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THE REACTION OF A MONOCHLOROCARBENOID WITH SOME METHOXYCYCLOALKENES—AN OBSERVATION ON THE MECHANISM OF THE INSERTION REACTION OF CARBENES AND CARBENOIDS INTO DOUBLE BONDS

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Abstract—The products from the reaction of the monochlorocarbenoid, derived from butyl lithium and dichloromethane, on 3- and 4-methoxycyclohexene and 3- and 4-methoxycyclopentene were examined. The major products have the chlorocyclopropane ring *syn* to the OMe group. In the products from the 4-methoxycycloalkenes the major *syn* product has the chloro group *exo*; the 3-methoxycycloalkenes are normal in this respect, having the chloro group *endo* in the major product. These results are discussed in terms of the non-linear approach which carbenes and carbenoids may adopt when they are being inserted into double bonds.

THE Simmons–Smith reaction on hydroxy,[1] methoxy,[2] and acetoxy[3] cyclohexenes and cyclopentenes gives the product which has the cyclopropane ring *syn* to the oxy substituent. This observation has been interpreted as being due to the formation of an intermediate carbenoid bonded to the O atom, followed by the delivery of the carbenoid to the nearer face of the double bond.

The addition of dichlorocarbene to 3-methoxycycloalkenes (e.g. **1**) has recently been shown[4] to give the products in which the cyclopropane ring is *anti* to the OMe group, and we have also observed that 4-methoxycyclopentene (**4**) with dichlorocarbene gives mainly (88:12) the *anti* product (**12c**).[5] In these cases, presumably, no intermediate is involved and dichlorocarbene attacks the less hindered face of the double bond.

We have now investigated the effectiveness of a methoxy group in delivering the monochlorocarbenoid,[6] derived from dichloromethane and butyl lithium, to the double bonds of the cyclohexenes (**1** and **2**) and the cyclopentenes (**3** and **4**). In this territory, intermediate between that of the methylene carbenoid of the Simmons–Smith reaction and the free dichlorocarbene, there is a further variable: the ratio of the *endo* chloro products to the *exo* chloro products. Usually for cyclohexenes and cyclopentenes[6,7] this ratio is close to three; that is, the *endo* chloro product is the major product.

RESULTS

The products of the reaction with dichloromethane and butyl lithium were separated, or partly separated, by GLC. In each of the *syn* cases (**5**,**7**,**9**,**11**), the *exo* and the *endo* product were separated from the other products and from each other. In the *anti* cases, **12a** and **12b** were obtained pure, (the latter by hydrogenation of **12c**), the mixture of **8a** and **8b** was separated from the *syn* isomers, but **6a** and **6b** and **10a**

and **10b** were not separated. This assignment of *exo* or *endo* configuration was made from the NMR spectra because of the large (~7 Hz) coupling constant for an *exo* hydrogen compared with an *endo* hydrogen (1–3 Hz)[6b]. The assignment of *syn* or *anti* configuration to the products was made by reduction (sodium in ammonia), which removed the chlorine.[6a] The products could then be compared with ethers of known configuration. The authentic *syn* ethers were prepared by Simmons–Smith reaction on the alcohols followed by methylation. The *anti* ethers were prepared from the Simmons–Smith products by oxidation to the ketone, reduction to the mixture of alcohols, methylation, and separation of the new ether. The only assignments of configuration which are in any doubt are the minor (*anti*) products from **1** and **3**, for which the *exo* or *endo* nature of the chloro group is not proved unambiguously. The order of elution by GLC for the products from **2** and **4** is *syn exo*, *anti exo*, *anti endo*, and finally *syn endo*. This is the order, too, for the products from **1** and **3** if the *anti* products have the *endo* chloro product the major one, as is the case for unsubstituted cyclopentenes and cyclohexenes and for their isomers from **2** and **4**.

The proportions of the different products are shown to the nearest whole number on the Scheme and the *syn:anti* ratios and the *endo:exo* ratios are recorded in Table 1.

TABLE 1. *Syn:anti* AND *endo:exo* RATIOS IN THE ADDITION OF THE MONOCHLOROCARBENOID TO THE ETHERS (**1**, **2**, **3**, AND **4**)

Starting material	*syn:anti*	*endo:exo* (*syn* products)	*endo:exo* (*anti* products)
Cyclohexene	—	3·2[6]	
Cyclopentene	—	3[7]	
1	27	3·6	1·6
2	3·1	0·4	1·5
3	6·6	1·9	2·4
4	3·1	0·4	4·3

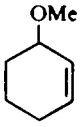
DISCUSSION

The first observation to be noted is that the OMe group exerts a mild *syn* directing effect in all four cases. It seems likely that the OMe group competes successfully with the double bond for the dichloromethyl lithium reagent and forms an intermediate which can then deliver a chlorocarbenoid species (or even chlorocarbene itself) to the nearer face of the double bond. This behaviour is intermediate between that of dichlorocarbene, which goes straight for the double bond, and the Simmons–Smith reagent, which is almost exclusively delivered from the methoxy group.

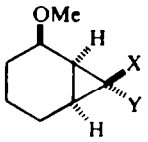
A second observation is that the allylic compounds (**1** and **3**) give a higher proportion of *syn* delivery than the homoallylic compounds (**2** and **4**). A third observation is that in the *syn* products (**7** and **11**), from the homoallylic ethers (**2** and **4**), the *exo* chloro compound is the major one. This is the unusual way round. Other cases in which the *exo* chloro compound is predominant include norbornene,[8] bicyclo[2,2,2]octene,[8] and Δ^3-carene;[9] in each case a steric effect is thought to be involved.

We should like to point out that both the greater *syn* selectivity in the allylic series and the change to predominantly *exo* chloro products in the *syn* homoallylic series are nicely explained by the Woodward and Hoffmann theory[10] of non-linear insertion

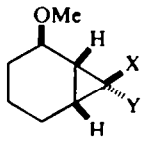
SCHEME



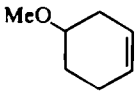
1



76% **5a** X = Cl, Y = H *syn endo*
21% **5b** X = H, Y = Cl *syn exo*



2% **6a** Y = H, Y = Cl *anti endo*
1% **6b** X = Cl, Y = H *anti exo*



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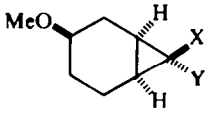
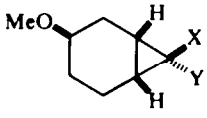
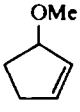


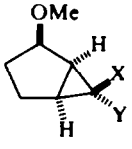
22% **7a** X = Cl, Y = H *syn endo*
53% **7b** X = H, Y = Cl *syn exo*



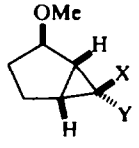
15% **8a** X = H, Y = Cl *anti endo*
10% **8b** X = Cl, Y = H *anti exo*



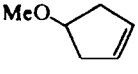
3



56% **9a** X = Cl, Y = H *syn endo*
30% **9b** X = H, Y = Cl *syn exo*



9% **10a** X = H, Y = Cl *anti endo*
4% **10b** X = Cl, Y = H *anti exo*



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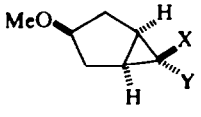
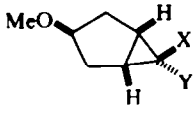
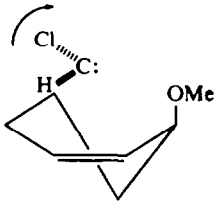


21% **11a** X = Cl, Y = H *syn endo*
54% **11b** X = H, Y = Cl *syn exo*

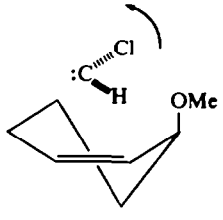


20% **12a** X = H, Y = Cl *anti endo*
5% **12b** X = Cl, Y = H *anti exo*
12c X = Y = Cl

of carbenes into double bonds. Delivery of the carbene* to one *end* of the face of the double bond looks to be easier from the allylic methoxy group than from the homoallylic methoxy group, whereas delivery to the *centre* of the face of the double bond ought to be easier from the more symmetrically disposed homoallylic OMe group. Thus our observation that there is more *syn* product in the allylic series is consistent with delivery to one end of the face of the double bond. Such delivery seems likely to be helpful to the non-linear motion of the carbene suggested by Woodward and Hoffmann. It is also consistent with the calculation[14] of the lowest energy path traversed by a carbene as it is inserted into a double bond. Secondly, the non-linear motion will develop an early and increasing steric interaction of the *endo* atom of the carbene and a homoallylic axial substituent. In the allylic case, however, the steric interaction is either much later and hence less than in the homoallylic series (if the carbene is being inserted as in III) or is actually decreasing (as in IV). The effect of a homoallylic substituent is therefore greater in deterring the chloro group from taking up the *endo* position than is the effect of an apparently closer allylic substituent. This is in contrast to the relative effects of allylic and homoallylic groups in (electrophilic) linear attack on cyclohexenes: in the work of Berti and his coworkers[15] on the bromination of 3- and 4-substituted cyclohexenes, allylic substituents were found to hinder *syn* axial (i.e. linear) attack more than do homoallylic substituents.

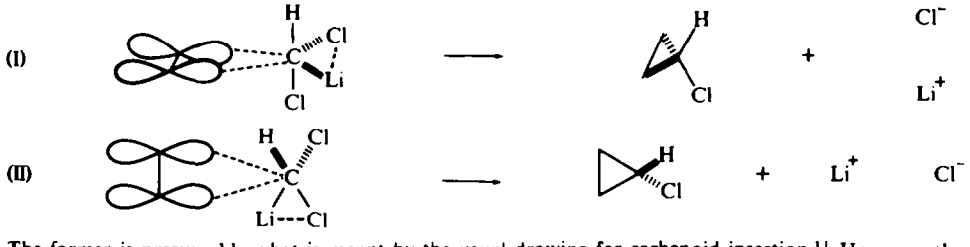


III



IV

* This argument is presented for a free chlorocarbene. Our ignorance of the precise species involved need not affect the discussion because the symmetry argument used by Woodward and Hoffmann appears to apply equally well to carbenoids. We can consider two likely transition states (I and II) corresponding to the linear and non-linear process respectively.



The former is presumably what is meant by the usual drawing for carbenoid insertion.[11] However, the latter would seem to be better on the grounds of symmetry. One way of looking at what takes place is to regard the events at the carbenoid carbon atom as simultaneous electrophilic substitution, with loss of Li^+, and nucleophilic substitution, with loss of Cl^-. Such events should be favoured by retention and inversion of configuration respectively, a condition which is met in II but not in I, where inversion in both processes is needed. A transition state very similar to II was drawn by Closs and Moss,[12] and, for an even more complicated situation, by Moser.[13]

We would like to stress that this explanation is by no means a necessary one. Product compositions on their own are notoriously weak guides to mechanism because the proportions of the different products represent such small relative changes in activation energy. Many factors, such as dipole–dipole interactions, and the conformational preferences of substituents,[16,17] could be contributing to disturb a quite different pattern. The particular reaction we have looked at is very far from being clearly defined; and the nature of the reactive species and the nature of the interaction with the OMe group are obvious gaps in our knowledge.

EXPERIMENTAL

NMR spectra were obtained for solns in CCl_4. IR spectra were obtained for liquid films. GLC investigations were carried out with the following:

1. An F and M 720 chromatograph fitted with a diethyleneglycol adipate column, 6 ft × 0·25 in, 10% on 60–80 mesh chromosorp W;
2. A Perkin–Elmer F11 chromatograph fitted with a 5% carbowax capillary column, 25 ft × 0·04 in.

3-Hydroxycyclohexene, 3-hydroxycyclopentene and 4-hydroxycyclopentene were prepared by established procedures.[1,2,18] 4-Hydroxycyclohexene was prepared by reduction of cyclohexa-1,4-diene monoepoxide with LAH.[17] Cyclohexa-1,4-diene monoepoxide was prepared from cyclohexa-1,4-diene by treatment of the corresponding monobromohydrin with NaOH aq using the conditions of Berchtold *et al.*[19] A 60% yield of the monoepoxide was obtained, based upon cyclohexa-1,4-diene. This is an improvement over the method[17] using per-acid directly on the diene. 3-Methoxycyclohexene (**1**),[17] 4-methoxycyclopentene (**4**)[5] were prepared by methylation of the corresponding alcohols using the general procedure described.[5]

Preparation of ethers of known configuration

The authentic *syn*-hydroxybicyclo[3,1,0]hexanes and *syn*-hydroxybicyclo[4,1,0]heptanes were prepared as described in the literature.[1,2,17] In each case the pure *syn*-isomer was isolated and methylated by the procedure described,[5] but purified by GLC (column 1). A new compound was syn-3-*methoxybicyclo*[4,1,0]-*heptane*. (Found: C, 75·9; H, 11·1. $C_8H_{14}O$ requires: C, 76·1; H, 11·2%), τ 6·84 (3H, s), 6·7–7·2 (1H, m), 7·6–9·6 (9H, m), 9·8–10·1 (1H, m).

The mixtures of *syn* and *anti* alcohols were prepared by the procedures described,[1,2] except for the 3-hydroxybicyclo[4,1,0]heptane mixture, when Meerwein–Ponndorf conditions were used in order to raise the proportion[17] of the *anti*-isomer. In each case the mixture of alcohols was methylated by the procedure described.[5] Two of the mixtures of ethers were separated by GLC (column 1) to give new ethers: anti-2-*methoxybicyclo*[4,1,0]*heptane*. (Found: C, 76·3; H, 11·1. $C_8H_{14}O$ requires: C, 76·1; H, 11·2%), τ 6·72 (3H, s), 6·5–6·9 (1H, m), 7·9–9·2 (8H, m), 9·3–9·7 (1H, m), 10·0–10·3 (1H, m), and anti-3-*methoxybicyclo*[3,1,0]*hexane*. (Found: C, 75·1; H, 11·00. $C_6H_{12}O$ requires: C, 74·9; H, 10·8%), τ 6·6 (1H, m), 6·86 (3H, s), 7·9 (2H, m), 8·2–8·5 (2H, m), 8·65–8·95 (2H, m), 9·5–9·9 (1H, m), 10·0–10·2 (1H, m). The mixture of 2-methoxybicyclo[3,1,0]hexanes was known and was not separated because the *syn* and *anti*-isomers could be distinguished in the NMR spectrum of the mixture by the position and appearance of the hydrogen on C-2, which is a broad doublet (J = 7 Hz) at τ 6·4 in the *anti*-isomer and a multiplet at τ 5·9–6·2 in the *syn*-isomer.[19] The mixture of 3-methoxybicyclo[4,1,0]heptanes (Found: C, 76·2; H, 11·1%) did not separate on GLC but the NMR showed the multiplets of the *syn* isomer described above and multiplets at τ 6·84 (3H, s), 6·7–7·3 (1H, m), 7·4–9·7 (9H, m), 10·1–10·3 (1H, m) due to the *anti*-isomer.

Addition of 'chlorocarbene' to the ethers (**1–4**) was carried out by slight modification of the method of Closs and Closs.[6] n-Butyl lithium (50 ml of a 2·35 M soln in hexane) was added dropwise over a period of 2 hr to a rapidly stirred mixture of the methoxycycloalkene (2–3 g) and dry dichloromethane (10 ml) under an atmosphere of dry N_2, the reaction vessel being immersed in a dry-ice/acetone bath maintained between −20° and −40°. The mixture was allowed to warm to room temp and stirred for 12 hr. Distilled water (25 ml) was slowly added and the aqueous and organic layers were separated. The aqueous layer was extracted with ether (3 × 25 ml), the organic fractions were combined, and dried ($MgSO_4$). The residue was distilled: b.p. 62–63°/2 mm (**5** and **6**) (65%), b.p. 72–82°/14 mm (**9** and **10**) (67%). In the cases of the 4-methoxy-cycloalkenes reaction was only half complete under these conditions and the product was

therefore recycled: b.p. 86–96°/15 mm (**7** and **8**) (80%), b.p. 78–82°/15 mm (**11** and **12**) (60%). The products were examined by GLC.

Products from **1**. Four peaks were detected: A, B, C, and D, with retention times 12·5, 14, 16·5, and 27·5 min, respectively (column 2). A and D were separated out (column 1). A, syn-2-*methoxy*-exo-7-*chlorobicyclo*-[4,1,0]*heptane* (**5b**) (Found: C, 60·1; H, 7·9. $C_8H_{13}OCl$ requires: C, 59·8; H, 8·2%), was identified as belonging to the *exo* series by spectroscopic data: τ 6·2–6·5 (1H, m, CH on C-2), 6·69 (3H, s), 7·13 (1H, t, J = 3 Hz, CH on C-7), 8·1–9·0 (8H, complex m). D, syn-2-*methoxy*-endo-7-*chlorobicyclo*[4,1,0]heptane (**5a**) (Found: C, 59·6; H, 7·9%), was identified as belonging to the *endo* series: τ 6·1–6·4 (1H, m, CH on C-2), 6·70 (3H, s), 6·81 (1H, t, J = 7 Hz, CH as C-7), 7·8–9·2 (8H, m). The C-7 proton in A is more shielded than in D, which is consistent with the above stereochemical assignments.[19] Because of the very low yield, B and C were not investigated or characterized; however their GLC behaviour, by analogy with the other series investigated below, is consistent with their being identified as the *anti exo* (**6b**) and *anti endo* (**6a**) isomers, respectively.

Products from **2**. Four peaks were detected, A, B, C, and D, with retention times 15·0, 16·5, 17·5, and 25·5 min, respectively (column 2). A and D were separated (column 1). A, syn-3-*methoxy*-exo-7-*chlorobicyclo*-[4,1,0]*heptane* (**7b**) (Found: C, 60·0; H, 8·1; Cl, 22·0. $C_8H_{13}OCl$ requires: C, 59·8; H, 8·2; Cl, 22·1%), was identified as belonging to the *exo* series: τ 6·7–7·0 (1H, m, CH on C-3), 6·82 (3H, s), 7·18 (1H, t, J = 1·8 Hz, CH on C-7), 7·2–8·9 (8H, m). D, syn-3-*methoxy*-endo-7-*chlorobicyclo*[4,1,0]*heptane* (**7a**) (Found: C, 59·6; H, 8·2; Cl, 22·3%), was identified as belonging to the *endo* series: τ 6·87 (3H, s), 6·7–7·3 (2H, m), 7·6–9·2 (8H, m), 7·5–8·2 (8H, m). B and C were separated out together. B, anti-3-*methoxy*-exo-7-*chlorobicyclo*-[4,1,0]*heptane* (**8b**), and C, anti-3-*methoxy*-endo-7-*chlorobicyclo*[4,1,0]*heptane* (**8a**). (Found: C, 59·9; H, 8·1; Cl, 22·3%), were identified as belonging to the *exo* and *endo* series, respectively, by spectroscopic analysis of their mixture: τ 6·78 (3H, s), 6·82 (3H, s), 6·85 (1H, t, J = 7 Hz), 6·6–7·3 (2H, m), 7·51 (1H, t, J = 3 Hz), 7·7–9·0 (16H, m).

Products from **3**. Four peaks were detected, A, B, C, and D, with retention times 13·5, 14·5, 18, and 30·5 min, respectively (column 2). A and D were separated (column 1). A, syn-2-*methoxy*-exo-6-*chlorobicyclo*-[3,1,0]*hexane* (**9b**) (Found: C, 57·2; H, 7·5. $C_7H_{11}OCl$ requires: C, 57·4; H, 7·6%), was identified as belonging to the *exo* series: τ 5·85–6·1 (1H, m, CH on C-2), 6·69 (3H, s), 7·05 (1H, t, J < 1 Hz, CH on C-6), 7·9–9·1 (6H, m). D, syn-2-*methoxy*-endo-6-*chlorobicyclo*[3,1,0]*hexane* (**9a**) (Found: C, 57·6; H, 7·6%), was identified as belonging to the *endo* series: τ 5·5–5·9 (1H, m, CH on C-2), 6·71 (3H, s), 6·73 (1H, t, J = 7 Hz, CH on C-6), 7·8–8·5 (6H, m). Because of the very low yield, B and C were not investigated or characterized, however their GLC behaviour, by analogy with the other series, is consistent with their being identified as the *anti exo* (**10b**) and *anti endo* (**10a**) isomers, respectively.

Products from **4**. Four peaks were detected, A, B, C, and D, with retention times 14, 15·5, 18, and 29 min, respectively (column 2). A, C, and D were separated out (column 1). A, syn-3-*methoxy*-exo-6-*chlorobicyclo*-[3,1,0]*hexane* (**11b**) (Found: C, 57·4; H, 7·3. $C_7H_{11}OCl$ requires: C, 57·4; H, 7·6%), was identified as belonging to the *exo* series: τ 6·25–6·45 (1H, m, CH on C-3), 9·90 (3H, s), 7·06 (1H, t, J = 2 Hz, CH on C-6), 7·8–8·7 (6H, m). C, anti-3-*methoxy*-endo-6-*chlorobicyclo*[3,1,0]*hexane* (**12a**) (Found: C, 57·4; H, 7·4), was identified as belonging to the *endo* series: τ 6·2–6·45 (1H, m, CH on C-3), 6·77 (1H, t, J = 7 Hz, CH on C-6), 6·87 (3H, s), 7·7–8·5 (6H, m). D, syn-3-*methoxy*-endo-6-*chlorobicyclo*[3,1,0]*hexane* (**11a**). (Found: C, 57·5; H, 7·7%), was identified as belonging to the *endo* series: τ 5·98 (1H, m, CH on C-3), 6·6 (1H, t, J = 7 Hz, CH on C-6), 6·86 (3H, s), 7·6–8·8 (6H, m). B was not characterized but its GLC retention time was the same as that of anti-3-*methoxy*-exo-6-*chlorobicyclo*[3,1,0]*hexane* (**12b**) prepared by hydrogenation of **12c**, see below.

Sodium and liquid ammonia reductions of the chlorocyclopropanes (**5–12**). The sodium and liquid ammonia reductions were carried out as described in the literature.[6a] The products were isolated and separated by GLC (column 1).

Reduction of products from **1**. The 2-methoxy-7-chlorobicyclo[4,1,0]heptane mixture (A–D) gave *syn*-2-methoxybicyclo[4,1,0]heptane, identified by GLC and spectroscopic comparison with the authentic material.

Reduction of products from **2**. A and D were separately reduced and the product in both cases was shown to be *syn*-3-methoxybicyclo[4,1,0]heptane by GLC and spectroscopic comparison with the authentic material. B and C were reduced together and the product was identified as *anti*-3-methoxybicyclo[4,1,0]-heptane by its GLC and spectroscopic behaviour: τ 6·86 (3H, s), 6·7–7·3 (1H, m), 7·4–9·2 (9H, m), 10·1–10·3 (1H, m).

Reduction of products from **3**. The 2-methoxy-6-chlorobicyclo[3,1,0]hexane mixture (A–D) gave a 10:1

mixture of *syn* and *anti*-2-methoxybicyclo[3,1,0]hexane, identified by GLC and spectroscopic comparison with the authentic materials.

Reduction of products from **4**. The 3-methoxy-6-chlorobicyclo[3,1,0]hexane mixture (A–D) gave *syn*- and *anti*-3-methoxybicyclo[3,1,0]hexanes, identified by GLC and spectroscopic comparisons with the authentic materials. A and D, when separately reduced, both gave *syn*-3-methoxybicyclo[3,1,0]hexane. A mixture of A, B and C, when reduced, gave a mixture of the *syn*- and *anti*-methoxybicyclo[3,1,0]hexanes.

Hydrogenation of 3-methoxy-6,6-dichlorobicyclo[3,1,0]*hexane*. The 9:1 mixture of *anti*- and *syn*-3-methoxy-6,6-dichlorobicyclo[3,1,0]hexane[5] (250 mg) was dissolved in methanol (10 ml, Analar) and KOH pellets (400 mg), distilled water (1 ml), and a small spatula load of Raney nickel (W4) were added. The mixture was stirred vigorously under hydrogen at room temp and pressure for 24 hr, after which no further H_2 was absorbed (72 ml of H_2 absorbed, 2·5 equivs). The catalyst was filtered off and the solvent removed. The residue was dissolved in ether, the ethereal soln washed with water, and dried ($MgSO_4$). The ether was removed and the product examined by GLC (column 1). Four product peaks could be seen (A, B, C, and D), ratios 6, 70, 14, and 10%. The peaks A, C and D corresponded with the *exo syn*, *endo anti*, and *endo syn*-3-methoxy-6-chlorobicyclo[3,1,0]hexane, respectively. The major product B corresponded to the small product peak from the mono-chlorocarbene addition to 4-methoxycyclopentene (**4**) which had not been characterized (B). It was separated out and identified as the missing anti-3-*methoxy*-exo-7-*chlorobicyclo*-[3,1,0]*hexane* (**12b**). (Found: C, 58·0; H, 7·3. $C_7H_{11}OCl$ requires: C, 57·3; H, 7·6%). τ 6·5–6·9 (1H, m), (3H, s), 7·54 (1H, t, $J < 1$ Hz), 7·7–8·5 (6H, m). Reduction of **12b** with sodium in liquid ammonia, gave only *anti*-3-methoxybicyclo[3,1,0]hexane, no *syn*-isomer being detected by GLC.

Hydrogenation of dihalocarbenes to halocarbenes is known,[20] but the stereoselectivity, to give *endo*-hydrogen is new.

TABLE 2. PRODUCT DISTRIBUTION FOR THE INSERTION REACTION IN DIFFERENT SOLVENT SYSTEMS

Starting material	Solvent	Products %			
		syn endo	*syn exo*	*anti endo*	*anti exo*
1	CH_2Cl_2/hexane	76	21	2	1
1	CH_2Cl_2	69	22	6	3
1	hexane	75	21	2	2
2	CH_2Cl_2/hexane	22	53	15	10
2	CH_2Cl_2	28	54	10	9
2	hexane	22	50	17	11
3	CH_2Cl_2/hexane	56	30	9	4
3	CH_2Cl_2	61	27	9	3
3	hexane	62	28	7	3
4	CH_2Cl_2/hexane	21	54	20	5
4	CH_2Cl_2	27	60	9	4
4	hexane	16	50	25	10

Effect of solvent on the exo:endo *and* syn:anti *ratios*. The addition of the chlorocarbenoid described above starts in dichloromethane solution but, as the addition of butyl lithium proceeds, the solvent becomes predominantly hexane. To check that a solvent effect was not important, as it is in some carbenoid insertions,[21] we repeated the reactions in solvent mixtures, (1) rich in hexane and (2) rich in dichloromethane. (1) n-BuLi (1 ml, 2M in hexane) was added over 20 min to a stirred soln of the methoxyalkene (50 μl) in dichloromethane (150 μl) in hexane (5 ml) under nitrogen at between −35° and −40°. (2) n-Butyl lithium (1 ml, 2M in hexane) was added over 20 min to a stirred solution of the methoxyalkene (40 μl) in dichloromethane (5 ml) under N_2 at between −35° and −40°. The results are recorded in Table 2, where it can be seen that, although the ratios are changed slightly, the change is not such as to alter our conclusions. The main change is an increase in the *syn:anti* ratio in dichloromethane for the homollylic ethers (**2** and **4**).

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REFERENCES

[1] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.* **83**, 3235 (1961);
E. J. Corey and R. L. Dawson, *Ibid.* **85**, 1782 (1963);
R. Ginsig and A. D. Cross, *Ibid.* **87**, 4629 (1965)

[2] W. G. Dauben and G. H. Berezin, *Ibid.* **85**, 468 (1963)

[3] S. Sawada, K. Takehana and Y. Inouye, *J. Org. Chem.* **33**, 1767 (1968)

[4] M. A. Tobia and B. E. Johnston, *Tetrahedron Letters* 2703 (1970)
D. Seyferth and V. A. Mai, *J. Am. Chem. Soc.* **92**, 7412 (1970)

[5] I. Fleming and E. J. Thomas, *Tetrahedron* **28**, 4989 (1972)

[6a] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.* **82**, 5723 (1960)

[b] G. L. Closs, R. A. Moss and J. J. Coyle, *Ibid.* **84**, 4985 (1962)

[c] G. L. Closs and J. J. Coyle, *Ibid.* **87**, 4270 (1965)

[7] M. S. Baird, D. G. Lindsay and C. B. Reese, *J. Chem. Soc.* (C) 1173 (1969)

[8] C. W. Jefford and W. Wojnarowski, *Tetrahedron* **25**, 2089 (1969)

[9] H. Frischlader, J. Graefe, H. van Phiet and M. Mühlstädt, *Ibid.* **25**, 2081 (1969)

[10] R. B. Woodward and R. Hoffmann, *Angew. Chem.* Internat. Edn. **8**, 781 (1969); for an earlier argument in favour of this mode, but not based on symmetry, see W. R. Moore, W. R. Moser and J. E. LaPrade, *J. Org. Chem.* **28**, 2200 (1963); and for a general review of carbene and carbenoid insertions see R. A. Moss, in B.S. Thyagarajan (Ed.) *Selective Organic Transformations* pp. 35–88. *Interscience*, New York (1970)

[11] G. Köbrich, *Angew. Chem.* Internat. Edn. **6**, 41 (1967)

[12] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.* **86**, 4042 (1964)

[13] W. R. Moser, *Ibid.* **91**, 1135, 1141 (1969)

[14] R. Hoffmann, *J. Am. Chem. Soc.* **90**, 1475 (1968)

[15] P. L. Barili, G. Bellucci, G. Berti, F. Marioni, A. Marsili, and I. Morelli. *Chem. Comm.* 1437 (1970)

[16] K. Sakashita, *Nippon Kagaku Zasshi* **81**, 49 (1960); *Chem. Abs.* **54**, 12015*b* (1960)
E. W. Garbisch, *J. Org. Chem.* **27**, 4249 (1962)
H. L. Goering, J. P. Blanchard and E. F. Silversmith, *J. Am. Chem. Soc.* **76**, 5409 (1954)
F. R. Jensen and C. H. Bushweller, *Ibid.* **91**, 5774 (1969)
E. J. Corey and R. A. Sneen, *Ibid.* **77**, 2505 (1955)

[17] J. H.-H. Chan and B. Rickborn, *Ibid.* **90**, 6406 (1968)

[18] K. Alder and F. H. Flock, *Chem. Ber.* **89**, 1732 (1956)

[19] T. N. Craig, G. R. Harvey and G. A. Berchtold, *J. Org. Chem.* **32**, 3743 (1967)

[20] K. Hoffmann, S. F. Orochena, S. M. Sax and G. A. Jeffrey, *J. Am. Chem. Soc.* **81**, 992 (1959)

[21] M. Schlosser and G. Heinz, *Angew. Chem.* Internat. Edn., **8**, 760 (1969)