham, *ibid.*, 1974, 433.

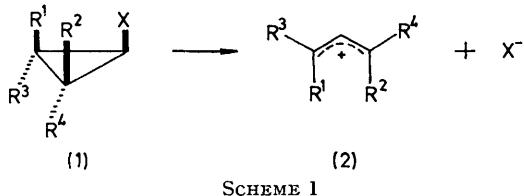
orbital symmetry² to the ring-expansion reaction and by the independent conclusions of De Puy *et al.*³ In essence, it was predicted that the concerted transformation of a cyclopropyl into an allylic cation is a disrotatory process in which the cyclopropyl substituents *cis* to the leaving group (R^1 and R^2 , Scheme 1) rotate inwards and those *trans* to the leaving group (R^3 and R^4) rotate outwards. These predictions were soon supported by the demonstration⁴ that the acetolysis rates of cyclopropyl tosylates

² R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

³ C. H. De Puy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, 1965, **87**, 4006.

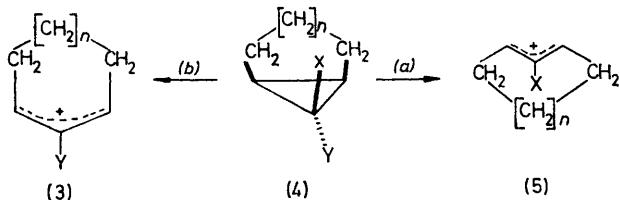
⁴ P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, 1966, **88**, 2668; C. H. De Puy, L. G. Schnack, and J. W. Hausser, *ibid.*, p. 3343.

(1; X = OTs) are enhanced by the presence of methyl or phenyl substituents at C(2) and C(3) and especially when these relatively bulky substituents are *trans* to the leaving group. The presence of bulky substituents *cis* to the leaving group would be expected to lead to a sterically hindered transition state and hence to a sterically hindered allylic cation (2).



SCHEME 1

If the principle of orbital symmetry conservation² is applied to bicyclic systems (4), two possible modes of ring opening can be envisaged (Scheme 2); (a) loss of the *exo*-leaving group (Y) to give a *trans,trans*-allylic cation (5), and (b) loss of the *endo*-leaving group (X) to give a *cis,cis*-allylic cation (3). Solvolysis studies by Schöllkopf, Schleyer, and their co-workers⁵ on the appropriate *endo*- and *exo*-tosylate esters [respectively (4; X = OTs, Y = H) and (4; X = H, Y = OTs)] have suggested that, except in cases where it would lead to exceptional ring strain in the transition state (*i.e.* when n < 3), (a) is the more favourable mode of ring-opening. Thus while *exo*-8-tosyloxybicyclo[5.1.0]octane (4; n = 3, X = H, Y = OTs) undergoes acetolysis at 2500 times the rate of cyclopropyl tosylate at 100 °C, *exo*-6-tosyloxybicyclo[3.1.0]hexane (4; n = 1, X = H, Y = OTs) is virtually unaffected at 150 °C. These studies⁵ clearly indicate that mode (a) is much favoured over mode (b) in the ring expansion of the bicyclo[5.1.0]octane and bicyclo[6.1.0]-nonane systems in that the *exo*-tosyloxy-derivatives (4 n = 3 or 4, respectively, X = H, Y = OTs) underwent acetolysis *ca.* 10³ times faster than their *endo*-epimers (4; n = 3 or 4, respectively, X = OTs, Y = H). The exceptionally high solvolysis rate of *endo*-6-tosyloxybicyclo[3.1.0]hexane (4; n = 1, X = OTs, Y = H), presumably with mode (b) ring-opening, is possibly due to the combined factors of ring strain in the ground state and a relatively strain-free transition state.



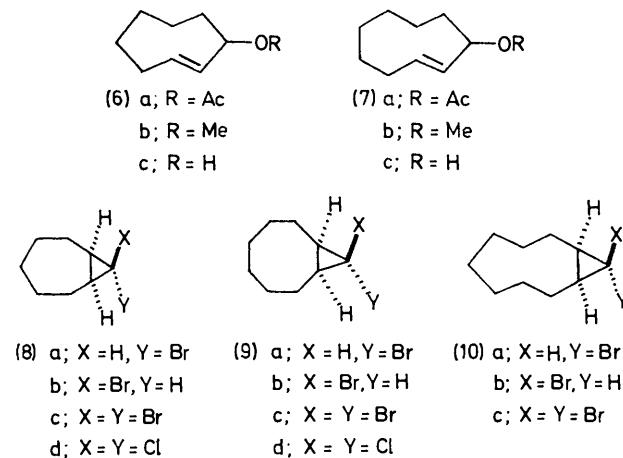
SCHEME 2

Although the solvolysis studies⁵ of Schöllkopf and Schleyer were mechanistically illuminating, they did not constitute a method for the synthesis of medium-

⁵ U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Letters*, 1967, 3639.

⁶ G. H. Whitham and M. Wright, *Chem. Comm.*, 1967, 294; *J. Chem. Soc. (C)*, 1971, 883.

sized ring *trans*-cycloalkene derivatives. Thus 3-acetoxy-*trans*-cyclo-octene (6a) and -cyclononene (7a) were not among the isolated acetolysis products of *exo*-8-tosyloxybicyclo[5.1.0]octane and *exo*-9-tosyloxybicyclo[6.1.0]nonane (4; n = 3 or 4, respectively, X = H, Y = OTs). This was almost certainly due to the comparatively drastic conditions required for acetolysis. The first successful preparation of a strained medium-sized ring cycloalkene derivative by this approach was that of *trans*-cyclo-oct-2-en-1-ol (6c) in 72% yield by heating *exo*-8-bromobicyclo[5.1.0]octane (8a) under reflux in aqueous dioxan in the presence of sodium hydrogen carbonate for 20 h.⁶ Only the corresponding *cis*-alcohol was obtained when the solvolysis was carried out in the presence of silver ion.



It is known that the ring-expansion reaction can be promoted thermally⁷ as well as solvolytically. Indeed there are a number of useful synthetic applications of the thermal reaction, especially in the bicyclo[3.1.0]hexane and bicyclo[4.1.0]heptane series. Unfortunately, the thermal reaction has not proved of much value in the synthesis of medium sized-ring *trans*-cycloalkene derivatives. Thus both *exo*-8-bromo-⁸ and 8,8-dibromo-bicyclo[5.1.0]octane⁷ (8a and c, respectively) are extremely stable to heat, and pyrolysis⁸ of *exo*-9-bromo- and 9,9 dibromo-bicyclo[6.1.0]nonane (9a and c, respectively) leads only to the less strained *cis*-cyclononene derivatives. The only clear example of the preparation of a medium-sized ring *trans*-cycloalkene by thermally promoted ring expansion is the conversion⁹ of 10,10-dibromobicyclo[7.1.0]decane (10c) into 2,3-dibromo-*trans*-cyclodecene. The failure to convert the bicyclo[6.1.0]nonanes (9a and c) into *trans*-cyclononene derivatives was probably due to the relatively high temperatures required.

In contrast to its thermal stability, we now report¹⁰ that when 8,8-dibromobicyclo[5.1.0]octane (8c) is treated with an excess of silver perchlorate in methanol solution

⁷ For some leading references, see M. S. Baird, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc. (C)*, 1969, 1174.

⁸ M. S. Baird and C. B. Reese, *J. Chem. Soc. (C)*, 1969, 1803.

⁹ C. B. Reese and A. Shaw, *J.C.S. Chem. Comm.*, 1972, 271.

¹⁰ For preliminary accounts see C. B. Reese and A. Shaw, *(a) J. Amer. Chem. Soc.*, 1970, **92**, 2566; *(b) Chem. Comm.*, 1970, 1365, 1367; *(c) J.C.S. Chem. Comm.*, 1972, 331, 332.

at 15–20 °C (Table 1, experiment no. 1) it is virtually quantitatively converted into 2-bromo-3-methoxy-*trans*-cyclo-octene (11a), which may be isolated as a colourless

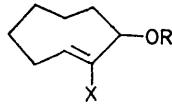
section). In order to ensure quantitative reaction, it is advisable to use a two-fold excess of silver perchlorate with an initial concentration of *ca.* 2M. Although there

TABLE 1
Silver perchlorate-promoted solvolysis of halogenocarbene adducts of cycloalkenes

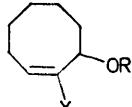
Experiment no.	Substrate	Solvent	Temp. (°C)	Time (min)	Product	Yield (%)	N.m.r. spectrum of product ^a			
							H(1) [J/Hz]	H(2)	H(3) [J/Hz]	OCH ₃ (OH) ^b
1	(8c)	MeOH	15–20	15	(11a)	84	3.89dd [4, 11.5]		6.36dd [6, 9]	6.83s
2	(8c)	Me ₂ CO–H ₂ O	15–20	15	(11b)	81	3.97dd [4, 12]		5.92dd [5.5, 10.5]	(7.22s)
3	(8a)	MeOH	15–20	10	(6b)	80	4.2–4.8m		6.36dt [5.5, 9]	6.81s
4	(8a)	Me ₂ CO–H ₂ O	15–20	10	(6c)	77	4.4–4.7m		5.9m	(5.69s)
5	(8b)	MeOH	45	180	(12a)	47	4.24–4.74m		6.02m	6.84s
6	(8b)	Me ₂ CO–H ₂ O	56	120	(12b)	56	4.4–4.7m		5.5m	(7.20s)
7	(8d)	MeOH	45	45	(11c)	80	4.12dd [4, 12]		6.24dd [5, 10]	6.80s
8	(9c)	MeOH	15–20	10	(13a) ^c	82	{3.80dd [5.5, 10.5] ^d	{6.09m ^d	{6.72s ^d	
							{3.99dd [5.5, 10]	{6.55dd [5.5, 10]	{6.83s	
							{3.66dd [6, 10] ^e	{5.59m ^e	{6.98br,s)	
							{4.04dd [5.5, 10]	{6.08dd [4, 10]		
10	(9a)	MeOH	0	15	(7b)	79	4.4–5.0m		{6.17m	6.82s
							{6.6m			
11	(9a)	Me ₂ CO–H ₂ O	0	15	(7c) ^f	82	4.6–4.8m		{5.58m	(7.12s)
							{6.0–6.3m			
12	(9b)	MeOH	70	60	(14a)	55	4.2–4.9m		5.9–6.2m	6.94s
13	(9b)	Me ₂ CO–H ₂ O	56	180	(14b)	55	4.3–4.75m		5.50m	(7.20s)
14	(9d)	MeOH	20	60	(13c)	70	{4.06dd [5.5, 11] ^g	{6.24m ^g	{6.74s ^g	
							{4.24dd [5, 10]	{6.42dd [4, 10]	{6.82s	
15	(10c)	MeOH	0	15	{(15a) ^h	81	3.88t [8]	6.44m	6.86s	
					{(16a)	3.92dd [6, 12.5]	5.76m	6.88s		
16	(10c)	Me ₂ CO–H ₂ O	0	15	{(15b) ⁱ	90	3.82t [8]	5.93dd [5, 8]	(7.45s)	
					{(16b)	4.14dd [5, 12]	5.33dd [6, 9]			
17	(10a)	MeOH	0	15	(15c)	91	4.2–4.85m	6.44m	6.86s	
18	(10b)	MeOH	65	60	{(15c) ^j	76	4.3–4.5m	5.7–6.0m	6.88s	
19	(19a)	MeOH	15–20	10	(20a)	90	4.16dd [6, 10]	6.49m	6.84s	
20	(19a)	Me ₂ CO–H ₂ O	15–20	20	(20b)	82	4.20dd [7, 8]	6.03dd [6, 10]		
21	(19b)	MeOH	20	20	(20c)	80	4.38dd [5, 10.5]	6.2–6.5m	6.84s	
22	(19b)	Me ₂ CO–H ₂ O	20	40	(20d)	73	4.42dd [5.5, 10]	5.86dd [6, 9]	(7.32s)	
23	(21)	MeOH	20	45	{(22a)	41	{3.80dd [2.5, 10.5]	{6.13m	{6.60s	
					{(23a)	{3.86dd [3, 10]	{6.35dd [3.5, 10.5]	{6.82s		
24	(21)	Me ₂ CO–H ₂ O	20	60	(22b)	42	{3.73dd [ca. 3, 10]	{6.34dd [3.5, 10.5]	{6.80s	
							{3.85dd [ca. 2, 10]	{5.70m		
								{5.95dd [3.5, 10.5]		

^a In CCl₄ except in experiments nos. 23 and 24 when CDCl₃ and CD₃OD, respectively, were used as solvents; protons numbered as in –CH(1)=CH(2)–C(OR)H(3). ^b Satisfactory integrals were obtained; hydroxy-signals in parentheses. ^c Contaminated with *ca.* 5% of *cis*-isomer (14c). When the solvolysis was carried out at 0 °C, pure *trans*-compound (13a) was obtained. ^d The ratio of the integrals of the first to the second of the bracketed signals was *ca.* 0.8 : 1. ^e The ratio of the integrals of the first to the second of the bracketed signals was *ca.* 0.4 : 1. ^f This compound has m.p. 64–65° and has probably been incorrectly described previously as *cis*-cyclononen-3-ol (14b) (H. Nozaki, T. Aratani, and R. Noyori, *Tetrahedron*, 1967, **23**, 3645). ^g The ratio of the integrals of the first to the second of the bracketed signals was *ca.* 0.6 : 1. ^h The proportions of (15a) and (16a) were *ca.* 7 : 3. ⁱ The proportions of (15b) and (16b) were *ca.* 2 : 1. ^j The proportions of (15c) and (16c) were *ca.* 1 : 3.

liquid in 84% yield. It is essential that the concentration of silver ions be high. Thus the reaction is fast in



(11) a; X = Br, R = Me
b; X = Br, R = H
c; X = Cl, R = Me



(12) a; X = H, R = Me
b; X = R = H
c; X = Br, R = Me

M-, slow in 0.1M-, and immeasurably slow in 1.44 × 10⁻²M-silver perchlorate solution (see Experimental

* It has recently been reported (R. D. Bach and C. L. Willis, *J. Amer. Chem. Soc.*, 1975, **97**, 3844) that the rate of reaction of 2-bromo-octane with AgClO₄ in methanol solution is proportional to [Ag⁺]².

are numerous reports ¹¹ of the silver ion-assisted solvolysis of halogenocarbene adducts of olefins, the dramatic effect of silver ion concentration on solvolysis rates does not appear to have been described. We believe that an adequate explanation of this phenomenon must await detailed kinetic measurements.*

When 8,8-dibromobicyclo[5.1.0]octane (8c) is treated with silver perchlorate in acetone–water (9 : 1 v/v) under similar conditions (Table 1, experiment no. 2), 2-bromo-*trans*-cyclo-oct-2-en-1-ol (11b) is obtained in high yield. In the same way, silver perchlorate-assisted solvolysis of *exo*-8-bromobicyclo[5.1.0]octane (8a) proceeds rapidly

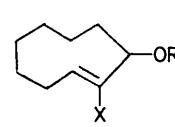
¹¹ For examples, see A. J. Birch, J. M. Brown, and F. Stansfield, *J. Chem. Soc.*, 1964, 5343; A. J. Birch, G. M. Iskander, B. I. Magboul, and F. Stansfield, *J. Chem. Soc. (C)*, 1967, 358; S. R. Sandler, *J. Org. Chem.*, 1967, **32**, 3876.

in methanol and in aqueous acetone (Table 1, experiments nos. 3 and 4) to give high yields of 3-methoxy- and 3-hydroxy-*trans*-cyclo-octenes (6b and c, respectively). The latter experiment is interesting in the light of Whitham and Wright's observations⁶ that solvolysis of (8a) leads to (6c) in the absence but to *cis*-cyclo-oct-2-en-1-ol (12b) in the presence of silver ions. While it is clear that the silver ion-assisted solvolysis proceeds under considerably milder conditions, the fact that a high concentration of silver ions is required is again emphasized. Whitham and Wright demonstrated⁶ that the isomerization of (6c) to (12b) was promoted by silver ions under the conditions they used for the solvolysis of (8a).

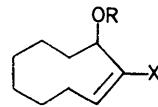
The conditions required for the silver perchlorate-promoted methanolysis of *endo*-8-bromobicyclo[5.1.0]-octane (8b) (Table 1, experiment no. 5) are much more drastic (3 h; 45 °C) than for the *exo*-isomer (8a) (experiment no. 3) and lead to *cis*-3-methoxycyclo-octene (12a) in only moderate yield. As the half-time of isomerization of (6a) to (12a) at 70 °C, in methanol containing silver perchlorate and perchloric acid, was found to be *ca.* 2 h, it is reasonable to conclude that *cis*-3-methoxycyclo-octene (12a) is the primary methanolysis product of *endo*-8-bromobicyclo[5.1.0] octane (8b). The silver perchlorate-promoted solvolysis of the latter in aqueous acetone (Table 1, experiment no. 6) again requires relatively drastic conditions (2 h; 56 °C) and leads only to a moderate yield of the *cis*-alcohol (12 b). We believe that (8a and b) are the first pair of epimeric halogenocyclopropane derivatives to be reported which both undergo ring-expansion to give pure *trans*- and *cis*-olefin derivatives in the manner predicted² on the basis of orbital symmetry considerations. In a final experiment in the bicyclo-[5.1.0]octane series, treatment of the 8,8-dichloro-derivative (8d) with silver perchlorate in methanol (Table 1, experiment no. 7) gave 2-chloro-3-methoxy-*trans*-cyclo-octene (11c) in good yield but, not surprisingly,⁷ the solvolytic conditions are more drastic than those required for the corresponding dibromo-compound (8a) (experiment no. 1).

A corresponding set of experiments was carried out in the bicyclo[6.1.0]nonane series. Thus the 9,9-dibromo-(9c) and *exo*-9-bromo-(9a) derivatives readily undergo silver perchlorate-promoted methanolysis (Table 1, experiments nos. 8 and 10) and hydrolysis (experiments nos. 9 and 11) to give the expected *trans*-cyclononene derivatives [(13a), (7b), (13b), and (7c), respectively] in high yields. It is desirable to carry out these solvolysis reactions at 0 °C and thereby prevent the formation of small amounts of the corresponding *cis*-isomers. For example, when (9c) is treated with silver perchlorate in methanol at 15–20 °C, the 2-bromo-3-methoxy-*trans*-cyclononene (13a) obtained (experiment no. 8) is contaminated with *ca.* 5% of *cis*-isomer (14c); at 0 °C, pure *trans*-isomer is obtained. As anticipated the methanolysis and hydrolysis of *endo*-9-bromobicyclo[6.1.0]nonane (9b) proceed more slowly (experiments nos. 12 and 13) to give moderate yields of the *cis*-cyclononene derivatives (14a and b, respectively) and the methanolysis of 9,9-dichlorobicyclo-

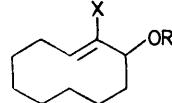
[6.1.0]nonane (experiment no. 14) leads to a high yield of 2-chloro-3-methoxy-*trans*-cyclononene (13c).



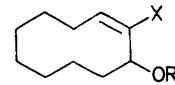
(13) a; X = Br, R = Me
b; X = Br, R = H
c; X = Cl, R = Me



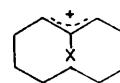
(14) a; X = H, R = Me
b; X = R = H
c; X = Br, R = Me



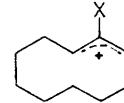
(15) a; X = Br, R = Me
b; X = Br, R = H
c; X = H, R = Me



(16) a; X = Br, R = Me
b; X = Br, R = H
c; X = H, R = Me



(17) a; X = H
b; X = Br

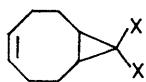


(18) a; X = H
b; X = Br

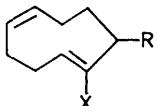
Silver perchlorate-promoted methanolysis and hydrolysis of 10,10-dibromobicyclo[7.1.0]decane (10c) (Table 1, experiments nos. 15 and 16) both proceed rapidly at 0 °C but mixtures of *ca.* 2 parts of the *trans*-isomers (15a and b, respectively) and 1 part of the *cis*-isomers (16a and b, respectively) are obtained. A possible explanation is that the *trans*,*trans*-cyclodecenylium ion (17b) is formed initially and then isomerizes to the *cis*,*trans*-allylic cation (18b) before solvolysis. Attempts to effect the direct separation of either of the two pairs of *cis*- and *trans*-isomers [(15a) and (16a); (15b) and (16b)] have been unsuccessful. However, it is possible to obtain pure samples of the *trans*- and *cis*-alcohols [(15b) and (16b), respectively] by separating and then saponifying their 3,5-dinitrobenzoate esters. Pure 2-bromo-3-methoxy-*trans*-cyclodecene (15a), required for variable temperature n.m.r. studies (see below), may readily be prepared by methylation of the pure alcohol (15b). Silver perchlorate-promoted methanolysis of *exo*-10-bromobicyclo[7.1.0]decane (10a) (experiment no. 17) proceeds rapidly at 0 °C to give, perhaps surprisingly, pure 3-methoxy-*trans*-cyclodecene (15c) in high yield; methanolysis of the *endo*-isomer (10b) (experiment no. 18) proceeds more slowly under the same reaction conditions to give a good yield of a *ca.* 3 : 1 mixture of *cis*- and *trans*-3-methoxy-cyclodecenes, (16c) and (15c).

We next turned our attention to the solvolysis of 9,9-dibromo- (19a) and 9,9-dichloro- (19b) bicyclo[6.1.0]non-4-enes. Both react rapidly with silver perchlorate in methanol (Table 1, experiments nos. 19 and 21) to give the corresponding 1-halogeno-9-methoxy-*trans*,*cis*-cyclonona-1,5-dienes (20a and c, respectively). Even the dichloro-compound (19b) undergoes rapid solvolysis:

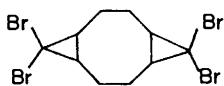
this correlates * with its being much more susceptible to heat-promoted ring expansion¹³ than its dihydro-derivative (9d). Compounds (19a and b) also readily undergo silver perchlorate-promoted hydrolysis in aqueous acetone (experiments nos. 20 and 22) to give 2-bromo- and 2-chloro-*trans*, *cis*-cyclonona-2,6-dienols (20b and d, respectively), which may be isolated as pure crystalline solids in high yields. Reaction between 2-bromo-*trans,cis*-cyclonona-2,6-dienol (20b) and phosphorus tribromide in benzene solution gives¹² 1,9-dibromo-*trans,cis*-cyclonona-1,5-diene (20; X = R = Br) which is readily distinguishable from its *cis,cis*-isomer (see below), obtained by the action of heat on (19a).



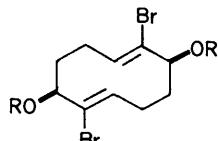
(19) a; X = Br
b; X = Cl



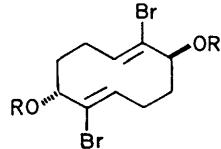
(20) a; X = Br, R = OMe
b; X = Br, R = OH
c; X = Cl, R = OMe
d; X = Cl, R = OH



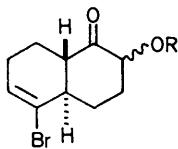
(21)



(22) a; R = Me
b; R = H



(23) a; R = Me
b; R = H



(24) a; R = Me
b; R = H

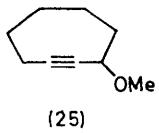
Finally the solvolysis of 5,5,10,10-tetrabromotricyclo-[7.1.0.0^{4,6}]decane (21) was examined. Treatment with silver perchlorate in methanol (Table 1, experiment no. 23) gives three products which were all isolated as pure crystalline solids. The major product, m.p. 63.5–65°, obtained in 41% yield, was characterized on the basis of n.m.r. spectroscopic (see below) and other data as 1,6-dibromo-*cis*-5,10-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (22a). The minor products (m.p.s 160–162° and 101–102°), obtained in 6 and 9% yields, were identified as the corresponding *trans*-5,10-dimethoxy-compound

* Duffin and Sutherland¹² have reported that 9,9-dibromo-bicyclo[6.1.0]non-4-ene (19a) undergoes silver acetate-promoted solvolysis in acetic acid [to give (20; X = Br, R = OAc)] at least 200 times as fast as its dihydro-derivative (9c).

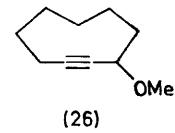
† The rapid elimination of the elements of hydrogen bromide from *trans*-2-bromocyclo-octene, -nonene, and -decene derivatives to give the corresponding cycloalkynes appears to be a general reaction.^{10,16,17} However, it may be necessary to protect hydroxy-functions (e.g. by tetrahydropyranylation^{10,18}) before carrying out this elimination. The elimination of the elements of hydrogen chloride from *trans*-2-chlorocycloalkene derivatives proceeds¹⁸ less rapidly.

(23a) and the bicyclic ketone (24a). It has not been established firmly that the rings in the latter compound are *trans*-fused but preliminary base-catalysed equilibration studies support this assignment. Silver perchlorate-promoted hydrolysis of (21) (experiment no. 24) gives 2,7-dibromo-*trans,trans*-cyclodeca-2,7-diene-*cis*-1,6-diol (22b) (42%) and the bicyclic ketol (24b). There is no indication that the *trans*-1,6-diol (23b) is also obtained. Methylation of (22b) gives (22a) in good yield.

It is clear, especially from thermochemical measurements,¹⁴ that *trans*-cyclo-octene, -cyclononene, and -cyclo-decene are more strained than the corresponding *cis*-cycloalkenes. It is therefore essential that the structures of all the *trans*-cycloalkene derivatives described above should be established unambiguously. In the cases of compounds (6b), (6c), (7b), and (7c), which are unsubstituted at C(2), the presence of strong i.r. bands at ca. 980 cm⁻¹ is good evidence¹⁵ for their being *trans*-isomers. Furthermore, these compounds are readily distinguishable from their *cis*-isomers [(12a), (12b), (14a), and (14b), respectively]. The structures of the 2-halogeno-*trans*-cycloalkene derivatives described above follow less clearly from spectroscopic measurements. The observation¹⁶ that they are rapidly converted into the corresponding cycloalkyne derivatives when treated with potassium t-butoxide in anhydrous dimethyl sulphoxide is perhaps the most convincing evidence for their assigned structures. Thus, as examples,† 3-methoxy-cyclo-octyne (25) and 3-methoxycyclononyne (26) are obtained¹⁶ in high yields when (11a) and (13a), respectively, are treated with an excess of potassium t-butoxide in dimethyl sulphoxide for 5 s at 20 °C. 1-Bromo-*cis*-cyclo-octene undergoes no detectable conversion into cyclo-octyne under these conditions.¹⁶ Less convincing evidence for the structures of 2-halogenocycloalkene derivatives comes from a study of their reduction with sodium in liquid ammonia. In contrast to a report¹⁸ that such reactions proceed stereospecifically with retention of configuration, reduction of 2-bromo-3-methoxy-*trans*-cyclo-octene (11a) leads to a ca. 1 : 1 mixture of *trans*- and *cis*-3-methoxycyclo-octenes [(6b) and (12a),



(25)



(26)

respectively] in high yield. Similar results are obtained in the reductions of 2-bromo-3-methoxy- and 2-bromo-3-hydroxy-*trans*-cyclononenes (13a and b, respectively) with sodium in liquid ammonia.

¹² D. Duffin and J. K. Sutherland, *Chem. Comm.*, 1970, 626.

¹³ M. S. Baird and C. B. Reese, *J. Chem. Soc. (C)*, 1969, 1808.

¹⁴ R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, 1957, 79, 4133.

¹⁵ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1954, p. 40.

¹⁶ C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1172.

¹⁷ C. B. Reese and A. Shaw, *J.C.S. Chem. Comm.*, 1972, 787.

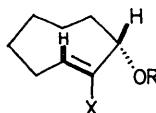
¹⁸ H. C. Hoff, K. W. Greenlee, and C. E. Board, *J. Amer. Chem. Soc.*, 1951, 73, 3329.

Further confirmation of the structures of the above 2-halogeno-*trans*-cycloalkene derivatives may be obtained from a study of their diastereoisomerism. 3-Substituted *trans*-cycloalkenes, such as 2-bromo-3-methoxy-*trans*-cyclo-octene (11a), have both a chiral plane, due to the presence of the *trans*-double bond, and an asymmetric carbon atom. Thus (11a) should exist in two diastereoisomeric forms [(27a) and (28a)] and the high optical stability of the pure enantiomers of *trans*-cyclo-octene¹⁹ indicates that these diastereoisomers should not be readily interconvertible. Examination of the H(1), H(3), and MeO signals in the ¹H n.m.r. spectrum of 2-bromo-3-methoxy-*trans*-cyclo-octene (11a), obtained by the silver perchlorate-promoted methanolysis of (8a) (Table 1, experiment no. 1), suggests that it is a pure diastereoisomer and thus that the solvolysis reaction is stereospecific. Indeed, the other *trans*-cyclo-octene derivatives obtained (experiments nos. 2—4 and 7) also appear to be pure diastereoisomers. It further seems (see below) that all these solvolysis products may be represented by the general formula (27). The products obtained when (27a) is heated at 190 °C for 50 min * contain starting material (27a), its diastereoisomer (28a), and 2-bromo-3-methoxy-*cis*-cyclo-octene (12c) in the proportions *ca.* 5 : 2 : 3. Both diastereoisomers of *trans*-cyclo-oct-2-enol (6c) have been prepared and characterized by Whitham and Wright.^{6,20}

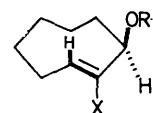
It is apparent from their n.m.r. spectra (Table 1) that 2-halogeno-*trans*-cyclononene derivatives (13) exist as mixtures of diastereoisomers at the ambient temperature (35 °C) of the n.m.r. spectrometer. Thus 2-bromo-3-methoxy-*trans*-cyclononene (13a) displays two double doublets for the resonance of H(1), a multiplet and a double doublet for the resonance of H(3), and two singlets for the resonance of the methoxy-protons. Furthermore, in each case [*i.e.* for H(1), H(3), and OMe], the integral of the lower field is *ca.* 0.8 times that of the higher field part of the signal. This evidence suggests that the two diastereoisomers [(29a) and (30a)] of (13a) are in equilibrium and that the equilibrium constant is *ca.* 0.8 in carbon tetrachloride solution at 35 °C. As the half-time of racemization of optically pure *trans*-cyclononene²¹ is 6 s at 30 °C, equilibration of (29a) and (30a) would be expected to occur rapidly at 35 °C but not too rapidly for the individual diastereoisomers to be observable by n.m.r. spectroscopy. Rotation of the *trans*-double bond through the loop of saturated carbon atoms in, say, diastereoisomer (29a) leads to the mirror image of diastereoisomer (30a), and *vice versa*. At higher temperatures, equilibration becomes rapid and the individual diastereoisomers are not then observable by n.m.r. spectroscopy. Thus at 92 °C, (13a) shows only a single methoxy-proton resonance. 2-Chloro-3-methoxy-*trans*-

cyclononene (13c) similarly appears from its n.m.r. spectrum at 35 °C to consist of an equilibrium mixture (*K ca.* 0.6) of two diastereoisomers [(29b) and (30b)]; the methoxy-proton signals of (13c) also coalesce reversibly at 92 °C.

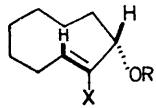
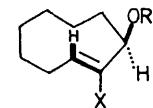
The higher field, more intense part of the H(3) signal in the n.m.r. spectrum of 2-bromo-3-methoxy-*trans*-cyclononene (13c) corresponds to the H(3) signal in the n.m.r. spectrum of (27a), the diastereoisomer of (11a) obtained directly from (8c) (Table 1, experiment no. 1). In both cases, a double doublet with one fairly large (9 or 10 Hz) and one smaller (6 or 5.5 Hz) coupling may be observed; such double doublets are suggestive of pseudo-axial protons. Similarly, the lower field, less intense part of the H(3) signal in the n.m.r. spectrum of (13c) is a multiplet assignable to a pseudo-equatorial methine proton and corresponds to the similar multiplet (τ 6.08) in the n.m.r. spectrum of (28a). Such comparisons may also be made between the n.m.r. spectra of (13b) and (11b) and of (13c) and (11c).



(27) a; X = Br, R = Me



(28) a; X = Br, R = Me

(29) a; X = Br, R = Me
b; X = Cl, R = Me(30) a; X = Br, R = Me
b; X = Cl, R = Me

As optically active *trans*-cyclononene is racemised rapidly²¹ at room temperature, it is much easier to detect chirality due to restricted rotation in *trans*-cyclononene derivatives by n.m.r. spectroscopy than by optical rotation measurements. The detection of the chirality of *trans*-cyclodecene by optical rotation measurements would almost certainly be impossible as racemisation would be expected to occur rapidly at temperatures well below 0 °C. The n.m.r. spectrum of 2-bromo-3-methoxy-*trans*-cyclodecene (15a), at 35 °C, exhibits only one peak each for H(1), H(3), and the methoxy-protons (see Table 1, experiment no. 15). Furthermore, the fact that H(1) resonates as a triplet suggests that the C-10 methylene protons are magnetically equivalent. This in turn suggests that H(1) is rotating rapidly through the loop of saturated carbon atoms at 35 °C. However, at -50°, the presence of a *ca.* 5 : 1 equilibrium mixture of diastereoisomers is apparent: the diastereoisomer with the higher-field signals and with a pseudoaxial methine proton again predominates. Coalescence of the methoxy signals occurs on warming to *ca.* 5 °C. Binsch and

* The half-time of racemization of optically active *trans*-cyclooctene¹⁹ is 60 min at 183.9 °C. Both polymerization and isomerization to *cis*-cyclo-octene occur to some extent under these conditions.

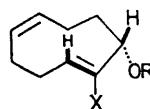
¹⁹ A. C. Cope and B. A. Pawson, *J. Amer. Chem. Soc.*, 1965, **87**, 3649.

²⁰ G. H. Whitham and M. Wright, *J. Chem. Soc. (C)*, 1971, 886.

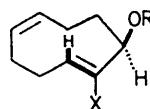
²¹ A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1965, **87**, 3644.

Roberts²² have also detected chirality due to restricted rotation in a *trans*-cyclodecene derivative by n.m.r. spectroscopy.

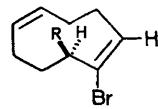
It is clear from n.m.r. spectroscopic data that solvolysis of 9,9-dibromo- and 9,9-dichloro-bicyclo[6.1.0]non-4-enes (19a and b, respectively) (Table 1, experiments nos. 19–22) leads to diastereoisomerically pure *trans,cis*-cyclonona-1,6-diene derivatives (20). Examination of their n.m.r. spectra also leads to the suggestion that the relative configurations of the *trans*-double bonds and asymmetric carbon atoms in the latter compounds (20) are the same as in the corresponding *trans*-cyclo-octene derivatives (11), obtained by the solvolysis of (8c and d) (see above). It follows that the barrier to rotation of the *trans*-double bond in the *trans,cis*-cyclononadiene (20) is greater than in the *trans*-cyclononene derivatives (13). However, when 1-bromo-9-methoxy-*trans,cis*-cyclonona-1,5-diene (20a) is heated at 70–80 °C for 1 h, a mixture of starting material (*ca.* 3 parts) and a less polar (by t.l.c.) product (1 part) is obtained. The latter compound, which may be isolated pure following adsorption chromatography of the mixture, may be assigned the structure (32a) on the grounds that its n.m.r. spectrum (Experimental section) bears the same relationship to that of (31a) as the n.m.r. spectrum of (27a) does to that of (28a).



(31a; X = Br, R = Me)



(32a; X = Br, R = Me)

(33a; a; R = Br
b; R = OMe)

Support for the assignment of structure (32a) may be obtained in the following way. Silver perchlorate-promoted methanolysis of 1,9-dibromo-*cis,cis*-cyclonona-1,5-diene¹³ (33a) gives (32a) and 1-bromo-9-methoxy-*cis,cis*-cyclonona-1,5-diene (33b) in the proportions *ca.* 3 : 2. None of the other *trans,cis*-diastereoisomer (31a) is detectable in the products. However, silver perchlorate-promoted methanolysis of either diastereoisomer of 1,9-dibromo-*trans,cis*-cyclonona-1,5-diene (20; X = R = Br) leads solely to (31a). Molecular models indicate that *S_N2'* methanolysis of the *cis,cis*-dibromide (33a) should lead stereospecifically to the *trans,cis*-ether (32a) if methanol attacks on the side of the molecule from which bromide ion departs. As the latter condition meets the stereoelectronic requirements²³ of the *S_N2'* reaction, this experiment provides convincing confirmation of the relative configuration of the *trans*-double bond.

* As 2-bromo- and 2-chloro-*trans-cis*-cyclonona-2,6-dien-1-ols (31; R = OH, X = Br or Cl) are both crystalline solids, it is possible that their structures could be established by X-ray crystallography.

and the asymmetric carbon atom in (32a) and hence in (31a).^{*} It also follows from a combination of this evidence and n.m.r. spectroscopy that the 2-halogeno-*trans*-cyclo-octene derivatives (11), obtained by the silver perchlorate-promoted solvolysis of (8c and d), most probably have the general structure (27). This correlates with the conclusion⁶ that the product obtained by the hydrolysis of *exo*-8-bromobicyclo[5.1.0]octane (8a) in the absence of silver ion has structure (27; X = R = H).

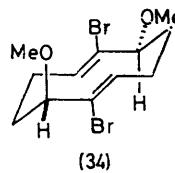
TABLE 2

Rates of equilibration of diastereoisomeric 1-bromo-9-methoxy-*trans,cis*-cyclonona-1,5-dienes (31a) and (32a)^a

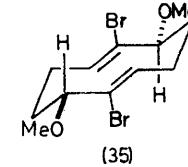
Temp. (°C)	$10^4(k_1 + k_2)/\text{s}^{-1}$ ^b	$t_{1/2}/\text{min}$
60	1.4	80
65	2.6	44
70	4.6	25
75	7.6	15

^a Pure (32a) was the starting material in all experiments.
^b k_1 and k_2 are the rate constants for the conversion of (32a) into (31a) and *vice versa*.

When (32a) is heated at either 65 or 75 °C for 18 h, the same equilibrium mixture containing starting material (24%) and (31a) (76%) is obtained. The interconversion of (31a) and (32a) is a first-order equilibration²⁴ which may conveniently be followed by measuring the relative intensities of the methoxy-proton signals of the two compounds after suitable time intervals. The equilibration rates and half-times determined in this way at four different temperatures are listed in Table 2. A straight-line Arrhenius plot may be obtained from these data and the energy of activation for the conversion of (32a) into (31a) estimated to be 25.5 kcal mol⁻¹. This may be compared with Cope's estimates^{19,21} of 35.6 ± 0.9 and 20 ± 2 kcal mol⁻¹ for the energies of activation for the racemisation of *trans*-cyclo-octene and *trans*-cyclononene, respectively.



(34)



As indicated above, the silver perchlorate-promoted methanolysis of 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]decane (21) (Table 1, experiment no. 23) gives two isomeric 1,6-dibromo-5,10-dimethoxy-*trans,trans*-cyclodeca-1,6-dienes [(22a) and (23a)]. The n.m.r. spectrum of the more abundant, lower melting isomer displays two doublet signals for its olefinic [H(2) and H(7)], a lower field multiplet and a higher field doublet [J 3.5 and 10.5 Hz] for its methine [H(5) and H(10)], and two singlets for its methoxy-protons. Thus the presence of one equatorially and one axially disposed proton is

²² G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 5157.

²³ W. G. Young, I. D. Webb, and H. L. Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076.

²⁴ A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 1st edn., Wiley, New York, 1953, p. 172.

suggested. The n.m.r. spectrum of the less abundant, higher melting isomer indicates that both olefinic, both methine, and both sets of methoxy-protons are in identical magnetic environments; furthermore, the chemical shifts and multiplicities of the signals observed correlate well with those of the higher field signals in the corresponding regions in the n.m.r. spectrum of the lower-melting isomer. This suggests that both methine protons in the higher melting isomer are axially disposed. On the basis of these n.m.r. data we have proposed^{10c} that the lower and higher melting compounds are 1,6-dibromo-*cis*- and -*trans*-5,10-dimethoxy-*trans,trans*-cyclo-deca-1,6-dienes [(22a) and (23a)] and that their preferred conformations at ambient temperature are (34) and (35), respectively. The proposed structure and conformation (at least, in the crystalline state) of (35) have been confirmed by X-ray crystallography.²⁵ The *cis*-dimethoxy-compound (22a) appears to display appreciable conformational stability in that a temperature of 158 °C is required for the coalescence of the methoxy-signals in the n.m.r. spectrum: the lower field region then resembles the corresponding region in the spectrum of 2-bromo-3-methoxy-*trans*-cyclodecene (15a) at ambient temperature.

The above discussion shows that 3-substituted 2-halo-gen (or unsubstituted) *trans*-cycloalkene derivatives can readily be distinguished from their *cis*-isomers on the basis of several different criteria. Perhaps the simplest to apply is a comparison of the chemical shifts of allylic methine protons [H(3)]. In a *cis*-cycloalkene derivative, this proton generally resonates between 0.3 and 0.75 p.p.m. downfield from H(3) in the corresponding *trans*-diastereoisomer with the higher-field methine proton resonance; H(3) in a *cis*-cycloalkene derivative usually, but not always, also resonates downfield from H(3) in the other *trans*-diastereoisomer. These generalisations are supported by the data in Table 1 and the Experimental section.

Finally, we comment on the detailed stereochemistry of the silver ion-assisted solvolysis of *exo*-8-bromo- and 8,8-dihalogeno-bicyclo[5.1.0]octanes (8a, c, and d) and of 9,9-dihalogenobicyclo[6.1.0]non-4-enes (19a and b). As the *exo*-halogeno-group departs, fission of the 1,8- or 1,9-bond occurs in a disrotatory fashion² so as to give a *trans,trans*-allylic system. Solvolysis of this allylic system appears to occur on the same side as the departing halogeno-group with resulting inversion of configuration at C-1 (or at C-8 or C-9). The stereochemistry observed is that expected on electronic grounds if the solvolytic process does not involve a free allylic cation. However, as steric factors would favour solvolysis of a free allylic cation on the side observed, such an *S_N1* process cannot be ruled out.

EXPERIMENTAL

N.m.r. spectra were measured at 100 MHz with Varian HA-100 and XL-100 spectrometers; unless otherwise stated Me₄Si was used as internal standard. U.v. spectra were measured with a Cary 14M-50 recording spectrophotometer. I.r. spectra of liquids and solids as films and Nujol

mulls, respectively, were taken with a Perkin-Elmer 257 (grating) and a Unicam SP 200 spectrometer. Mass spectra were obtained with A.E.I. MS 9 and 12 spectrometers, by using a heated inlet system. Both analytical and preparative g.l.c. were carried out with an F & M 720 chromatograph with hydrogen as carrier gas; polyphenyl ether, SE 30, Carbowax 20M, diethylene glycol adipate, and Apiezon C were used as stationary phases. T.l.c. was carried out on 20 × 5 cm glass plates coated with Merck Kieselgel GF²⁵⁴.

Silver Perchlorate-promoted Methanolysis of 8,8-Dibromobicyclo[5.1.0]octane (with A.C. RISIUS).—(a) A solution of 8,8-dibromobicyclo[5.1.0]octane (0.99 g, 3.7 mmol) in methanol (1 ml) was added dropwise during 2 min to a stirred solution of silver perchlorate (1.58 g, 7.6 mmol) in methanol (6.4 ml) at 20 °C. After a further 10 min, the products were filtered to give silver bromide (0.54 g, 78%). T.l.c. of the filtrate revealed only a trace of unchanged starting material.

(b) A solution of 8,8-dibromobicyclo[5.1.0]octane (1.25 g, 4.66 mmol) and silver perchlorate (2.09 g, 10.1 mmol) in methanol (100 ml) was stirred at 20 °C in the dark. A precipitate had formed after 20 min. After 22 h, the products were filtered to give silver bromide (0.15 g, 17%) and the filtrate was found (t.l.c.) to contain starting material (major component) and another component. After a further 7 days, t.l.c. of the products revealed only a trace of starting material.

(c) A solution of 8,8-dibromobicyclo[5.1.0]octane (0.103 g, 0.38 mmol) and silver perchlorate (0.15 g, 0.72 mmol) in methanol (50 ml) was stirred at 20 °C in the dark. After 24 h, no precipitation of silver bromide was detected.

2-Bromo-3-methoxy-trans-cyclo-octene (11a).—8,8-Dibromobicyclo[5.1.0]octane²⁶ (2.6 g, 9.7 mmol) was added dropwise over 5–10 min to a stirred, cooled (15–20 °C) solution of silver perchlorate (4.0 g, 19.3 mmol) in methanol (10 ml). After a further 5 min, the products were poured, with swirling, into aqueous sodium carbonate (0.25M; 75 ml). The mixture was then filtered and the precipitate washed thoroughly with acetone. The filtrate and washings were extracted with ether (3 × 25 ml) and the combined ether layers washed with distilled water (3 × 20 ml). The dried (MgSO₄) organic layer was evaporated under reduced pressure to give 2-bromo-3-methoxy-trans-cyclo-octene (Found: C, 49.2; H, 6.7; Br, 36.5. C₉H₁₅BrO requires C, 49.3; H, 6.85; Br, 36.5%) as a liquid [single component by g.l.c. (Carbowax 20M)]; yield 1.8 g (84%); τ (CCl₄) 3.89 (1 H, dd, J 4 and 11.5 Hz), 6.36 (1 H, dd, J 6 and 9 Hz), 6.83 (3 H, s), and 7.1–9.5 (10 H, m); ν_{max} (film) 1 625m and 1 120s cm⁻¹; m/e 218/220 (M⁺, 20%) and 61 (100%).

Action of Heat on 2-Bromo-3-methoxy-trans-cyclo-octene (11a).—(a) 2-Bromo-3-methoxy-trans-cyclo-octene (0.5 g) was heated in an oil-bath, under N₂, at 180 °C for 150 min and then at 200 °C for 20 min. G.l.c. (Carbowax 20M) indicated that only a trace of starting material remained. The products were distilled under reduced pressure to give 2-bromo-3-methoxy-cis-cyclo-octene (Found: C, 49.1; H, 6.7; Br, 36.3. C₉H₁₅BrO requires C, 49.3; H, 6.85; Br, 36.5%) as a liquid, b.p. 44° at 0.5 mmHg; yield 0.15 g (30%); τ (CCl₄) 3.78 (1 H, t, J 8.5 Hz), 5.90 (1 H, t, J 7.5 Hz), 6.80 (3 H, s), and 7.6–8.8 (10 H, m); ν_{max} (film) 1 625m and 1 100s cm⁻¹; m/e 218/220 (M⁺, 5%) and 107 (100%).

(b) 2-Bromo-3-methoxy-trans-cyclo-octene (1.5 g) was heated in an oil-bath, under N₂, at 190 °C for 50 min, and

²⁵ D. N. J. White, *Helv. Chim. Acta*, 1973, **56**, 1347.

²⁶ G. Wittig and H. L. Dorsch, *Annalen*, 1968, **711**, 46.

the products were cooled to room temperature and dissolved in benzene-petroleum (b.p. 60—80°) (1 : 4 v/v). The solution was allowed to percolate through a short column of Mallinckrodt SilicAR CC7 and the eluate was evaporated to give an oil (1.1 g). The n.m.r. spectrum of this material suggested that it contained starting material (*ca.* 50%), the above *cis*-isomer (*ca.* 30%), and a third component (*ca.* 20%). T.l.c. (benzene) confirmed the presence of a product with R_F higher than that of the starting material and its *cis*-isomer. A solution of this mixture in petroleum (b.p. 60—80°) was applied to a column of SilicAR CC7 (25 g) which was eluted with benzene-petroleum (b.p. 60—80°) (2 : 98 v/v). Concentration of the appropriate early fractions gave the less polar *diastereoisomer* of 2-bromo-3-methoxy-trans-cyclo-octene (Found: C, 49.2; H, 6.7; Br, 36.7%); yield 0.11 g (7%); τ (CCl₄) 3.64 (1 H, dd, *J* 4 and 11 Hz), 6.08 (1 H, m), 6.74 (3 H, s), and 7.1—9.4 (10 H, m); ν_{max} (film) 1 645m and 1 100s cm⁻¹; *m/e* 218/220 (M^+ , 16%) and 71 (100%). Concentration of the appropriate later fractions gave a mixture (0.75 g, 50%) of starting material and its *cis*-isomer.

2-Bromo-trans-cyclo-oct-2-enol (11b).—8,8-Dibromobicyclo[5.1.0]octane (2.6 g, 9.7 mmol) was added dropwise over 10 min to a stirred, cooled (15—20 °C) solution of silver perchlorate (4.0 g, 19.3 mmol) in acetone-water (9 : 1 v/v; 10 ml). The products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give 2-bromo-trans-cyclo-oct-2-enol (Found: C, 46.5; H, 6.3; Br, 39.3. C₈H₁₃BrO requires C, 46.8; H, 6.35; Br, 39.0%) as an oil [single component by t.l.c. in ethyl acetate-benzene (1 : 19 v/v)]; yield 1.6 g (81%); τ (CCl₄) 3.97 (1 H, dd, *J* 4 and 12 Hz), 5.92 (1 H, dd, *J* 5.5 and 10.5 Hz), 7.22 (1 H, s), and 7.1—9.4 (10 H, m); ν_{max} (film) 3 400s and 1 625m cm⁻¹; *m/e* 204/206 (M^+ , 21%) and 81 (100%).

2-Chloro-3-methoxy-trans-cyclo-octene (11c).—8,8-Dichlorobicyclo[5.1.0]octane (1.0 g, 5.6 mmol) was added to a stirred solution of silver perchlorate (2.0 g, 9.6 mmol) in methanol (5 ml) and the reactants were maintained at 45 °C (water-bath) for 45 min. The products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give 2-chloro-3-methoxy-trans-cyclo-octene (Found: C, 62.2; H, 8.6; Cl, 20.15. C₉H₁₅ClO requires C, 61.9; H, 8.6; Cl, 20.4%) as an oil (0.79 g, 80%); τ (CCl₄) 4.12 (1 H, dd, *J* 4 and 12 Hz), 6.24 (1H, dd, *J* 5 and 10 Hz), 6.80 (3 H, s), and 7.0—9.4 (10 H, m); ν_{max} (film) 1 640m cm⁻¹; *m/e* 174/176 (M^+ , 14 and 16%) and 131 (100%).

3-Methoxy-trans-cyclo-octene (6b).—*exo*-8-Bromobicyclo[5.1.0]octane⁶ (1.82 g, 9.6 mmol) was added dropwise over 5 min to a stirred, cooled (15—20 °C) solution of silver perchlorate (4.0 g, 19.3 mmol) in methanol (10 ml). After a further 5 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene, except that the final ethereal solution was evaporated in a stream of N₂ at atmospheric pressure, to give 3-methoxy-trans-cyclo-octene (Found: C, 77.1; H, 11.2. C₉H₁₆O requires: C, 77.1; H, 11.4%) as a liquid [single component by g.l.c. (polyphenyl ether)]; yield 1.1 g (80%); τ (CCl₄) 4.2—4.8 (2 H, m), 6.36 (1 H, dt, *J* 5.5 and 9 Hz), 6.81 (3 H, s), and 7.9—9.4 (10 H, m); ν_{max} (film) 1 640m, 1 090s, and 980s cm⁻¹; *m/e* 140 (M^+ , 18%) and 97 (100%).

trans-Cyclo-oct-2-enol (6c).—*exo*-8-Bromobicyclo[5.1.0]-octane (1.5 g, 7.9 mmol) was added dropwise over 5 min to a stirred solution of silver perchlorate (3.0 g, 14.5 mmol) in acetone-water (9 : 1 v/v; 10 ml) at 20 °C. The products were worked up as described in the preparation of 3-methoxy-trans-cyclo-octene to give *trans*-cyclo-oct-2-enol (Found:

C, 76.0; H, 10.9. Calc. for C₈H₁₄O: C, 76.2; H, 11.1%) as a viscous oil [single component by t.l.c. in ethyl acetate-benzene (1 : 19 v/v)]; yield 0.77 g (77%); τ (CCl₄) 4.4—4.7 (2 H, m), 5.69 (1 H, s), 5.8—6.0 (1 H, m), and 7.5—9.5 (10 H, m); ν_{max} (film) 3 320s, 1 640m, and 980s cm⁻¹; *m/e* 126 (M^+ , 9%) and 27 (100%).

Purification of endo-8-Bromobicyclo[5.1.0]octane and Higher Homologues.—Reduction of dibromocarbene adducts of cycloalkenes with tri-n-butyltin hydride by the published procedure usually gives the corresponding *endo*-monobromo-compounds contaminated with *ca.* 10% of their *exo*-isomers. The following procedure for the partial purification of *endo*-8-bromobicyclo[5.1.0]octane may be applied generally to the purification of *endo*-bromobicyclo[n.1.0]alkanes in which *n* > 4.

Redistilled *endo*-8-bromobicyclo[5.1.0]octane⁸ (containing *ca.* 10% of *exo*-isomer) (3.0 g, 15.9 mmol) was added to a stirred solution of silver perchlorate (1.5 g, 7.2 mmol) in acetone-water (9 : 1 v/v; 15 ml) at 20 °C. When precipitation of silver bromide became slow, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene. A solution of the oil obtained in petroleum (b.p. 30—40°) was allowed to percolate through a short column of Mallinckrodt SilicAR CC7. Evaporation of the eluate followed by distillation gave *endo*-8-bromobicyclo[5.1.0]octane (2.5 g, 83%), which was shown by g.l.c. (Carbowax 20M) to contain only 2—3% of *exo*-isomer.

3-Methoxy-cis-cyclo-octene (12a).—*endo*-8-Bromobicyclo[5.1.0]octane (1.0 g, 5.3 mmol) was added to a stirred solution of silver perchlorate (2.1 g, 10.1 mmol) in methanol (6 ml) and the reactants were maintained at 45 °C (water-bath) for 3 h. The products were worked up as described above in the preparation of 3-methoxy-trans-cyclo-octene to give 3-methoxy-cis-cyclo-octene (Found: C, 77.0; H, 11.65. C₉H₁₆O requires C, 77.1; H, 11.4%) as a mobile, discoloured liquid [single component by g.l.c. (polyphenyl ether) with a slightly lower *t*_R than its *trans*-isomer]; yield 0.35 g (47%); τ (CCl₄) 4.24—4.74 (2 H, m), 6.02 (1 H, m), 6.84 (3 H, s), and 7.7—9.0 (10 H, m); ν_{max} (film) 1 640m and 1 100s cm⁻¹; *m/e* 140 (M^+ , 20%) and 97 (100%).

Stability of 3-Methoxy-trans-cyclo-octene to Silver Perchlorate—Perchloric Acid in Methanol.—Hydrogen chloride was bubbled into a solution of silver perchlorate (0.5 g, 2.4 mmol) in methanol (6 ml) until no further precipitation occurred. The mixture was filtered and silver perchlorate (2.0 g, 9.6 mmol) was added to the filtrate, followed by 3-methoxy-trans-cyclo-octene (1.4 g, 10.0 mmol). The solution was maintained at 70 °C (water-bath) with stirring. Samples were worked up after suitable intervals of time and examined by g.l.c. (polyphenyl ether). The half-time for the conversion of 3-methoxy-trans-cyclo-octene into its *cis*-isomer was found to be *ca.* 2 h.

Under the same conditions (*i.e.* at 70 °C), the reaction between *endo*-8-bromobicyclo[5.1.0]octane (0.5 g, 2.6 mmol) and silver perchlorate (1.0 g, 4.8 mmol) in methanol (3 ml) [to give 3-methoxy-cis-cyclo-octene] was complete within 1 h. At no time during this reaction was it possible to detect more than a trace of 3-methoxy-trans-cyclo-octene by g.l.c.

Reduction of 2-Bromo-3-methoxy-trans-cyclo-octene with Sodium in Liquid Ammonia.—A solution of 2-bromo-3-methoxy-trans-cyclo-octene (7.2 g, 33 mmol) in petroleum ether (b.p. 30—40°; 20 ml) was added dropwise over 15 min to a solution of sodium (2.3 g, 100 mmol) in liquid ammonia (150 ml). After the reactants had been stirred for 15 min at reflux temperature, an excess of ammonium chloride was

added. The ammonia was then allowed to evaporate and the residue partitioned between petroleum (b.p. 30–40°) and water. Careful evaporation of the dried ($MgSO_4$) organic layer at atmospheric pressure gave a liquid (3.9 g, 93%), which was shown by g.l.c. (Carbowax 20M) to contain *trans*- and *cis*-3-methoxycyclo-octenes in approximately equal proportions. This mixture was separated into its pure constituents by extracting its solution in petroleum (b.p. 30–40°; 50 ml) with aqueous 20% silver nitrate (3 × 50 ml). Pure *cis*-isomer remained in the organic layer and pure *trans*-isomer was extracted with petroleum from the aqueous layer after addition of ammonia (*d* 0.88; 50 ml).

cis-Cyclo-oct-2-enol (12b).—*endo*-8-Bromobicyclo[5.1.0]-octane (1.0 g, 5.3 mmol) was added to a solution of silver perchlorate (4.0 g, 19.3 mmol) in acetone–water (9 : 1 v/v; 10 ml) and the reactants heated, under reflux, for 2 h. During this time more silver perchlorate (1.0 g, 4.8 mmol) was added in portions. The products were worked up as described in the preparation of 3-methoxy-*trans*-cyclo-octene to give *cis*-cyclo-oct-2-enol⁶ (Found: C, 76.2; H, 11.0. $C_8H_{14}O$ requires C, 76.2; H, 11.1%) as a discoloured oil [single component by t.l.c. in ethyl acetate–benzene (1 : 19, v/v)]; yield 0.375 g (56%); τ (CCl_4) 4.4–4.7 (2 H, m), 5.4–5.6 (1 H, m), 7.20 (1 H, s), and 7.7–7.8 (10 H, m); ν_{max} (film) 3 310s, 1 650m, and 1 050s cm^{-1} ; *m/e* 126 (M^+ , 34%) and 83 (100%).

2-Bromo-3-methoxy-*trans*-cyclononene (13a).—(a) 9,9-Dibromobicyclo[6.1.0]nonane²⁷ (4.0 g, 14.2 mmol) was added dropwise over 5–10 min to a stirred, cooled (15–20 °C) solution of silver perchlorate (5.7 g, 27.5 mmol) in methanol (15 ml). After a further 5 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene. Distillation of the oil so obtained gave 2-bromo-3-methoxy-*trans*-cyclononene (Found: C, 51.6; H, 7.3; Br, 34.3. $C_{10}H_{11}BrO$ requires C, 51.5; H, 7.3; Br, 34.3%) as a liquid [*ca.* 95% pure by g.l.c. (polyphenyl ether, SE30, Carbowax 20M, diethylene glycol adipate)], b.p. 72–75° at 0.5 mmHg; yield 2.7 g (82%); τ (CCl_4) 3.80 and 3.99 (1 H, dd and dd, *J* 5.5 and 10.5; 5.5 and 10 Hz, respectively), 6.09 and 6.55 (1 H, m and dd, *J* 5.5 and 10 Hz, respectively), 6.72 and 6.83 (3 H, s and s), and 7.3–9.2 (12 H, m) [the integrals of the signals at 3.80, 6.09, and 6.72 were *ca.* 0.8 times those of the signals at 3.99, 6.55 and 6.83]; ν_{max} (film) 1 635m and 1 105s cm^{-1} ; *m/e* 232/234 (M^+ , 38%) and 71 (100%). The impurity in this material had the same *t_R* (on each of the above four stationary phases) as 2-bromo-3-methoxy-*cis*-cyclononene.

(b) 9,9-Dibromobicyclo[6.1.0]nonane (1.0 g, 3.5 mmol) was added dropwise over 10 min, to a stirred, cooled (ice–water) solution of silver perchlorate (4.0 g, 19.3 mmol) in methanol (7 ml). Work-up after 15 min gave 2-bromo-3-methoxy-*trans*-cyclonene, free (g.l.c., Carbowax 20M) from its *cis*-isomer.

2-Bromo-*trans*-cyclonon-2-enol (13b).—9,9-Dibromobicyclo[6.1.0]nonane (5.0 g, 17.7 mmol) was added dropwise over 5–10 min to a stirred, cooled (15–20 °C) solution of silver perchlorate (7.35 g, 35.5 mmol) in acetone–water (9 : 1 v/v; 18 ml). After a further 5 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene to give 2-bromo-*trans*-cyclonon-2-enol (Found: C, 49.5; H, 6.8; Br, 36.5. $C_9H_{15}BrO$ requires C, 49.3; H, 6.85; Br, 36.5%) as an oil (3.0 g, 80%); τ (CCl_4) 3.66 and 4.04 (1 H, dd and dd, *J* 6 and 10; 5.5 and

10 Hz, respectively), 5.59 and 6.08 (1 H, m and dd, *J* 4 and 10 Hz, respectively), 6.98br (1 H, s), and 7.4–9.2 (12 H, m) (the integrals of the signals at 3.66 and 5.59 were *ca.* 0.4 times those of the signals at 4.04 and 6.08); ν_{max} (film) 3 350s, 1 630m, and 1 130s cm^{-1} ; *m/e* 218/220 (M^+ , 25%) and 41 (100%). The n.m.r. spectrum suggested that the material was contaminated with the *cis*-isomer (*ca.* 5%).

2-Chloro-3-methoxy-*trans*-cyclononene (13c).—(a) 9,9-Dichlorobicyclo[6.1.0]nonane (0.50 g, 2.6 mmol) was rapidly stirred at 20 °C with saturated methanolic silver perchlorate (2 ml). After 1 h, the products were worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene. The material thus obtained was purified by chromatography on a column of Mallinckrodt SilicAR CC7. Elution with petroleum (b.p. 60–80°)–benzene (19 : 1 v/v) gave 2-chloro-3-methoxy-*trans*-cyclononene (Found: C, 63.6; H, 9.1; Cl, 18.6. $C_{10}H_{11}ClO$ requires C, 63.6; H, 9.0; Cl, 18.8%) as an oil [shown by n.m.r. (see below) to be uncontaminated with the *cis*-isomer]; yield 0.35 g (70%); τ (CCl_4) 4.06 and 4.24 (1 H, dd and dd; *J* 5.5 and 11; 5 and 10 Hz, respectively), 6.24 and 6.42 (1 H, m and dd, *J* 4 and 10 Hz, respectively), 6.74 and 6.82 (3 H, s and s), and 7.2–9.2 (12 H, m) (the integrals of the signals at 4.06, 6.24, and 6.74 were *ca.* 0.6 times those of the signals at 4.24, 6.42, and 6.82); ν_{max} (film) 1 640m cm^{-1} ; *m/e* 188/190 (M^+ , 6 and 2%) and 40 (100%).

(b) When the solvolysis was carried out at 45 °C, under the conditions described for the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene, the material obtained was shown (n.m.r. spectroscopy) to consist of 2-chloro-3-methoxy-*trans*-cyclononene (*ca.* 60%) and a second product (*ca.* 40%) believed to be its *cis*-isomer.

Effect of Temperature on the N.m.r. Spectra of (a) 2-Chloro-11c and (b) 2-Bromo- (11b) 3-methoxy-*trans*-cyclononene.—(a) The n.m.r. spectrum of a solution in tetrachloroethylene displayed two singlets at τ 6.75 and 6.82 ($W_{1/2}$ 2.5 and 4 Hz, respectively) at ambient temperature (34.5 °C). At 92.5 °C, the signals had coalesced to a single singlet (τ 6.79, $W_{1/2}$ 8 Hz). Narrowing of this signal was observed at higher temperatures (107 °C, $W_{1/2}$ 5 Hz; 117.5 °C, $W_{1/2}$ 4.5 Hz). When the temperature was lowered to 34.5 °C, the original spectrum was again observed.

(b) The n.m.r. spectrum of a solution in tetrachloroethylene similarly displayed two singlets at τ 6.79 ($W_{1/2}$ 2 Hz) and 6.88 ($W_{1/2}$ 3.5 Hz), at 34.5 °C. The two signals again had coalesced to a singlet at *ca.* 92 °C and further narrowing was again observed at higher temperatures (94 °C, $W_{1/2}$ 7.5 Hz; 111.5 °C, $W_{1/2}$ 3.5 Hz). This process was again completely reversible.

3-Methoxy-*trans*-cyclononene (7b).—*exo*-9-Bromobicyclo[6.1.0]nonane²⁸ (1.0 g, 4.9 mmol) was added dropwise to a stirred, cooled (ice–water) solution of silver perchlorate (2.0 g, 9.6 mmol) in methanol (5 ml). After a further 10 min, the products were allowed to warm to room temperature and then worked up as described in the preparation of 3-methoxy-*trans*-cyclo-octene to give 3-methoxy-*trans*-cyclononene (Found: C, 78.1; H, 11.9. $C_{10}H_{18}O$ requires C, 78.0; H, 11.7%) as a liquid [single component by g.l.c. (Carbowax 20M)]; yield 0.61 g (79%); τ (CCl_4) 4.4–5.0 (2 H, m), 6.17 and 6.5–6.7 (1 H, m and m), 6.82 (3 H, s), and 7.6–9.2 (12 H, m) [the integral of the signal at 6.17 was *ca.* 0.15 times that of the signal at 6.5–6.7]; ν_{max} (film) 1 650m, 1 110s, and 985s cm^{-1} ; *m/e* 154 (M^+ , 10%) and 97 (100%).

²⁷ P. D. Gardner and M. Narayana, *J. Org. Chem.*, 1961, **26**, 3518.

²⁸ C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Cardenas, and P. D. Gardner, *Chem. and Ind.*, 1965, 766.

trans-Cyclonon-2-enol (7c).—*exo-9-Bromobicyclo-[6.1.0]-nonane* (0.60 g, 2.95 mmol) was added dropwise to a stirred, cooled (water-bath at 15 °C) solution of silver perchlorate (1.0 g, 4.85 mmol) in acetone–water (9 : 1 v/v; 5 ml). After a further 10 min, the products were allowed to warm to room temperature and then worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene to give a solid (0.37 g). Recrystallization from n-hexane gave *trans-cyclonon-2-enol* (Found: C, 76.9; H, 11.3. $C_9H_{16}O$ requires C, 77.1; H, 11.4%) as feathery crystals, m.p. 64–65°; yield 0.34 g (82%); τ (CCl_4) 4.6–4.8 (2 H, m), 5.58 and 6.0–6.3 (1 H, m and m), 7.12 (1 H, s), and 7.6–9.2 (12 H, m) (the integral of the signal at 5.58 was *ca.* 0.3 times that of the signal at 6.0–6.3); ν_{max} (CCl_4) 3 600m, 3 300s, 1 640m, 1 020s, and 980s cm^{-1} ; m/e 140 (M^+ , 20%) and 83 (100%).

3-Methoxy-cis-cyclononene (14a).—*endo-9-Bromobicyclo-[6.1.0]nonane*²⁹ (1.0 g, 4.9 mmol) was added to a solution of silver perchlorate (2.0 g, 9.6 mmol) in methanol (5 ml) and the stirred reactants were maintained at 65 °C for 1 h. During this period, more silver perchlorate (1.0 g, 4.8 mmol) was added in portions. The products were then worked up as described in the preparation of 3-methoxy-*trans*-cyclo-octene to give *3-methoxy-cis-cyclononene* (Found: C, 77.8; H, 11.4. $C_{10}H_{18}O$ requires C, 78.0; H, 11.7%) as a discoloured oil [largely one component by g.l.c. (Carbowax 20M)]; yield 0.42 g (55%); τ (CCl_4) 4.2–4.9 (2 H, m), 5.9–6.2 (1 H, m), 6.94 (3 H, s.), and 7.8–8.9 (12 H, m); ν_{max} (film) 1 650m and 1 100s cm^{-1} ; m/e 154 (M^+ , 14%) and 97 (100%).

cis-Cyclonon-2-enol (14b).—*endo-9-Bromobicyclo-[6.1.0]-nonane* (1.0 g, 4.9 mmol), silver perchlorate (2.0 g, 9.6 mmol), and acetone–water (9 : 1 v/v; 10 ml) were heated together, under reflux, for 3 h. During this period, more silver perchlorate (1.0 g, 4.8 mmol) was added in portions. The products were then worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene to give a yellow oil [0.42 g (*ca.* 55%); largely one component on t.l.c. in ethyl acetate–benzene (1 : 19 v/v)]. G.l.c. gave *cis-cyclonon-2-enol* (Found: C, 77.2; H, 11.1. $C_9H_{16}O$ requires C, 77.1; H, 11.4%); τ (CCl_4) 4.3–4.75 (2 H, m), 5.50 (1 H, m), 7.20 (1 H, s), and 7.7–8.8 (12 H, m); ν_{max} (film) 3 340s and 1 645m cm^{-1} ; m/e 140 (M^+ , 6%) and 83 (100%).

Reduction of 2-Bromo-3-methoxy-trans-cyclononene with Sodium in Liquid Ammonia.—The reaction was carried out as described in the corresponding reduction of 2-bromo-3-methoxy-*trans*-cyclo-octene. A solution of substrate (1.0 g, 4.3 mmol) in petroleum (b.p. 30–40°; 10 ml) was added dropwise to a stirred solution of sodium (1.0 g, 43 mmol) in liquid ammonia (50 ml; distilled from the cylinder). Work up gave an oil (0.495 g, 75%) shown [n.m.r. spectroscopy; g.l.c. (Carbowax 20 M)] to be a 3 : 2 mixture of *trans*- and *cis*-3-methoxycyclonenes.

Reduction of 2-Bromo-trans-cyclonon-2-enol with Sodium in Liquid Ammonia.—The reaction was carried out as described for the reduction of 2-bromo-3-methoxy-*trans*-cyclo-octene. A solution of the substrate (1.0 g, 4.6 mmol) in petroleum (b.p. 30–40°; 10 ml) was added to a solution of sodium (2.0 g, 86 mmol) in liquid ammonia (75 ml). Work up gave an oil (0.45 g, 70%) shown (n.m.r. spectroscopy) to be a 1 : 1 mixture of *trans*- and *cis*-cyclonon-2-enols.

1-Bromo-9-methoxy-trans,cis-cyclonona-1,5-diene (20a).—9,9-Dibromobicyclo[6.1.0]non-4-ene³⁰ (2.0 g, 7.15 mmol) was added dropwise over 5–10 min to a stirred, cooled (15–20 °C) solution of silver perchlorate (2.75 g, 13 mmol) in

methanol (10 ml). After a further 5 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene to give *1-bromo-9-methoxy-trans,cis-cyclonona-1,6-diene* (Found: C, 52.3; H, 6.3; Br, 34.7. $C_{10}H_{16}BrO$ requires C, 52.0; H, 6.5; Br 34.6%) as a pure [n.m.r. (see below) and g.l.c.] liquid (1.48 g, 90%); τ (CCl_4) 4.16 (1 H, dd, J 6 and 10 Hz), 4.5–4.9 (2 H, m), 6.49 (1 H, m), 6.84 (3 H, s), and 7.5–8.5 (8 H, m); ν_{max} (film) 1 640m and 1 110s cm^{-1} ; m/e 91 (base peak; no M^+).

Action of Heat on 1-Bromo-9-methoxy-trans,cis-cyclonona-1,5-diene.—1-Bromo-9-methoxy-*trans,cis-cyclonona-1,5-diene* (0.75 g), obtained as above from 9,9-dibromobicyclo[6.1.0]non-4-ene, was heated (water-bath) at 70–80 °C for 1 h. The products, which were found [t.l.c. (benzene)] to consist of starting material and a higher R_F component, were adsorbed on a column of Mallinckrodt SilicAR CC7 (20 g). Elution with petroleum (b.p. 60–80°)–benzene (98 : 2, v/v) gave the less polar *diastereoisomer* of *1-bromo-9-methoxy-trans,cis-cyclonona-1,5-diene* (Found: C, 52.0; H, 6.5; Br, 34.3. $C_{10}H_{16}BrO$ requires C, 52.0; H, 6.5; Br, 34.6%); yield 0.105 g (14%); τ (CCl_4) 3.94 (1 H, dd, J 6 and 9.5 Hz), 4.55–4.9 (2 H, m), 6.07 (1 H, m), 6.71 (3 H, s), and 7.65–8.45 (8 H, m); ν_{max} (film) 1 650m and 1 100s cm^{-1} ; m/e 43 (base peak; no M^+). When this compound was heated at 70–80 °C (water-bath) for 1 h, t.l.c. (benzene) again indicated the presence of a mixture of diastereoisomers.

Determination of the Equilibrium Constant for the Interconversion of the Diastereoisomeric 1-Bromo-9-methoxy-trans,cis-cyclonona-1,5-dienes.—To each of two n.m.r. tubes was added the less polar diastereoisomer (*ca.* 0.01 g). The tubes were maintained for 18 h at 65 and 75 °C, respectively. The n.m.r. spectra (CCl_4) of the products revealed (by integration of the methoxy signals at τ 6.71 and 6.84) that the equilibrium constant for the interconversion of the less into the more polar (obtained directly by methanolysis of 9,9-dibromobicyclo[6.1.0]non-4-ene) diastereoisomer was 3.15 at both 65 and 75 °C.

Determination of the Rate of Equilibration of the Diastereoisomers of 1-Bromo-9-methoxy-trans,cis-cyclonona-1,5-diene.—To each of eight n.m.r. tubes was added the less polar diastereoisomer (*ca.* 0.01 g). The tubes were then immersed in a thermostatically-controlled oil-bath, maintained at 60 ± 0.2 °C. At 10 min (± 2 s) intervals tubes were removed and cooled (ice–methanol) and the n.m.r. spectra (CCl_4) of their contents were measured. Integration of the methoxy-signals at τ 6.71 and 6.84 indicated the proportions of the two diastereoisomers present and provided rate data (Table 2).

Similar experiments were carried out at 65 °C (10 min intervals), 70 °C (8 min intervals), and 75 °C (6 min intervals); eight different measurements were made at each temperature. The data obtained are given in Table 2.

2-Bromo-trans,cis-cyclonona-2,6-dienol (20b).—9,9-Dibromobicyclo[6.1.0]non-4-ene (5.5 g, 19.6 mmol) was added dropwise over 10 min to a cooled (15–20 °C), stirred solution of silver perchlorate (7.35 g, 35.5 mmol) in acetone–water (9 : 1 v/v; 20 ml). After a further 10 min the products were worked up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene to give a solid (3.84 g). Recrystallization from petroleum (b.p. 60–80°) gave *2-bromo-trans,cis-cyclonona-2,6-dienol* (Found: C, 49.55; H, 5.95; Br, 36.5. $C_9H_{13}BrO$ requires C, 49.7; H, 6.0; Br, 36.8%).

²⁹ D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, 1963, **28**, 703.

³⁰ L. Skattebøl, *Tetrahedron Letters*, 1961, 167.

as needles, m.p. 87°; yield 3.48 g (82%); τ (CCl_4) 4.20 (1 H, dd, J 7 and 8 Hz), 4.5—4.9 (2 H, m), 6.03 (1 H, dd, J 6 and 10 Hz), and 7.5—8.6 (9 H, m); ν_{max} (Nujol) 3 310s and 1 635m cm^{-1} ; m/e 216/218 (M^+ , 2%) and 91 (100%).

1-Chloro-9-methoxy-trans,cis-cyclonona-1,5-diene (20c).—9,9-Dichlorobicyclo[6.1.0]non-4-ene (0.50 g, 2.6 mmol) was added to a saturated solution of silver perchlorate in methanol (2.0 ml) at 20 °C. The mixture was stirred for 20 min and then worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give 1-chloro-9-methoxy-trans,cis-cyclonona-1,5-diene (Found: C, 64.7; H, 8.0; Cl, 18.8. $\text{C}_{10}\text{H}_{15}\text{ClO}$ requires C, 64.4; H, 8.05; Cl, 19.0%); yield 0.39 g (80%); τ (CCl_4) 4.38 (1 H, dd, J 5 and 10.5 Hz), 4.5—4.9 (2 H, m), 6.2—6.5 (1 H, m), 6.84 (3 H, s), and 7.4—8.5 (8 H, m); ν_{max} 1 650m and 1 115s cm^{-1} ; m/e 186/188 (M^+ , 3 and 1%).

2-Chloro-trans,cis-cyclonona-2,6-dienol (20d).—9,9-Dichlorobicyclo[6.1.0]non-4-ene (0.15 g, 0.78 mmol) was added to a saturated solution of silver perchlorate in acetone-water (19 : 1 v/v; 1.0 ml) at 20 °C. The mixture was stirred for 40 min and then worked-up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give an oil (0.098 g) which slowly crystallized. Recrystallization from petroleum (b.p. 60—80°) gave 2-chloro-trans,cis-cyclonona-2,6-dienol (Found: C, 62.3; H, 7.5; Cl, 20.35. $\text{C}_9\text{H}_{13}\text{ClO}$ requires C, 62.6; H, 7.55; Cl, 20.6%) as crystals, m.p. 66—68°; yield 0.085 g (73%); τ (CCl_4) 4.42 (1 H, dd, J 5.5 and 10 Hz), 4.55—4.9 (2 H, m), 5.86 (1 H, dd, J 6 and 9 Hz), 7.32 (1 H, s), and 7.5—8.6 (8 H, m); ν_{max} (Nujol) 3 320 br,s and 1 650m cm^{-1} ; m/e 172/174 (M^+ , 6 and 2%) and 119 (100%).

1,9-Dibromo-trans,cis-cyclonona-1,5-diene (20; X = R = Br).—A solution of 2-bromo-trans,cis-cyclonona-2,6-dienol (20b) (2.0 g, 9.2 mmol) in benzene (20 ml) was added dropwise over 30 min to a stirred solution of phosphorus tribromide in benzene (20 ml) at 20 °C, with exclusion of moisture. After a further 15 min, the products were diluted with ether (50 ml) and then an excess of aqueous sodium carbonate was added. The dried (MgSO_4) organic layer was evaporated to give an oil. A solution of this in petroleum (b.p. 60—80°) was applied to a column of Mallinckrodt SilicAR CC7 (20 g) which was then eluted with benzene-petroleum (b.p. 60—80°) (2 : 98 v/v). Crystallization of the solid product from ethanol gave 1,9-dibromo-trans,cis-cyclonona-1,5-diene as crystals, m.p. 46.5—47.5°; yield 0.59 g (23%); τ (CCl_4) 4.12 (1 H, dd, J 7 and 9 Hz), 4.5—4.8 (2 H, m), 6.52 (1 H, dd, J 7 and 11 Hz), and 7.5—8.5 (8 H, m); ν_{max} (Nujol) 1 630m cm^{-1} ; m/e 278/280/282 (M^+ , 5, 10, and 5%) and 91 (100%).

Methanolysis of 1,9-Dibromo-trans,cis-cyclonona-1,5-diene.—1,9-Dibromo-trans,cis-cyclonona-1,5-diene (0.17 g, 0.6 mmol) was added to a stirred solution of silver perchlorate (0.20 g, 1.0 mmol) in methanol (10 ml) at 20 °C. After 10 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give the more polar diastereoisomer of 1-bromo-9-methoxy-trans,cis-cyclonona-1,5-diene * (0.095 g, 68%) as the sole product [as indicated by t.l.c. (benzene) and n.m.r. spectroscopy].

* The starting material in this solvolysis experiment was the more polar diastereoisomer of 2,9-dibromo-trans,cis-cyclonona-1,5-diene. When this compound was heated at 70 °C, under N_2 , it was converted into an equilibrium mixture containing starting material and what is believed to be its less polar diastereoisomer [τ (CCl_4) 3.40 (1 H, dd, J 5 and 10.5 Hz), 4.4—4.9 (2 H, m), 5.16 (1 H, m), and 7.2—8.5 (8 H, m)]. When the latter was treated with silver perchlorate in methanol solution, the more polar diastereoisomer of 1-bromo-9-methoxy-trans,cis-cyclonona-1,5-diene was again obtained as virtually the sole product.

Methanolysis of 1,9-Dibromo-cis,cis-cyclonona-1,5-diene.—1,9-Dibromo-cis,cis-cyclonona-1,5-diene¹³ (1.5 g, 5.36 mmol) was added to a stirred solution of silver perchlorate (3.0 g, 14.5 mmol) in methanol (10 ml) at 20 °C. After 90 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give an oil (1.01 g) shown by t.l.c. (benzene) to consist of two main components. A solution of this material in petroleum (b.p. 60—80°) was applied to a column of Mallinckrodt SilicAR CC7 (30 g) which was then eluted with benzene-petroleum (b.p. 60—80°) (2 : 98, v/v). Early fractions gave the less polar diastereoisomer of 1-bromo-9-methoxy-trans,cis-cyclonona-1,5-diene (0.51 g, 41%), identical with the material described above. Later fractions gave 1-bromo-9-methoxy-cis,cis-cyclonona-1,5-diene (Found: C, 52.1; H, 6.65; Br, 34.35. $\text{C}_{10}\text{H}_{15}\text{BrO}$ requires C, 52.0; H, 6.65; Br, 34.6%) as an oil (0.41 g, 33%); τ (CCl_4) 3.60 (1 H, t, J 9.5 Hz), 4.2—4.65 (2 H, m), 6.18 (1 H, dd, J 4.5 and 11 Hz), 6.91 (3 H, s), and 7.7—8.6 (8 H, m); ν_{max} (film) 1 630m and 1 100s cm^{-1} ; m/e 230/232 (M^+ , 13%) and 43 (100%).

Methanolysis of 10,10-Dibromobicyclo[7.1.0]decane.—10,10-Dibromobicyclo[7.1.0]decane³¹ (2.0 g, 6.75 mmol) was added dropwise over 5 min to a cooled (ice-water) solution of silver perchlorate (3.0 g, 14.5 mmol) in methanol (10 ml). After a further 10 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give an oil (1.36 g, 81%). G.l.c. (diethylene glycol adipate) and n.m.r. spectroscopy suggested that this material was a ca 70 : 30 mixture of trans- and cis-2-bromo-3-methoxycyclodecenes (see below).

2-Bromo-cis- and -trans-cyclodec-2-enols (16b and 15b, respectively).—10,10-Dibromobicyclo[7.1.0]decane (1.5 g, 5.07 mmol) was added in three portions to a cooled (ice-water) solution of silver perchlorate (2.0 g, 9.6 mmol) in acetone-water (9 : 1 v/v; 10 ml). After a further 10 min, the products were worked up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene to give an oil (1.06 g, 90%). T.l.c. [benzene-ethyl acetate (19 : 1)] and n.m.r. spectroscopy suggested that this material was a ca. 2 : 1 mixture of trans- and cis-2-bromocyclodec-2-enols.

To a stirred solution of the latter mixture of bromo-alcohols (1.4 g, 6.0 mmol) in dioxan (10 ml) and pyridine (1.5 g, 19 mmol) at 20° was added recrystallized 3,5-dinitrobenzoyl chloride (2.8 g, 12 mmol) over 10 min. After a further 20 min, the products were concentrated and the residue was partitioned between chloroform and aqueous sodium carbonate. The chloroform layer was washed with dilute hydrochloric acid and water, then dried (MgSO_4), and evaporated. A solution of the residue in hot petroleum (b.p. 60—80°) was adsorbed on Mallinckrodt SilicAR CC4 silicic acid (15 g) and the slurry was added to the top of a column of the same support (45 g). The column was eluted with petroleum (b.p. 60—80°)-benzene (93.5 : 6.5 to 89 : 11 v/v) and the middle fractions were rechromatographed. Concentration of the early fractions and crystallization from petroleum (b.p. 60—80°) gave 2-bromo-cis-cyclodec-2-enyl 3,5-dinitrobenzoate (Found: C, 47.75; H, 4.5; N, 6.4; Br 18.85. $\text{C}_{17}\text{H}_{19}\text{BrN}_2\text{O}_6$ requires C, 47.7; H, 4.4; N, 6.5; Br, 18.7%); yield 0.43 g; m.p. 149—151°. Concentration of the later fractions and crystallization from petroleum (b.p. 60—80°) gave the trans-isomer (Found: C, 47.95; H, 4.5; N, 6.4; Br, 18.5%); yield 0.93 g; m.p. 98—100°. The intermediate fractions contained 0.6 g of mixed cis- and trans-isomers.

A solution of the 3,5-dinitrobenzoate of the *trans*-alcohol (0.92 g) in dioxan (10 ml) was added dropwise to a stirred solution of potassium hydroxide (0.6 g) in water (10 ml). After a further 10 min, the products were neutralized with toluene-*p*-sulphonic acid and the dioxan was removed by evaporation under reduced pressure. The aqueous residue was then extracted with ether and the dried ($MgSO_4$) ethereal layer evaporated to give 2-bromo-*trans*-cyclodec-2-enol as an oil (0.49 g); τ (CCl_4) 3.82 (1 H, t, J 8 Hz), 5.93 (1 H, dd, J 5 and 8 Hz), 6.80 (1 H, s), and 7.5—9.1 (14 H, m); ν_{max} 3 350s, 1 640m, and 1 050s cm^{-1} ; m/e 232/234 (M^+ , 10%) and 41 (100%).

In the same way, 2-bromo-*cis*-cyclodec-2-enol (0.20 g) was obtained from its 3,5-dinitrobenzoate (0.42 g); it crystallized from petroleum (b.p. 60—80°) in hexagonal prisms, m.p. 55—56°; τ (CCl_4) 4.14 (1 H, dd, J 5 and 12 Hz), 5.33 (1 H, dd, J 6 and 9 Hz), 7.45 (1 H, s), and 7.8—9.0 (14 H, m); ν_{max} 3 350s and 1 630m cm^{-1} ; m/e 232/234 (M^+ , 11%) and 41 (100%).

2-Bromo-3-methoxy-*trans*-cyclodecene (15a).—Methyl iodide (0.50 g, 3.5 mmol) and barium oxide (0.50 g, 3.3 mmol) were added to a stirred solution of 2-bromo-*trans*-cyclodec-2-enol (0.485 g, 1.46 mmol) in anhydrous dimethyl sulphoxide (5 ml) at 20 °C. After 16 h, more methyl iodide (0.50 g, 3.5 mmol) and barium oxide (0.50 g, 3.3 mmol) were added and, after a further 8 h, the products were poured into water (25 ml). The aqueous mixture was extracted with ether (3 × 20 ml) and the combined extracts were dried ($MgSO_4$) and evaporated to give a yellow oil (0.45 g). This was adsorbed on a column of SilicAR CC7 (10 g), which was eluted with petroleum (b.p. 60—80°)—benzene (19 : 1 v/v) to give 2-bromo-3-methoxy-*trans*-cyclodecene (Found: C, 53.5; H, 7.7; Br, 32.1. $C_{11}H_{19}BrO$ requires C, 53.5; H, 7.7; Br, 32.4%) as an oil (0.27 g, 52%); τ (CCl_4) (a) at 35 °C: 3.88 (1 H, t, J 8 Hz), 6.44 (1 H, m), 6.86 (3 H, s), and 7.4—9.1 (14 H, m); (b) at —50 °C: ca. 3.75 and 3.89 (1 H, m and dd, J 6 and 8.5 Hz, respectively), 6.22 and 6.54 (1 H, m and dd, J 5 and 9.5 Hz, respectively), 6.78 and 6.94 (3 H, s and s), and 7.3—9.5 (14 H, m) (the integrals of the signals at 6.22 and 6.78 are ca. 0.2 times those of the signals at 6.54 and 6.94); (c) at ca. 5 °C, the signals at 6.78 and 6.94 have coalesced; ν_{max} (film) 1 645m and 1 110s cm^{-1} ; m/e 246/248 (M^+ , 52%) and 162/164 (100%).

Reduction of a Mixture of *cis*- and *trans*-2-Bromo-3-methoxycyclodecenes with Sodium in Liquid Ammonia.—The reaction was carried out as described for the reduction of 2-bromo-3-methoxy-*trans*-cyclo-octene. A solution of a 2 : 1 mixture of *trans*- and *cis*-2-bromo-3-methoxycyclodecenes (1.5 g, 6.1 mmol), obtained by the silver perchlorate-assisted methanolysis of 10,10-dibromobicyclo[7.1.0]decane (see above), in petroleum (b.p. 30—40°; 15 ml) was added to a solution of sodium (1.0 g, 43 mmol) in liquid ammonia (50 ml). Work up gave an oil (0.81 g, 83%) shown [n.m.r. spectroscopy and g.l.c. (polyphenyl ether)] to be a ca. 1 : 1 mixture of *cis*- and *trans*-3-methoxycyclodecenes (see below).

exo-10-Bromobicyclo[7.1.0]decane (10a).—A solution of sodium methylsulphonylmethanide [from sodium hydride (1.0 g, 42 mmol) and dimethyl sulphoxide (50 ml)] was added dropwise over 30 min to a stirred solution of 10,10-dibromobicyclo[7.1.0]decane (5.0 g, 16.9 mmol) in anhydrous dimethyl sulphoxide (50 ml) under nitrogen. After 1 h, water (150 ml) was added and the mixture obtained extracted with ether (3 × 50 ml). Distillation of the dried ($MgSO_4$) extract gave material (2.0 g), b.p. 30—70° at 0.2 mmHg; Redistillation gave a fraction (1.2 g, 33%), b.p. 52—54° at

0.1 mmHg; ν_{max} (film) 1 250s, 1 180m, and 970m cm^{-1} ; m/e 216/218 (M^+ , 1%) and 95 (100%).

endo-10-Bromobicyclo[7.1.0]decane (10b).—Tri-n-butyltin hydride (5.5 g, 19 mmol) was added over 1 h to cooled, stirred 10,10-dibromobicyclo[7.1.0]decane (5.0 g, 16.9 mmol) with the exclusion of moisture. The reactants were then kept at 20 °C for 16 h and distilled to give 90% pure (contaminated with ca. 10% of *exo*-isomer) *endo*-10-bromobicyclo[7.1.0]decane (Found: C, 55.1; H, 7.5; Br, 36.85. Calc. for $C_{10}H_{17}Br$: C, 55.3; H, 7.8; Br, 36.8%), b.p. 60—64° at 0.2 mmHg; yield 2.1 g (57%); τ (CCl_4) 6.94 (1 H, t, J 7.5 Hz) and 7.9—8.3 (16 H, m); ν_{max} (film) 1 250 cm^{-1} ; m/e 216/218 (M^+ , 1%) and 91 (100%).

cis-3-Methoxycyclodecene (16c).—A solution of the above (90% pure) *endo*-10-bromobicyclo[7.1.0]decane (0.7 g, 3.2 mmol) and silver perchlorate (1.35 g, 6.4 mmol) in methanol (4 ml) was heated under reflux for 1 h. During this period more silver perchlorate (0.7 g, 3.2 mmol) was added. Work up as in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene gave a slightly discoloured oil (0.41 g, 76%), found [n.m.r. spectroscopy and g.l.c. (polyphenyl ether)] to be a 3 : 1 mixture of *cis*- and *trans*-3-methoxycyclodecenes. Pure *cis*-3-methoxycyclodecene (Found: C, 78.8; H, 12.1. $C_{11}H_{20}O$ requires C, 78.6; H, 11.9%) was isolated by preparative g.l.c.; τ (CCl_4) 4.3—5.0 (2 H, m), 5.7—6.0 (1 H, m), 6.88 (3 H, s), and 7.4—8.9 (14 H, m); ν_{max} (film) 1 090s cm^{-1} ; m/e 168 (M^+ , 21%) and 97 (100%).

trans-3-Methoxycyclodecene (15c).—*exo*-10-Bromobicyclo[7.1.0]decane (0.44 g, 2.03 mmol), as prepared above, was added to a cooled (ice-water) stirred solution of silver perchlorate (0.75 g, 3.6 mmol) in methanol (3 ml). Precipitation of silver bromide was rapid and the reaction was soon complete. Work up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene gave *trans*-3-methoxycyclodecene (Found: C, 78.3; H, 11.7%) as a liquid (0.31 g, 91%); τ (CCl_4) 4.2—4.85 (2 H, m), 6.44 (1 H, m), 6.86 (3 H, s), and 7.6—9.0 (14 H, m); ν_{max} (film) 1 630m, 1 100m, and 980s cm^{-1} ; m/e 168 (M^+ , 25%) and 97 (100%).

Silver Perchlorate-promoted Methanolysis of 5,5,10,10-Tetrabromotricyclo[7.1.0.0^{4,6}]decane.—(a) Finely powdered 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]decane³⁰ (9.0 g, 20 mmol) was added over 30 min to a cooled, stirred solution of silver perchlorate (12.0 g, 58 mmol) in methanol (50 ml). After a further 15 min at 20 °C, work up as described in the preparation of 2-bromo-3-methoxy-*trans*-cyclo-octene gave a clear, viscous oil (6.8 g). T.l.c.(benzene) revealed the presence of three main components [R_F values (a) ca. 0.4 (major component), (b) ca. 0.35, and (c) ca. 0.1] and a number of minor components. SilicAR CC7 (200—325 mesh; 20 g) was added to a solution of this material in petroleum (b.p. 60—80°) and the resultant slurry applied to a column of the same support (65 g). Elution of the column with petroleum (b.p. 60—80°)—benzene (94 : 6) gave (i) virtually pure component (a) (2.2 g) isolated as an oil and (ii) a mixture of components (a) and (b). Rechromatography of the mixed fractions gave more (0.7 g) virtually pure component (a). This material (2.9 g, 43%), which was first obtained crystalline following preparative t.l.c., crystallized from absolute ethanol to give 1,6-dibromo-*cis*-5,10-dimethoxy-*trans*,*trans*-cyclodeca-1,6-diene (Found: C, 40.6; H, 5.1; Br, 44.9. $C_{12}H_{18}Br_2O_2$ requires C, 40.7; H, 5.1; Br, 45.2%) as plates, m.p. 63.5—65°; τ (CCl_4) * 3.80 (1 H, dd,

* $\tau(C_6Cl_6)$ at 190 °C 3.92 (1 H, t, J 7 Hz), 6.37 (1 H, m), and 6.85 (3 H, s); coalescence of the methoxy signals occurs at 158 °C in hexachlorobuta-1,3-diene solution.

J 2.5 and 10.5 Hz), 3.86 (1 H, dd, *J* 3 and 10.5 Hz), 6.13 (1 H, m), 6.35 (1 H, dd, *J* 3.5 and 10.5 Hz), 6.60 (3 H, s), 6.82 (3 H, s), and 6.9—8.5 (8 H, m); ν_{max} (film) 1 650m and 1 100s cm^{-1} ; *m/e* 352/354/356 (M^+ , 0.5, 1, and 0.5%) and 32 (100%).

Elution of the column with benzene gave virtually pure component (c). Crystallization from petroleum (b.p. 60—80°) gave 7-bromo-3-methoxybicyclo[4.4.0]dec-7-en-2-one (Found: C, 51.1; H, 5.65; Br, 30.7. $C_{11}H_{15}BrO_2$ requires: C, 51.0; H, 5.8; Br, 30.8%) as needles, m.p. 101—102°; yield 0.46 g (9%); τ (CDCl_3) 3.92 (1 H, m), 6.35 (1 H, m), 6.65 (3 H, s), and 7.4—8.8 (10 H, m); ν_{max} (Nujol) 1 720s and 1 640m cm^{-1} ; *m/e* 260/258 (M^+ , 15%) and 71 (100%).

(b) The experiment was repeated on the same scale; the crude products (5.8 g) were dissolved in petroleum (b.p. 40—60°; 15 ml) and the solution was kept under nitrogen at —10 °C. After 3 days, the resultant solid precipitate (1.1 g) was collected by filtration. T.l.c. (benzene) revealed the presence of components (b) and (c) (see above). Chromatographic separation on SilicAR CC7, evaporation of the fractions containing component (b), and crystallization of the residue from acetone gave 1,6-dibromo-trans-5,10-dimethoxy-trans,trans-cyclodeca-1,6-diene (Found: C, 40.5; H, 4.9; Br, 45.4. $C_{12}H_{18}Br_2O_2$ requires C, 40.7; H, 5.1; Br, 45.2%) as crystals, m.p. 160—162°; yield 0.44 g (6%); τ (CDCl_3) 3.88 (2 H, dd, *J* 3.5 and 10.5 Hz), 6.34 (2 H, dd, *J* 3.5 and 10.5 Hz), 6.80 (6 H, s), and 7.0—8.5 (8 H, m); ν_{max} (Nujol) 1 650m and 1 100s cm^{-1} ; *m/e* 352/354/356 (M^+ , 4, 8, and 4%) and 183 (100%).

Silver Perchlorate-promoted Hydrolysis of 5,5,10,10-Tetrabromotricyclo[7.1.0.0^{4,6}]decane.—Finely powdered 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}] decane (7.8 g, 17.3 mmol) was added over 30 min to a cooled, stirred solution of silver perchlorate (12.0 g, 58 mmol) in acetone—water (9 : 1 v/v; 50 ml). After a further 30 min at 20 °C, work up as described in the preparation of 2-bromo-3-methoxy-trans-cyclo-octene, except that the dried ethereal extracts were concentrated to small volume and then cooled (ice—methanol slurry), gave a precipitate which was found by t.l.c. [benzene—

ethyl acetate (19 : 1)] to contain virtually a single component (R_F 0.2). The mother liquors were concentrated and the residual oil was chromatographed on SilicAR CC7 (50 g) to give (i) an oil with R_F 0.4 and (ii) an additional quantity of the above lower R_F (0.2) product. Crystallization of the latter from acetonitrile gave 2,7-dibromo-trans,trans-cyclodeca-2,7-diene-cis-1,6-diol (Found: C, 38.0; H, 4.5; Br, 49.4. $C_{10}H_{14}Br_2O_2$ requires C, 37.8; H, 4.3; Br, 49.1%), m.p. 155—157°; yield of crude material 2.4 g (42%); τ (CD_3OD) 3.73 (1 H, dd, *J* ca 3 and 10 Hz), 3.85 (1 H, dd, *J* ca. 2 and 10 Hz), 5.70 (1 H, m), 5.95 (1 H, dd, *J* 3.5 and 10.5 Hz), and 6.7—8.6 (8 H, m); ν_{max} (Nujol) 3 300br,s and 1 660m cm^{-1} ; *m/e* 324/326/328 (M^+ , 12, 24, and 12%) and 91 (100%).

Crystallization of the minor (R_F 0.4) product from cyclohexane gave 7-bromo-3-hydroxybicyclo[4.4.0]-dec-7-en-2-one (Found: C, 49.1; H, 5.4; Br, 32.3. $C_{10}H_{13}BrO_2$ requires C, 49.0; H, 5.3; Br, 32.6%), m.p. 155°; yield (before crystallization) 0.3 g (7%); τ (CDCl_3) 3.88 (1 H, m), 5.88 (1 H, m), 6.28 (1 H, m), and 7.3—8.8 (10 H, m); ν_{max} (Nujol) 3 480br, s, 1 700s, and 1 630m cm^{-1} ; *m/e* 244/246 (M^+ , 36%) and 28 (100%).

Methylation of 2,7-Dibromo-trans,trans-cyclodeca-2,7-diene-cis-1,6-diol.—Methyl iodide (1.0 g) and barium oxide (1.5 g) were added to a solution of the diol (0.25 g) in anhydrous dimethyl sulphoxide (10 ml). The reactants were stirred at 20 °C, with the exclusion of moisture, for 48 h and then more methyl iodide (1.5 g) and barium oxide (1.5 g) were added. After a further 24 h the products were poured into water (50 ml) and the mixture was extracted with ether (4 × 50 ml). The dried (MgSO_4) combined ether layers were evaporated to a yellow oil (0.21 g). The major component (ca. 80%) of this material was isolated by preparative t.l.c. and identified (i.r. and n.m.r. spectroscopy) as 1,6-dibromo-cis-5,10-dimethoxy-trans,trans-cyclodeca-1,6-diene.

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