Tetrahedron Vol. 28, pp. 4989 to 5001. Pergamon Press 1972. Printed in Great Britain

THE REARRANGEMENT OF CYCLOPROPYL CHLORIDES TO ALLYL CHLORIDES

STEREOSPECIFICITY IN THE RECAPTURE OF THE CHLORIDE ION

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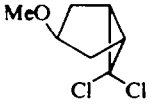
(*Received in the UK* 27 *March* 1972; *Accepted for publication* 22 *June* 1972)

Abstract—The cyclopropyl chlorides (**1** and **2**) rearrange on heating to give stereospecifically the allyl chlorides (**3** and **4**, respectively). In the presence of nucleophiles such as methoxide ion, the corresponding allyl ethers (**5** and **6**, respectively) are formed. Analysis of the stereochemistry of these products indicates that they are formed from the corresponding allyl chlorides (**3** and **4**), which are evidently the first-formed products of the reaction even in the presence of strong nucleophiles. The reaction of the allyl chlorides (**3** and **4**) with sodium phenylthioxide in aprotic non-polar solvents goes predominantly with retention of configuration, but in methanol is normal in giving predominantly inversion of configuration.

WE DESCRIBED in a preliminary communication[1] our evidence that the rearrangement of cyclopropyl chlorides to allyl chlorides is stereospecific. In particular, the cyclopropyl chlorides (**1** and **2**) gave, under a variety of conditions (Table), the same products in the same ratio as the allyl chlorides (**3** and **4** respectively). We concluded that all the reactions proceeded by a stereospecific rearrangement of the cyclopropyl chlorides to the allyl chlorides (**1** → **3**), and (**2** → **4**), followed by further reaction of the allyl



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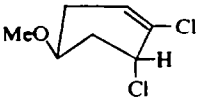

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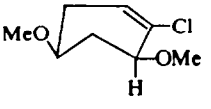

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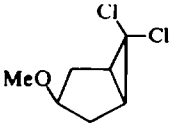

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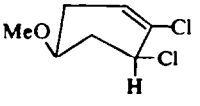

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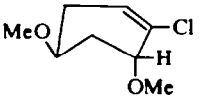

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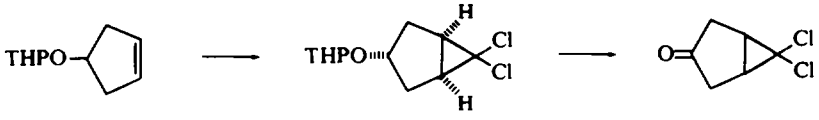
chlorides. Thus, with sodium methoxide in methanol, both **1** and **3** gave largely the *cis*-methyl ether (**5**), and both **2** and **4** gave largely the *trans*-methyl ether (**6**). In this, the full paper on our work, we record the synthesis of the starting materials

and the proof of configuration for all the compounds involved, and we somewhat amplify our earlier discussion.

SYNTHESIS OF STARTING MATERIALS

anti-6,6-Dichloro-3-methoxybicyclo[3,1,0]hexane (**1**) was the major product from the reaction of sodium methoxide and ethyl trichloroacetate with 4-methoxycyclopentene.[2] It was freed from the small amount of the *syn*-isomer by preparative GLC. The *syn*-isomer (**2**) was prepared by a short sequence starting from the tetrahydropyranyl ether (**7**) of 4-hydroxycyclopentene. With chloroform and potassium t-butoxide, this ether gave a mixture of the *syn* and *anti* isomers, consisting largely of the *anti*-isomer (**8**). The mixture was hydrolysed and then oxidised to give the crystalline ketone (**9**) which was reduced with lithium aluminium hydride, to give, stereoselectively,[3] the *syn* alcohol. Methylation of this alcohol gave the ether (**2**).



7 **8** **9**

When **1** and **2** were heated alone at 160° for 4 hr, a mixture of the allyl chlorides (**3** and **4**) was obtained in each case (Table). This was a simple synthesis of the allyl chlorides; but it was not possible to separate them from each other by gas chromatography because, under all the conditions that we tried, they were partially interconverted on the column. We therefore prepared the pure isomers by a different route.

The mixture of dichlorocyclopropanes (**1** and **2**) was treated with silver perchlorate in aqueous acetone[4] to give a mixture of the allylic alcohols (**10** and **11**) in approximately 50:50 ratio. These were separated from each other by column chromatography and then separately treated with triphenylphosphine dichloride.[5] The *cis*-alcohol (**10**) gave the *trans*-chloride (**3**), and the *trans*-alcohol (**11**) gave the *cis*-chloride (**4**). In each case the purity of the chlorides was judged by NMR spectroscopy, using the $Eu(DPM)_3$ shift reagent[6] to separate the signals, otherwise almost coincident, of the methoxy groups.

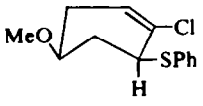
10 **11**

PROOF OF CONFIGURATION

The configuration of the 6,6-dichloro-3-methoxy-bicyclo[3,1,0]hexanes (**1** and **2**) was established by reduction with sodium in liquid ammonia to the 3-methoxybicyclo[3,1,0]hexanes of known configuration.[2] Methylation of the separated alcohols (**10** and **11**) gave the methyl ethers (**5** and **6**), hydrogenation of which gave the dimethyl ethers of the cyclohexan-1,3-diols. Authentic samples of these ethers were

prepared from the *cis*- and *trans*-cyclohexan-1,3-diols of known configuration.[7] This established the configuration of the alcohols (**10** and **11**) and of the ethers (**5** and **6**). On the basis of the known stereochemistry of substitutions using triphenylphosphine dihalide,[5,8] the *cis*-alcohol (**10**) was expected to give the *trans*-chloride (**3**) and the *trans*-alcohol (**11**) to give the *cis*-chloride (**4**). This enables us to assign configurations to the chlorides (**3** and **4**), and our assignment was supported by the displacement of the chlorine of **3** and **4**, again with inversion, to give the ethers (**5** and **6** respectively), the configuration of which we had already established unambiguously. Finally, the alcohols (**10** and **11**) were treated with thionyl chloride; this time, the products were predominantly the opposite allyl chlorides (**4** and **3** respectively) from those obtained with the triphenylphosphine dichloride reagent. This is exactly what we expected from the well-known[9] SNi′ pathway for the reaction of thionyl chloride with allyl alcohols. The reaction with thionyl chloride was not used for the preparation of the chlorides (**3** and **4**), because it was not quite so cleanly stereospecific as the reaction with triphenylphosphine dichloride.

The only products the stereochemistry of which was not rigorously established were the thioethers (**12** and **13**). These could not be separated from each other, but it was possible to identify and distinguish them by their NMR spectra using the $Eu(DPM)_3$ shift reagent.



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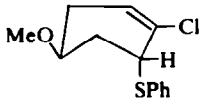

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The isomer to which we assign the structure (**12**) showed features in its NMR spectrum similar to those in the NMR spectra of the corresponding chloride (**4**), ether (**5**), and alcohol (**10**); and the isomer to which we assign structure (**13**) showed features in its NMR spectrum similar to those in the NMR spectra of the chloride (**3**), the ether (**6**), and the alcohol (**11**). In particular, the width of the signal due to the allylic hydrogen next to the heteroatom is greater for the *cis* isomers (**12**, **4**, **5**, and **10**) than for the *trans* isomers (**13**, **3**, **6**, and **11**), as one would expect for a pseudoaxial allylic hydrogen.[10] The shapes of the signals are also similar within each series, the former having a simple broad hump, but the latter having in each case a broadened overlapping triplet. The signal of the vinyl hydrogen is also diagnostic: in the *trans* isomers it appears as a double doublet, but in the *cis* isomers, as a result of extra (allylic) coupling,[11] it appears as a broad hump.

The likely conformation of these isomers deserves some comment. The *trans* isomers (**13**, **3**, and **6**) are almost certainly in the conformation illustrated because it is well-established[12] that most allylic groups preferentially adopt the pseudoaxial position. The *cis* isomers (**12**, **4**, and **5**), on the other hand, may not find the conformation shown especially favourable; thus they may well be in conformational equilibrium with other conformations. In agreement with this possibility, and further supporting our assignment for **12** and **13**, is the observation that the $Eu(DPM)_3$-induced shifts of the signals from the methoxy groups in the *trans*-thioether (**13**) and in the *trans*-chloride (**3**) are greater than they are in the *cis* isomers (**12** and **4**). It is known[13] that

equatorial methoxy groups are generally shifted more than axial methoxy groups.

The *cis*-thioether (**12**) is kinetically less stable to heat and to base than is the *trans* isomer (**13**). This too is in line with the relative reactivities of the chlorides (**4** and **3**), as far as thermal stability is concerned, and with the ethers (**5** and **6**), as far as sensitivity to base is concerned (see below). Finally, the stereochemistry of the substitution in methanol is the one more likely to give inversion of configuration, and this is what our assignment is consistent with. It then follows that retention of configuration occurs with sodium phenylthioxide in diglyme.

THE STEREOSPECIFIC REARRANGEMENT OF THE CYCLOPROPYL CHLORIDES TO THE ALLYL CHLORIDES

When the cyclopropyl chlorides (**1** and **2**) were heated in sealed tubes at 160° for 4 hr, the allyl chlorides (**3** and **4**) were obtained (Table). Under these conditions, however, the allyl chlorides (**3** and **4**) are slowly interconverting, so that the proportion of each detected underestimates the degree of stereospecificity. Thus, in our preliminary work[1] we relied on circumstantial evidence to support our claim that the rearrangement was at least 95% stereospecific. By taking the reaction to lower conversion, we have now found directly that, in each case, the first-formed allyl chloride is the result of a highly stereospecific reaction. By extrapolation of several runs back to zero conversion we observe that the *syn* isomer (**2**) is rearranging with $100 \pm 3\%$ stereospecificity, and the *anti* isomer (**1**) with about $95 \pm 3\%$ stereospecificity.

The rearrangement, which we have now shown to be stereospecific in the neat liquid and in solution in polar and non-polar solvents, could be a concerted [σ2s + σ2a] process (as it is sometimes represented[14]), or it could be an ion-pair process (as reports[15] of kinetic studies have usually considered it). The latter mechanism is supported by analogy with the gas phase chemistry of many alkyl halides.[16] What we have now shown is that, if ion-pairs are involved, they must remain intimate enough to preserve the distinction between the upper and lower surfaces of the six-membered ring, in which case the distinction between the two mechanisms is not necessarily a clear one. That some charge separation is involved is, however, not in doubt: the reaction in methanol is a good deal faster than the reaction in non-polar solvents, and it is also known, for example, that cyclopropyl bromides in general open faster than corresponding chlorides.[17] That the initial reaction in methanol is a stereospecific rearrangement followed by solvolysis is further supported by our observation that at 100° for six hrs, when the reaction is incomplete, the allyl chlorides (**3** from **1**, and **4** from **2**) were present in addition to the ethers (**5** and **6**). This observation is in line with some results of Skell[18], who found kinetic evidence for the intermediacy of allyl bromides in the solvolysis of 6,6-dibromobicyclo[3,1,0]hexane in aqueous methanol.

In spite of our having used powerful nucleophiles such as phenylthioxide ion in aprotic solvents, we have been unable to persuade a nucleophile to participate directly

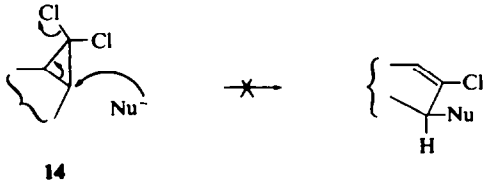

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TABLE. PRODUCT DISTRIBUTIONS IN THE REACTIONS OF 1, 2, 3 AND 4

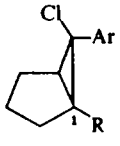
Reaction Conditions	Starting Material	% Reaction[a]	Production Distribution %		
			3[b]	4[b]	
160°[c]	1	95	91	9	
4 hrs.[c,d,e]	3	—	94	6	
	2	100	14	86	
	4[f]	—	19	81	
160°	1	74	95	5	
2·5 hrs.[c]	2	92	18	82	
160°	1	45	89	11	
1·12 hrs.[c]	2	77	5	95	
160°	1	26	95	5	
0·5 hrs.[c]	2	59	2	98	
			PhCl[g]	5[g]	6[g]
1 N NaOMe in	1	62	41	51[i]	8
MeOH at 100°[c,e,h]	3	100	37	57	6
6 hr. for 1 and 2. .	2	37	69	5[i]	26
15 min. for 3 and 4	4[f]	100	72	4	24
MeOH[c,d,e]	1	100	0	53	47
140°	3	100	0	54	46
6 hr.	2	100	0	23	77
	4[f]	100	0	25	75
1 N $AgClO_4$ in	1	100	0	60	40
MeOH	3	100	0	62	38
68°	2	90	0	41	59
1 hr.	4[f]	100	0	46	54
			12[b]	13[b]	
0·23 N PhSNa in	1	100	86	14	
MeOH[c,d,e,j,k]	3	100	90	10	
120°	2	100	5	95	
5 hr.	4[f]	100	4	96	
PhSNa suspended in	1	100	12	88	
diglyme at 161°	3	100	11	89	
3.5 hr for 1 and 2[k]	2[f]	100	65	35	
5 min. for 3 and 4	4[f]	100	65	35	

[a] Estimated from the amount of recovered starting material. [b] Estimated by NMR. [c] The reactions were performed in a sealed tube. [d] The results are reproducible to ±4%. [e] The results are the average of two or more runs. [f] The results are corrected for about 4% of 3 in the starting material. [g] Estimated by GLC. [h] The results are reprodubible to ±3%. [i] Corrected for about 4% decomposition of this isomer under the reaction conditions; the product of the decomposition was anisole (see text). [j] This reaction gives about 10% of 5 and 6, as well as 12 and 13. [k] A small amount of 1-chloro-4-methoxy-2-phenylthiocyclohexene was formed in this reaction, the amount was usually less than 5%.

(**14**, arrows) in the opening of the cyclopropane ring. Evidently, the chloride ion stays closely attached to the rest of the molecule until it is in a position to be displaced by a nucleophile. Our evidence that direct participation (**14**) does not occur is both stereochemical and kinetic: the stereochemistry observed is always the same as that obtained from the corresponding allyl chloride (Table), and the rate of the reaction is not markedly affected by the addition of sodium methoxide or sodium phenylthioxide to the methanol.

The close association of the chloride ion with the rest of the molecule may be maintained even in the presence of silver ions, where, once again, the same proportion of products is obtained from the cyclopropyl chlorides (**1** and **2**) as from the allyl chlorides (**3** and **4**). The closeness of this association may also explain the most unusual observation of an allylic bromide product in a silver-ion catalysed opening of a cyclopropyl bromide.[19]

Although direct nucleophilic participation in the ring opening was what we originally set out to find, its absence is perhaps not surprising. In the compounds (**15**), the rate of ring opening[20] is only ten times faster when R = Ph than when R = H; thus, not much positive charge is developed at C-1 in the transition state of this reaction. With other compounds, though, the reaction is made much easier by the presence of groups which help to delocalise the developing positive charge. Thus the adducts of dihalocarbenes with indene,[21] with cyclopentadiene[18], with 4,5-dihydrofuran[18], and with methoxy -[22] and ethoxy-[23] cyclohexene, all rearrange very readily, most of them at about 60°. One of our compounds too, namely the ketone (**9**), rearranges with very great ease (room temperature for 3 hr) in the presence of base to give *p*-chlorophenol. In this case, presumably the enol or enolate (**16**) is the reactive intermediate, and we note that in this compound the assisted and concerted breaking of two sigma bonds (**16**, arrows) takes place in spite of an appallingly bad arrangement of orbitals for continuous overlap. With these analogies in mind, we are still hopeful that it may be possible to find nucleophilic participation in a ring-opening reaction of this kind, perhaps by incorporating an internal nucleophile into the molecule. A nucleophilic displacement with inversion has been observed[24] with a carbon atom leaving group in the case of the cyclopropane (**17**). Certainly we expected to observe inversion in our compounds had a direct nucleophilic substitution (as in **14**) been possible. We expected it because such a process is, in essence, the reverse of the cyclopropanone-forming step in the Favorskii reaction, a step which is known[25] to go with inversion of configuration in non-polar solvents.



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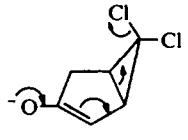

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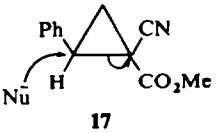

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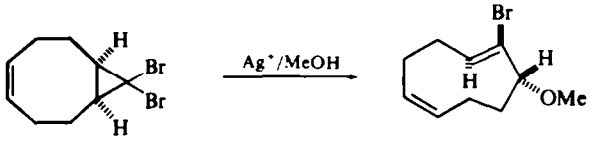
The low degree of stereoselectivity in the silver-ion catalysed reactions of **1** and **2** (Table) is in contrast to the highly stereoselective process which has been observed[4,19,26] in the silver-ion catalysed opening of several cyclopropyl halides in which the cyclopropane ring is fused to a medium sized ring. Thus, Reese and Shaw[26] obtained only

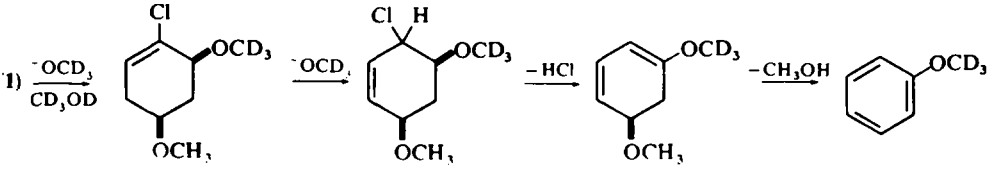
one diastereoisomer of the *trans*-cyclononadiene (**19**) from the silver-ion catalysed reaction of the cyclopropyl bromide (**18**). In the light of our results, it seems likely that the stereoselectivity in this medium-sized ring series results from a preferred formation of one diastereoisomer rather than from an inherent demand for inversion of configuration at the carbon atom which accepts the nucleophile[27]. In other words, it is a stereoselective reaction and not a stereospecific one—using the distinction between these words suggested by Zimmerman[28], and here found to be exceptionally useful.



18 **19**

An unexpected result was the observation that anisole, in addition to the expected chlorobenzene, was a product from the reaction of the cyclopropyl chlorides (**1** and **2**) with sodium methoxide. It was found that chlorobenzene was stable under the reaction conditions, and that the anisole was produced by partial decomposition of the *cis*-methyl ether (**5**). The reaction took place only in the presence of sodium methoxide.

We did one experiment to identify the pathway for the formation of the anisole from the methyl ether (**5**). When the directly prepared mixture of cyclopropyl chlorides (**1** and **2**, with **1** predominating) was heated with $NaOCD_3$ in CD_3OD for 6 hr at 120°, conversion to anisole was observed. The anisole was isolated and found by NMR spectroscopy to be fully deuterated in the methoxy group but not detectably deuterated in the ring. We suggest that a base-catalysed allylic rearrangement takes place (of the kind Cram and his co-workers[29] have found does not involve extensive exchange with solvent deuterons), followed by dehydrochlorination and loss of methanol.



THE "SN2′ PRODUCTS"

There remain the anomalous results with sodium phenylthioxide in non-polar solvents. As usual, the results with the cyclopropyl chlorides and the corresponding allyl chlorides are the same. The anomaly comes in the stereochemistry observed in the displacement of the allyl chlorides. Whereas inversion of configuration is the predominant result in methanol (**3** → **12** and **4** → **13**), the displacement in diglyme (and in DME and benzene) proceeds mainly with retention of configuration (**3** → **13** and **4** → **12**). This result is exactly what would be expected if an SN2′ process predominates in the non-polar solvent[30]. It is for reactions in non-polar solvents that SN2′ processes are most often claimed. However, the reaction is possibly heterogeneous, and, of course, we

have not proved that the nucleophile has bonded to a different carbon atom from the one which the chloride ion left. Indeed, this would be difficult to prove because of the very great ease of allylic rearrangement we can expect[9] for the allylic chlorides. So we do not claim, in the present climate of opinion[31,32], that we certainly have a concerted SN2′ reaction. What we do have is an unusually clear case of synfacial[32] displacement of an allylic chloride in non-polar aprotic solvents and an apofacial[32] displacement in a polar protic solvent.

EXPERIMENTAL

NMR spectra were obtained for solns in CCl_4. Eu(DPM)$_3$ was sublimed before use and stored *in vacuo*. IR spectra were taken as films or nujol mulls. Light petroleum refers to the faction b.p. 40–60°. GLC was carried out with the following columns:

1. A Perkin–Elmer F11 hot-wire chromatograph fitted with an LAC-1R-296 column, 6 ft × 0·125 in, 20% on 60–80 mesh chromosorp P (column 1). 2. A Perkin–Elmer F21 flame ionization chromatograph fitted with a glass column packed with LAC-1R-296, 3 ft × 0·375 ins, 20% on 60–80 mesh chromosorp P (column 2). 3. An F. and M 720 chromatograph fitted with a diethylene glycol adipate column, 6 ft × 0·25 in, 10% on 60–80 mesh chromosorp W (column 3).

4-Methoxycyclopentene. 4-Hydroxycyclopentene[33] (17 g) was added dropwise to a stirred suspension of sodium hydride (15 g of the 50% dispersion) in anhydrous ether (200 ml) under N_2. After 2 hr at room temp, an excess of MeI was added and the mixture stirred for 48 hr. Water (100 ml) was then added, the ether layer dried ($MgSO_4$) and the ether distilled off through a Vigreux column and the residue distilled to give *4-methoxycyclopentene* (15·5 g, 80%), b.p. 99°/760 mm. (Found: C, 73·6; H, 10·4. $C_6H_{10}O$ requires: C, 73·4; H, 10·3%), τ 4·3–4·5 (2H, M, olefinic C<u>H</u>), 5·8–6·2 (1H, m, C<u>H</u> on C-4), 6·8 (3H, s, OMe), and 7·4–7·8 (4H, m, 2 × C<u>H</u>$_2$).

anti-6,6-*Dichloro-3-methoxybicyclo*[3,1,0]*hexane* (**1**). NaOMe (from 13·5 g Na, dried at 100°/0·2 mm for 3 hr) was suspended in hexane (150 ml) and 4-methoxycyclopentene (15 g) added. The mixture was stirred at 0° under N_2 as ethyl trichloroacetate (90 g) was added cautiously over 30 min.[34] After a further 12 hr water was added, the ether layers dried ($MgSO_4$), the solvent evaporated and the residue distilled (25·3 g, 91%), b.p. 59–61°/0·4 mm. GLC (column 1, oven 150°) showed two components (A and B) in the ratio of 7:1 with retention times of 3·3 and 4·5 min respectively. The component (A) was separated (column 2, oven 140°) to give anti-6,6-*dichloro-3-methoxybicyclo* [3,1,0] *hexane* (**1**). (Found: C, 46·4; H, 5·7; Cl, 39·1. $C_7H_{10}OCl_2$ requires: C, 46·4; H, 5·6; Cl, 39·1%), ν_{max}. 3040 w, 2860 m, 2830 m, and 1100 s cm^{-1}, τ 6·1–6·5 (1H, m, C<u>H</u> on C-3), 6·88 (3H, s, OMe), and 7·6–8·3 (6H, m). The minor component (B) was also collected to give syn-6,6-*dichloro-3-methoxybicyclo*[3,1,0]*hexane*(**2**). (Found: C, 46·7; H 5·5%), ν_{max} 3040 w, 2870 m, 2830 m and 1120 cm^{-1}, τ 5·8–6·2 (1H, m), 6·84 (3H, s), 7·4–7·8 (2H, m), 7·9–8·15 (2H, m cyclopropyl <u>H</u>), and 8·25–8·6 (2H, m).

Proof of configuration of anti- *and* syn-6,6-*dichloro-3-methoxybicyclo*[3,1,0]*hexanes* (**1** and **2**). The isomer (A) (100 mg), described in the preparation above, in ether (0·5 ml) was added to a soln of Na (150 mg) in liquid ammonia (6 ml) and stirred for 1 hr. Only one product was detected by GLC (column 3), and this proved to be identical (NMR, GLC) to *anti*-3-methoxybicyclo[3,1,0]hexane, see below. The minor isomer (B), actually obtained from the longer route described below, was reduced in the same way and gave only one product identical (IR, NMR, GLC with *syn*-3-methoxybicyclo[3,1,0]hexane, see below.

Authentic anti- *and* syn-3-*methoxybicyclo*[3,1,0]*hexanes*. The *syn*-methyl ether was prepared by methylation of *syn*-hydroxybicyclo[3,1,0]hexane[2] using the procedure described above for 3-methoxycyclopentene. It is a known compound.[35]

The *anti*-methyl ether was prepared by similarly methylating the mixture of *syn*- and *anti*-alcohols obtained by Meerwein-Ponndorf reduction[2] of bicyclo [3,1,0]hexan-3-one, and separating the *anti*-product from the *syn*-product (column 3) to give pure anti-3-*methoxybicyclo*[3,1,0]*hexane*. (Found: C, 75·1; H, 11·0. $C_6H_{12}O$ requires: C, 74·9; H, 10·8%), τ 6·6 (1H, m, CH on C-3), 6·86 (3H, w), 7·9 (2H, m), 8·2–8·5 (2H, m), 8·65–8·95 (2H, m), 9·5–9·9 (1H, m), and 10·0–10·2 (1H, m).

4-Hydroxycyclopentene tetrahydropyranyl ether (**7**). This ether was made by the method of Parham and Anderson.[36] The crude product was redistilled through a short vigreux column to give *4-hydroxycyclopentene tetrahydropyranyl ether* (79%), *b.p. 89–93 /9 mm.* (*Found*: C, 71·6; H, 9·5. $C_{10}H_{16}O_2$ requires: C, 71·4; H, 9·6%), ν_{max} 3060 w, 2870 m, and 2850 m cm^{-1}, τ 4·2–4·4 (2H, m, olefinic protons), 5·0–5·6 (2H, m), 5·9–6·3 (1H, m), 6·4–6·7 (1H, m), 7·0–7·8 (4H, m), and 7·9–8·6 (6H, m).

syn-*and* anti-6,6-*Dichlorobicyclo*[3,1,0]*hexan-3-ol tetrahydropyranyl ether.* Potassium t-butoxide (from 36 g K) was suspended in light petroleum (600 ml) and 7 (31 g, 0·2 mole) added. The mixture was stirred at 0° under dry N_2 for 10 min before chloroform (122 g, 0·94 mole) was added dropwise over a period of 3 hr. The mixture was stirred for a further 12 hr at room temp and then distilled water was added. The organic layers were dried ($MgSO_4$), the ether was removed and the product fractionally distilled to give recovered 7 (12·6 g), b.p. 44–48°/0·25 mm and a mixture of syn *and* anti-6,6-*dichlorobicyclo*[3,1,0]*hexan-3-ol tetrahydropyranyl ethers* (24 g, 86% allowing for recovered starting material), b.p. 95–97°/0·25 mm. (Found: C, 52·9; H, 6·3; Cl, 28·0. $C_{11}H_{16}O_2Cl_2$ requires: C, 52·6; H, 6·4; Cl, 28·2%), ν_{max} 3040 w, 2870 m, and 2850 cm^{-1}, τ 5·0–6·0 (2H, m), 6·0–6·5 (1H, m), 6·5–6·8 (1H, m), 7·2–8·2 (5H, m), and 8·2–8·8 (6H, m).

syn-*and* anti-6,6-*Dichlorobicyclo*[3,1,0]*hexan-3-ol.* A mixture of *syn-* and *anti-*6,6-dichlorobicyclo[3,1,0]-hexan-3-ol tetrahydropyranyl ethers (20 g, 0·08 mole) and toluene-*p*-sulphonic acid (2·1 g) were refluxed in ethanol (600 ml) for 1 hr, cooled, diluted with water, and extracted into ether. The ether extracts were washed with dilute sodium hydroxide, water, and dried ($MgSO_4$). The ether was removed and the product distilled to give a mixture of syn-*and* anti-6,6-*dichlorobicyclo*[3,1,0]*hexan-3-ol* (11·6 g, 88%), b.p. 64–68°/0·2 mm, ν_{max} 3350s and 1080s cm^{-1}, τ 5·4–5·9 (1H, m, C<u>H</u> on C-3), 6·2–6·5 (1H, broad s, —O<u>H</u>), and 7·0–8·3 (6H, m). A satisfactory analysis could not be obtained for this mixture, but methylation of a small portion using the procedure described above for the methylation of 4-hydroxycyclopentene gave *syn-* and *anti-*6,6-dichloro-3-methoxybicyclo[3,1,0]hexane (**1** and **2**) identical with authentic samples (GLC, column 1, oven 150°), in the ratio *syn:anti* = 1:10.

6,6-*Dichlorobicyclo*[3,1,0]*hexan-3-one* (**9**). A soln of CrO_3 (8·0 g) in H_2SO_4 (7·0 ml) and water (to make up to 30 ml) was added over a period of 5 min to the mixture of *syn-* and *anti-*6,6-dichlorobicyclo[3,1,0]hexan-3-ol (9·0 g) in acetone (400 ml, distilled off $KMnO_4$ and deoxygenated). The mixture was stirred for a further 5 min before MeOH (20 ml) was added. The green soln was then decanted off the Cr salts, which were washed with acetone: the acetone extracts were combined and the acetone removed. The residue was dissolved in ether and the ethereal soln washed 3 times with sat NaCl aq, dried ($MgSO_4$) and the ether removed. The crude product crystallized on cooling and was recrystallized from ether–light petroleum to give 6,6-*dichlorobicyclo*[3,1,0]*hexan-3-one* (**9**: 5·6 g, 62%), m.p. 56–56·5° (Found: C, 44·0: H, 3·9: Cl, 43·1. $C_6H_6OCl_2$ requires: C, 43·7: H, 3·7: Cl, 43·0%), ν_{max} 3065w and 1740s cm^{-1}, τ 7·4–7·9 (m).

syn-6,6-*Dichlorobicyclo*[3,1,0]*hexan-3-ol.* 6,6-Dichlorobicyclo[3,1,0]hexan-3-one (5·6 g,) in dry ether (20 ml) was added to a suspension of LAH (0·65 g,) in dry ether (100 ml) at room temp under dry N_2. The mixture was stirred for 40 min at room temp and then refluxed for a further 90 min.

Aqueous work-up using sat NH_4Cl aq (50 ml) gave an organic residue, which was distilled, giving syn-6,6-*dichlorobicyclo*[3,1,0]*hexan-3-ol* (4·7 g, 84%), b.p. 69–70°/0·15 mm. (Found: C, 42·8; H, 4·7; Cl, 42·2. $C_6H_8OCl_2$ requires: C, 43·1; H, 4·8; Cl, 42·5%), ν_{max} 3330s, 3040w, and 1070s cm^{-1}, τ 5·6 (1H, quartet, J = 8 Hz, C<u>H</u> on C-3), 7·16 (1H, s, —O<u>H</u>), 7·3–7·75 (2H, m), 7·9–8·15 (2H, m, cyclopropyl protons), and 8·25–8·6 (2H, m). The colourless liquid crystallized on standing to give prisms, m.p. 35–39°.

syn-6,6-*Dichloro-3-methoxybicyclo*[3,1,0]*hexane* (**2**). *syn-*6,6-Dichlorobicyclo[3,1,0]hexan-3-ol (4·6 g, was methylated using the procedure described for the methylation of 4-hydroxycyclopentene to give **2** (1·7 g, 37%), b.p. 99–100°/14 mm, identical (GLC, NMR) with the minor isomer (B) obtained by the addition of dichlorocarbene to 4-methoxycyclopentene.

cis *and* trans-2-*Chloro-5-methoxycyclohex-2-enol* (**10** and **11**) A mixture of **1** and **2** (10 g, *syn:anti* = 1:7) was refluxed in aqueous acetone (200 ml, acetone:water = 95:5) with $AgClO_4$ (41·4 g,) for 2 hr. The ppt was filtered off and the soln diluted with water and extracted into ether. The extracts were dried ($MgSO_4$), and the ether removed leaving a pale yellow oil. Two components, A and B, were detected both by GLC (column 1, oven 180°, retention times 5·8 and 6·0 min, respectively, in the ratio 1:1) and by TLC (silica gel, 4% EtOH in $CHCl_3$). They were separated on a silica column (Mallinkrodt CC-7, eluting with $CHCl_3$). The separated products were dissolved in ether, the solns washed twice with sat NaCl aq and once with distilled water, dried ($MgSO_4$), and the ether removed under vacuum. A, the faster on TLC (2·7 g) was cis-2-*chloro-5-methoxycyclohex-2-enol* (**10**). (Found: C, 51·4; H, 6·7. $C_7H_{11}O_2Cl$ requires: C, 51·7; H, 6·8%), ν_{max} 3400s, 3040w, 2830m, and 1650m cm^{-1}, τ 4·32 (1H, t, J = 4 Hz, olefinic proton), 5·95–6·15 (1H, m, C<u>H</u> on C-3), 6·25–6·42 (1H, quintet, J = 4 Hz, C<u>H</u> on C-5), 6·7 (3H, s,—OMe), 6·97 (1H, broad s, —O<u>H</u>), 7·6–7·8 (2H, m, —C<u>H</u>$_2$), and 7·84–8·02 (2H, m, C<u>H</u>$_2$). The *cis* configuration was assigned by correlation, see below, with *cis*-cyclohexan-1,3-diol and is consistent with this isomer being the faster on TLC. B, the slower on TLC (2·7 g) was identified as **11**, but a satisfactory analysis could not be obtained; ν_{max} 3370s, 3040w, 2830m, and 1650 cm^{-1}, τ 4·15–4·32 (1H, m, olefinic proton), 5·74–5·92 (1H, m, C<u>H</u> on C-3), 6·2–6·5 (2H, m, C<u>H</u> on C-5 and —O<u>H</u>), 6·7 (3H, s, —OMe), and 7·3–9·4 (4H, m, 2xCH_2). The *trans* configuration was assigned by

correlation with *trans*-cyclohexan-1,3-diol and is consistent with this isomer being the slower on TLC. A mixed fraction (0·9 g) was also obtained (total yield 6·3 g, 68%).

cis- *and* trans-1,6-*Dichloro*-4-*methoxycyclohexene* (**3** and **4**). When mixtures of the chlorides (**3** and **4**) were required they were prepared by heating mixtures of the *syn*- and *anti*-dichlorocyclopropanes (**1** and **2**) in a sealed tube at 170° for 6 hr; the products were purified (not separated) down a column of silica (Mallinkrodt CC-7, eluted with CH_2Cl_2); yields were usually about 80%.

For the pure, separated allyl chlorides, the following procedure was used. Chlorine was bubbled through a soln of triphenylphosphine (4·0 g,) in CCl_4 (100 ml, AR) until a permanent yellow colour was formed in the mixture. The CCl_4 was then removed under vacuum leaving triphenylphosphine dichloride as a white solid, which was dried at room temp under vacuum (0·2 mm). The triphenylphosphine dichloride was dissolved in dry acetonitrile (100 ml) and **10** or **11** (1 g, 0·006 mole) added to the soln under N_2 at room temp. The mixture was stirred at room temp for 90 min, then diluted with Na_2CO_3aq and extracted into light petroleum. The light petroleum extracts were dried ($MgSO_4$) and the solvent removed. The crude allyl chlorides were freed from triphenylphosphine oxide by chromatography on silica (Mallinkrodt CC-7, 100 g). Using this technique, **10** was converted into **3**, which contained less than 1% of the *cis* isomer (**4**), and *trans*-**11** was converted into *cis*-**4** which contained 4% of the *trans*-isomer (**3**). Yields were greater than 90%. The *trans*-isomer (**3**) showed ν_{max} 3060w, 2840m, and 1650m cm^{-1}, τ 4·10–4·25 (1H, m, olefinic C<u>H</u>), 5·4–5·6 (1H, m, half-height width 10Hz, C<u>H</u> on C-3), 6·1–6·5 (1H, m, C<u>H</u> on C-5), 6·70 (3H, s, OMe), and 7·2–8·2 (4H, m, 2C<u>H</u>$_2$); there was no allylic coupling detectable by spin decoupling. The *cis*-isomer (**4**) showed ν_{max} 3060w, 2840m, and 1650 cm^{-1}, τ 4·05–4·25 (1H, m), 5·4–5·7 (1H, m, half-height width 20 Hz), 6·5–6·8 (1H, m), 6·72 (3H, s) and 7·2–8·2 (4H, m); a small allylic coupling ($\sim$1 Hz) was detectable by spin decoupling.

The compositions of mixtures of the allyl chlorides (**3** and **4**) could not be measured by GLC (the allyl chlorides decomposed extensively in the injection port of the analytical chromatograph), instead they were measured by NMR in the presence of $Eu(DPM)_3$[6] which shifted all the peaks downfield and separated those of each isomer. The peaks from the *trans*-isomer (**3**) were shifted downfield more than the corresponding peaks from the *cis* isomer (**4**). A graph was plotted of the shift of the methoxy singlet from the *trans*-isomer (**3**) against the shift of the methoxy singlet of the *cis*-isomer (**4**). It was a straight line, slope 1·18, and was used to detect small impurities of one of the isomers in the other.

The allyl chlorides were also obtained in a less pure state from **10** and **11** using thionyl chloride in ether. Thionyl chloride (120 mg, purified by fractional distillation twice through a 10 in packed column off triphenyl phosphite) in dry ether (5 ml) was added to **10** or **11** (100 mg) under a dry atmosphere and the mixture stirred at room temp for 24 hr before being diluted with ether and washed with Na_2CO_3 aq and water. The ethereal soln was dried ($MgSO_4$) and the ether removed leaving **3** and **4**. Using this technique, **11** was converted to *trans*-**3** containing less than 5% of the *cis* isomer (**4**) and **10** was converted into *cis*-**4** containing about 25% of the *trans*-isomer (**3**). These reactions were repeated several times using different reaction times and temps but the stereospecificities could not be improved upon.

cis- *and* trans-1-*Chloro*-4,6-*dimethoxycyclohexene* (**5** and **6**)

Preparation I. A mixture of **1** and **2** (2 g, *syn*:*anti* = 1:7) was heated in a sealed tube for 6 hr at 140° in MeOH (20 ml). The soln was then diluted with water and extracted into ether. The ether extracts were combined, dried ($MgSO_4$) and the ether removed. The residue (approx 2·0 g) was examined by GLC (column 1, oven 150°) which detected two products A and B, relative retention times 3·5 and 5·0 min, respectively, ratio approx 1:1, which were separated by preparative GLC (column 2, oven 140°). A was identified as trans-1-*chloro*4,6-*dimethoxycyclohexene* (**6**). (Found: C, 54·5; H, 7·3; Cl, 20·3. $C_8H_{13}O_2Cl$ requires: C, 54·5; H, 7·4; Cl, 20·1%). ν_{max} 3060w, 2840m, and 1655 cm^{-1}, τ 4·15–4·35 (1H, m, olefinic proton), 6·2–6·4 (1H, m, C<u>H</u> on C-3), 6·3–6·8 (1H, m, C<u>H</u> on C-5), 6·75 (3H, s, —OMe), 6·80 (3H, s, —OMe), and 7·3–8·65 (4H, m, 2xCH_2). B was identified as cis-1-*chloro*-4,6-*dimethoxycyclohexene* (**5**). (Found: C, 54·4; H, 7·3; Cl, 20·3%). ν_{max} 3060w, 2840m, and 1655m cm^{-1}, τ 4·15–4·35 (1H, m, olefinic proton), 6·0–6·4 (1H, m, C<u>H</u> on C-3), 6·5–7·1 (1H, m, C<u>H</u> on C-5), 6·69 (3H, s, —OMe), 6·76 (3H, s, —OCH_3), and 7·4–8·6 (4H, m, 2xCH_2).

Preparation II. Small portions of **10** and **11** were methylated separately using the procedure described above for the methylation of 4-hydroxycyclopentene. The *cis*-alcohol (**10**) gave *cis*-**5** identical with an authentic sample (GLC, NMR, IR), and the *trans*-alcohol (**11**) gave *trans*-**6** identical with an authentic sample (GLC, NMR, IR).

cis- *and* trans-1,3-*Dimethoxycyclohexane*

Preparation I. *cis*- and *trans*-**5** and **6** (100 mg) were separately dissolved in absolute EtOH (1·5 ml)

containing KOH (100 mg) and 5% Pd-C (50 mg) and the mixtures stirred under H_2 at room temp for 2 hr, after which time the absorption of H_2 had stopped. The mixtures were diluted with water and extracted into ether, and the ether extracts combined, dried ($CaCl_2$) and the ether removed by careful distillation through a packed column. The products were examined and isolated by GLC (columns 1 and 3). *cis*-**5** gave cis-1,3-*dimethoxycyclohexane* identical with a sample prepared by methylation of *cis*-cyclohexane-1,3-diol. (Found: C, 66·8; H, 11·1. $C_8H_{16}O_2$ requires: 66·6; H, 11·2), ν_{max} 2870m, 2830m, and 1105 cm^{-1}, τ 6·3–7·2 (2H, m, CH on C-1 and C-3), 6·78 (6H, s, 2x-OMe), 7·5–7·85 (1H, m), 7·9–8·4 (3H, m), and 8·6–9·2 (4H, m). *trans*-**6** gave trans-1,3-*dimethoxycyclohexane* identical with a sample prepared by methylation of *trans*-cyclohexane-1,3-diol (Found: C, 66·6; H, 11·2%), ν_{max} 2870m, 2830m, and 1100 cm^{-1}, τ 6·3–7·0 (2H, m, CH on C-1 and C-3), 6·8 (6H, s, 2x-OMe), and 8·1–8·9 (8H, m, 4xCH_2). No *trans*-1,3-dimethoxycyclohexane was detected in the product mixture from the *cis*-allyl ether (**5**) (GLC), nor was any *cis*-1,3-dimethoxycyclohexane detected in the product mixture from the *trans*-allyl ether (**6**).

Preparation II. Dimethyl sulphate (0·4 ml), then NaOH (2 ml of 40% soln in water), and then more Me_2SO_4 (0·6 ml) were added to a soln of *cis*- or *trans*-cyclohexane-1,3-diol[37] (100 mg) in the minimum amount of water. The mixtures were stirred and refluxed for 4 hr, cooled and extracted into ether. The ether extracts were combined, dried ($MgSO_4$), and the ether was removed by careful distillation through a packed column. The products were examined and isolated by GLC (column 3) as described above.

cis- *and* trans-1-*Chloro*-4-*methoxy*-6-(*phenylthio*)*cyclohexene* (**12** and **13**). Mixtures of **1** and **2** (0·54 g, *syn*:*anti* = 1:7) were heated in MeOH, or dimethoxyethane, or dimethyl sulphoxide (15 ml) with sodium phenylthioxide (10% excess in MeOH; 100% excess in dimethoxyethane and dimethyl sulphoxide) for several hr (5 hr at 120° in MeOH; 3 hr at 160° in dimethoxyethane; and 1 hr at 133° in dimethyl sulphoxide). The mixtures were then diluted with water and extracted into light petroleum. The light petroleum extracts were combined, dried (anhyd $MgSO_4$) and the solvent removed under vacuum. The residues were then examined by TLC (silica gel, eluting with 20% ether in light petroleum).

The residues from the reactions in MeOH showed three components on TLC, A, B, and C, and these were separated by column chromatography on silica (Mallinkrodt CC-7, 50 g). A, the fastest component on TLC, was identified as diphenyl disulphide by comparison (TLC, m.p.) with an authentic sample. B was identified as a mixture of cis- *and* trans-1-*chloro*-4-*methoxy*-6-(*phenylthio*)*cyclohexene* (**12** and **13**) (0·45 g, 60%), in the ratio *cis*:*trans* = 73:27. (Found: C, 61·0; H, 5·7; Cl, 14·2. $C_{13}H_{15}OClS$ requires: C, 61·3; H, 5·9; Cl, 13·9%), ν_{max} 3065m, 3060w, 2830m, 1645m, 1587m, 1576m, 1484m, and 1110s cm^{-1}, τ 2·4–2·9 (5H, m, aromatic protons), 4·1–4·4 (1H, m, olefinic protons), 6·1–6·9 (2H, m, CH on C-3 and CH on C-5), 6·78 (3H, s, –OMe), and 7·3–8·5 (4H, m, 2xCH_2). C, the slowest component on TLC was identified as a mixture of *cis*- and *trans*-**5** and **6** (0·1 g) by comparison (NMR) with the authentic materials.

The residues from the reactions in dimethoxyethane showed two main components on TLC, A and B, and these were separated by chromatography on silica (Mallinkrodt CC-7 50 g). A, the fastest component was identified as diphenyl disulphide by comparison (TLC, m.p.) with an authentic sample. B, the slower component, was identified as a mixture of *cis* and *trans*-**12** and **13**, *cis*:*trans* = 16:84. (Found: C, 61·4; H, 5·9; Cl, 14·1%), ν_{max} 3070m, 3060m, 3020w, 2830m, 1650m, 1590m, 1580m, 1487m, and 1100 cm^{-1}, τ 2·4–2·9 (5H, m, aromatic protons), 4·1–4·4 (1H, m, olefinic protons), 6·1–6·9 (2H, m, CH on C-3 and CH and CH on C-5), 6·78 (3H, s, –OMe), and 7·3–8·5 (4H, m, 2xCH_2).

The residues from the reactions in dimethyl sulphoxide showed two major components on TLC which were separated and shown to be diphenyl disulphide and a mixture of *cis*- and *trans*-**12** and **13**, in the ratio of *cis*:*trans* = 73:27.

Mixtures of the allyl thioethers (**12** and **13**) were analysed by NMR in the presence of $Eu(DPM)_3$ which shifted all the peaks downfield and separated those due to each isomer. The peaks from the *trans*-thioether (**13**) were shifted more than those from the *cis*-thioether (**12**). A graph was plotted of the shift of the methoxy singlet from the *trans*-isomer (**13**) against the shift of the methoxy singlet of the *cis*-isomer (**12**). It had a straight line, slope 1·61, and was used to check the line assignments made in later spectra. The methoxy singlets were used in the quantitative analysis of the allyl thioether mixtures.

Thermal rearrangements in the absence of solvent. Portions (30 mg) of *syn*- and *anti*-6,6-dichloro-3-methoxybicyclo[3,1,0]hexane (**1** and **2**) were heated separately in sealed tubes immersed in an oil bath maintained at 160° (±1°). The crude product mixtures were shown by NMR to consist of *cis*- and *trans*-**3** and **4**, together with unchanged starting material and a small amount of aromatic (elimination?) product. Stability tests on samples of *cis*- and *trans*-**3** and **4** (20 mg portions) were also carried out using this technique.

Rearrangements of syn- *and* anti-,6-*dichloro*-3-*methoxybicyclo*[3,1,0]*hexane* (**1** *and* **2**) *in solutions of sodium methoxide in methanol. syn*- and *anti*-**1** and **2** and *cis*- and *trans*-**3** and **4** (40 mg portions) were heated

separately in solns of NaOMe in MeOH (2 ml 1N) in sealed tubes immersed in an oil bath at the required temp. The reactions were worked up by the addition of distilled water (10 ml) and extraction into light petroleum (3 × 10 ml). The light petroleum extracts were combined, dried ($MgSO_4$) and the solvent removed by slow distillation through a packed column. The product mixtures were analysed by GLC (column 1; oven 80° for the elimination products, and 150° for the substitution products), the products being identified by co-injection with authentic materials. The composition of a mixture of chlorobenzene, anisole, starting dichlorocyclopropanes, and product allyl ethers did not change when the mixtute was dissolved in MeOH and put through the extraction procedure. The results were corrected for relative response factors and for the decomposition of the *cis*-methyl ether (**5**). The absolute GLC response was determined before and after each analysis and hence the recovery in each experiment estimated. The errors in these estimations were quite large, but the results did show that more than 80% of the starting materials could usually be accounted for.

Rearrangements of 6,6-dichlorobicyclo[3,1,0]*hexan-3-one* (**9**). 6,6-Dichlorobicyclo[3,1,0]hexan-3-one (50 mg) was dissolved in MeOH (1 ml) and a soln of NaOMe in MeOH (1 ml, 1N) was added. The mixture was stirred under dry N_2 for 3 hr at room temp, after which time no starting material was left (TLC, eluting with 4% EtOH in $CHCl_3$). The soln was then diluted with water, acidified, extracted into ether, and the ether extracts combined, dried ($MgSO_4$), and the ether removed. One product was detected and purified by TLC and shown to be *p*-chlorophenol by comparison (NMR, TLC, IR) with an authentic sample. No reaction took place under these conditions in the absence of NaOMe.

Rearrangements in methanol alone. Portions (40 mg) of *syn*- and *anti*-**1** and **2** and *cis*- and *trans*-**3** and **4** were heated separately in MeOH (2 ml) in sealed tubes at 100° and 140°. The product mixtures were worked up and analysed as described above, the products being identified by co-injection with the authentic materials.

The dichlorocyclopropane reactions performed at 100° were incomplete after 6 hr heating, and the intermediate allyl chlorides (**3** and **4**) could be detected in the product mixtures (GLC, NMR). In the product mixture from the *anti*-**1** no *cis*-allyl chloride (**4**) could be detected (GLC) although some *trans*-allyl chloride (**3**) was present (NMR). In the product mixture from the *syn*-**2**, *cis*-allyl chloride (**4**) could be detected (GLC) but the absence of the *trans*-allyl chloride (**3**) could not be unambiguously established. (GLC was unsuitable because both **5** and **4** have the same retention time; NMR was unsuitable because of the complexity of the mixture and the presence of the *cis*-allyl chloride).

Rearrangements in methanol in the presence of silver perchlorate. syn and *anti*-**1** and **2** and *cis*- and *trans*-**3** and **4** (40 mg portions) were added separately to solns of silver perchlorate in MeOH (2 ml, 1N) and the mixtures refluxed (usually for 1 hr). The product mixtures were filtered and then worked up and analysed as described above.

Rearrangements in the presence of sodium phenylthioxide. syn and *anti*-**1** and **2** and *cis*- and *trans*-**3** and **4** (36 mg portions) were dissolved separately in the solvent (1 ml of methanol, dimethoxyethane, or diglyme) together with sodium phenylthioxide (30 mg, 12% excess, dissolved in MeOH 53 mg, 100% excess, suspended in dimethoxyethane or diglyme) and the mixtures heated in tubes sealed under N_2 for the MeOH and dimethoxyethane runs, and refluxed under dry N_2 for the diglyme runs. The mixtures were then cooled, added to distilled water (10 ml) and extracted into light petroleum. The light petroleum extracts were combined, dried ($MgSO_4$) and the solvent removed. The crude products were examined by TLC (eluting with 20% ether in light petroleum) which showed the presence of diphenyl disulphide and the expected **12** and **13**. The *cis*- and *trans*-**12** and **13** could not be separated by TLC. They were isolated together by preparative TLC and analysed by NMR in the presence of $Eu(DPM)_3$.

Checks on the stability of the allyl thio-ethers (**12** and **13**). Mixtures of *cis*- and *trans*-**12** and **13** (30 mg portions) were heated in the solvent (1 ml, methanol or demethoxyethane, or 2 ml diglyme), in some cases in the presence of sodium phenylthioxide (30 mg in MeOH; 53 mg in dimethoxyethane or diglyme) or NaOMe (normal soln in MeOH) for several hr. The mixtures were then worked up and analysed as described above. The results showed that **12** and **13** isomerised only in the presence of base, to a compound to which we assign the structure 1-*chloro*-4-*methoxy*-2-(*phenylthio*)*cyclohexene* (Found: C, 61·4, H, 5·9. $C_{13}H_{15}OClS$ requires: C, 61·3; H, 5·9%), ν_{max} 3080m, 2910m, 1630m, 1590m, cm^{-1}, τ 2·4–3·0 (5H, m, aromatic protons), 6·4–6·8 (1H, m, C<u>H</u> on C-4), 6·85 (3H, s, OCH_3), 7·2–7·7 (2H, m, $-CH_2-$), 7·7–7·95 (2H, $-CH_2-$) and 7·95–8·4 (2H, m, $—CH_2—$). However this isomerisation did not occur extensively during the quantitative investigations of the rearrangement reactions.

REFERENCES

[1] I. Fleming and E. J. Thomas, *Tetrahedron Letters* 2485 (1971)—
[2] See also I. Fleming and E. J. Thomas, following paper, *Tetrahedron* **28**, 5003 (1972)
[3] Cf. S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.* **83**, 3235 (1961)
[4] C. B. Reese and A. Shaw, *Ibid.* **92**, 2566 (1970)
[5] G. A. Wiley, R. L. Hershkowitz, B. M. Rein and B. C. Chung, *Ibid.* **86** 964 (1964);
G. A. Wiley, B. M. Rein and R. L. Hershkowitz, *Tetrahedron Letters* 2509 (1964)
[6] J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.* **93**, 641 (1971) and references therein
[7] L. P. Kuhn, *Ibid.* **74**, 2492 (1952)
H. Finegold and H. Kwart, *J. Org. Chem.* **27**, 2361 (1962)
[8] J. P. Schaeffer and D. S. Weinberg, *Ibid.* **30**, 2635 (1965)
[9] J. D. Roberts, W. G. Young and S. Winstein, *J. Am. Chem. Soc.* **64**, 2157 (1942)
H. L. Goering, T. D. Nevitt and E. F. Silversmith, *Ibid.* **77**, 4042 (1955)
See also C. W. Jefford and J. A. Gunsher, *Helv. Chim. Acta* **54**, 1482 (1971)
[10] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. A. Schneider, *J. Am. Chem. Soc.* **80**, 6098 (1958)
[11] D. J. Collins, J. J. Hobbs and S. Sternhell, *Austral. J. Chem.* **16**, 1030 (1963)
[12] H. L. Goering, J. P. Blanchard and E. F. Silversmith, *J. Am. Chem. Soc.* **76**, 5409 (1954)
K. Sakashita, *Nippon Kagaku Zasshi* **81**, 49 (1960); *Chem. Abs.* **54**, 12015b (1960);
E. W. Garbisch, *J. Org. Chem.* **27**, 4249 (1962)
A. Laplanche and F. Venien, *C. R. Acad. Sci. Paris* c. **273**, 671 (1971).
[13] J. E. Herz, V. M. Rodriguez and P. Joseph-Nathan, *Tetrahedron Letters* 2949 (1971)
[14] C. W. Jefford, *Chimia* **24**, 357 (1970)
K. A. W. Parry and P. J. Robinson, *J. Chem. Soc.* (B) 49 (1969)
R. Fields, R. N. Hazeldine and D. Peter, *Ibid.* (C) 165 (1969)
[15] K. A. Holbrook and K. A. W. Parry, *Ibid.* (B) 1019 (1970)
[16] A. Maccoll, *Chem. Rev.* **69**, 33 (1969)
[17] M. S. Baird, D. H. Lindsay and C. B. Reese, *J. Chem. Soc.* (C) 1173 (1969)
[18] L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron* **21**, 1315 (1965)
[19] D. Duffin and J. K. Sutherland, *Chem. Comm.* 626 (1970)
[20] D. T. Clark and G. Smale, *Ibid.* 868 (1969)
[21] W. E. Parham, H. F. Reiff and P. Schwartzentruber, *J. Am. Chem. Soc.* **78**, 1437 (1956)
[22] D. G. Lindsay and C. B. Reese, *Tetrahedron* **21**, 1673 (1965)
[23] W. E. Parham, R. W. Soeder and R. M. Dodson, *J. Am. Chem. Soc.* **84**, 1755 (1962)
[24] E. W. Yankee and D. J. Cram. *Ibid.* **92**, 6329 (1970)
[25] G. Stork and I. J. Borowitz, *Ibid.* **82**, 4307 (1960)
H. O. House and W. F. Gilmore, *Ibid.* **83**, 3980 (1961)
C. R. Engel, S. K. Roy, J. Capitaine, J. Bilodeau, C. McPherson-Foucar and P. Lachance, *Canad. J. Chem.* **48**, 361 (1970)
[26] C. B. Reese and A. Shaw, *Chem. Comm.* 1365 (1970)
M. S. Baird and C. B. Reese, *Ibid.* 1644 (1970)
[27] See also G. H. Whitham and M. Wright, *J. Chem. Soc.* (C) 883 (1971), where a similar stereoselectivity has been found in the medium-sized ring series, but without the use of silver ions.
[28] H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *J. Am. Chem. Soc.* **81**, 108 (1959), footnote 16
[29] D. J. Cram, *Fundamentals of Carbanion Chemistry*, pp. 175–193. Academic Press, New York (1965)..
[30] G. Stork and W. N. White, *J. Am. Chem. Soc.* **75**, 4119 (1953)
[31] F. G. Bordwell, *Accts. Chem. Res.* **3**, 281 (1970)
F. E. Lutz and E. F. Kiefer, *Chem. Comm.* 1722 (1970)
J. A. Hemmingson and B. D. England, *J. Chem. Soc.* (B) 1347 (1971)
P. B. D. de la Mare and C. A. Vernon, *Ibid.* 1699 (1971)
[32] C. W. Jefford, A. Sweeney, D. T. Hill and F. Delay, *Helv. Chim. Acta* **54** 1517 (1971)
[33] E. L. Allred, J. Sonnenberg and S. Winstein, *J. Org. Chem.* **25**, 26 (1960)
[34] W. E. Parham, E. E. Schweizer, and S. A. Mierzwa, *Org. Synth.* **41**, 76 (1961)
[35] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.* **30**, 771 (1965)
[36] W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.* **70**, 4187 (1948)
[37] M. F. Clarke and L. N. Owen, *J. J. Chem. Soc.* 2103 (1950)