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STUDIES IN ORGANOPHOSPHORUS CHEMISTRY

REACTION OF EPOXIDES WITH TERTIARY PHOSPHINE DIHALIDES[*]

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Abstract—The reaction of tertiary phosphine dichlorides and dibromides with epoxides gives vicinal dihalides. The reaction involves initial cleavage of the epoxide carbon–oxygen bond emanating from the most highly substituted epoxide carbon. Haloalkoxyphosphonium salts are thus formed which undergo subsequent reaction giving vicinal dihalides and tertiary phosphine oxides. The vicinal dihalides which result from epoxides of cyclohexenes are mixtures of *cis* and *trans* isomers in which the *cis* isomer is formed by backside attack of halogen at both epoxide carbons.

THE CONVERSION of alkenes to vicinal dihalides through ionic halogenation invariably proceeds in a *trans* fashion. Only in the case of chlorination with iodobenzene dichloride can *cis* halogenation be efficiently achieved.[1][‡] In this case halogen is introduced from the least hindered side of the alkene. Free radical halogenation of alkenes proceeds in a stereorandom fashion.[2] Although data are lacking one would expect the *cis*-dihalo product formed from free radical halogenations of cycloalkenes to be that resulting from attack from the least hindered side. We have investigated the reaction of epoxides with tertiary phosphine dibromides and dichlorides as a method for the conversion of cyclic (*cis*) alkenes to *cis* vicinal dihalides.[3]

The reaction of tertiary phosphine dihalides with alcohols[4] and ethers[5] produces high yields of alkyl halides. The reaction with alcohols has been reported to proceed in most instances with inversion of configuration at the reacting carbon center.[4a,b,f,i,j,n] Retention and racemization in the alcohol-alkyl halide transformation are observed only in those

$$R_3PX_2 + ROH \rightarrow R_3\overset{\oplus}{P}\text{—OR}\ \overset{}{X^{\ominus}} \rightarrow R\text{—}X + HX + R_3P \rightarrow 0$$

$$R_3PX_2 + R\text{—}O\text{—}R \rightarrow 2R\text{—}X + R_3P \rightarrow O$$

cases where the sometimes isolatable[4d,i,l,m] alkoxyphosphonium halide salt intermediates involved in these reactions may ionize to an exceptionally stable carbonium ion[4j,k] or where inversion at the reacting carbon center is sterically[4d] unfavorable.

Based on these reports it appears that a practical method for transformation of cycloalkenes to *cis* vicinal dihalocycloalkanes might lie in the conversion of the alkene to an epoxide followed by reaction of the epoxide with a tertiary phosphine dihalide. If inversion at each epoxide carbon occurred during the second reaction as depicted in Scheme I (Path B) then one would be able to introduce *cis* halogens from

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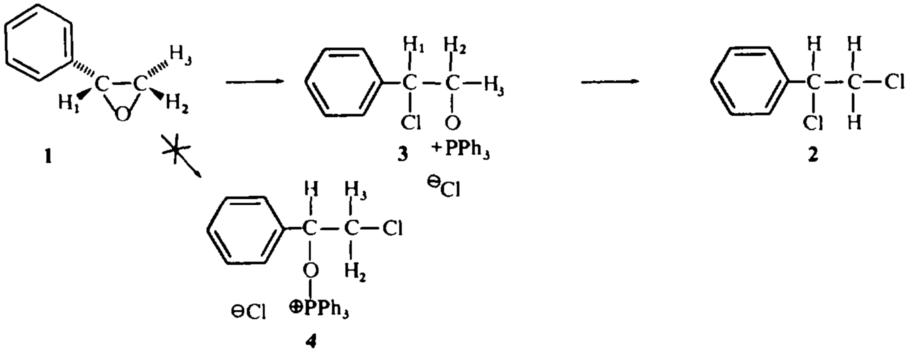
[‡] Bromination with iodobenzene although useful for selective brominations of alkenes proceeds in a *trans* fashion.

the sterically most hindered side of cycloalkenes by reaction of the epoxide derived from epoxidation from the least hindered side of the alkene. As can be seen from Table 1 the conversion of epoxides to vicinal dihalides with triphenylphosphine dibromide and dichloride is a moderately efficient and general reaction. The structure and stereochemistry of the dihalide products were determined by analysis of NMR and mass spectral data.

Since several investigations[6] have indicated that tertiary phosphine dihalides exist in solution as halophosphonium halide salts ($R_3\overset{\oplus}{P}X\overset{\ominus}{X}$), initial complexation of electrophilic phosphorus with the expoxide oxygen seemed probable in the present cases. As in related epoxide openings, if this complexation is significant it would be expected to direct the initial opening reaction of unsymmetrically substituted epoxides toward the most substituted carbon. That this is indeed the case was demonstrated by following the conversion of styrene oxide **1** to 1,2-dichlorophenylethane, **2**, in an NMR probe.

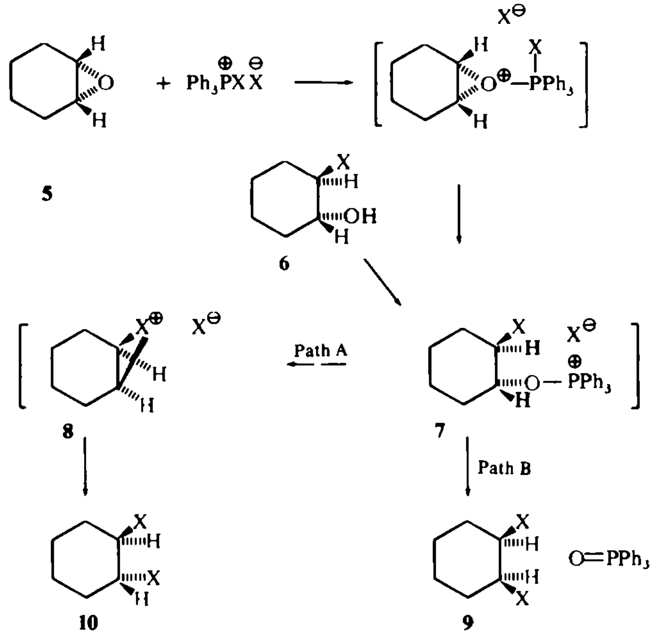
When styrene epoxide was mixed with a slight excess of triphenylphosphine dichloride in MeCN, the quartet signals due to H_1, H_2 and H_3 of **1** immediately vanished and three triplets at δ 5·55 (H = 5 Hz), δ 5·16 (J = 7 Hz) and δ 4·63 (J = 5 Hz) and a doublet at δ 4·03 appeared. These were due to 1,2-dichlorophenylethane and increased with time until after 12 hr at room temperature they were the only resonances in the δ 4–δ 6 region. The triplets at δ 5·55 and δ 4·63 decreased correspondingly with time. These signals are assigned to H_1 and H_2, H_3 of **3**. The latter hydrogens are observed as a triplet because the coupling of H_1 with H_2 and H_3 is very similar to the P–O–C–$H_{2,3}$ coupling.[4f] The alternate alkoxyphosphonium salt, **4**, would be expected to give rise to a doublet (H_2, H_3) and a quartet or sextet (H_1).



The reaction of epoxides of *cis* cyclic alkenes with tertiary phosphine dihalides gave both *cis* and *trans* vicinal dihalides (Table 1). In the case of cyclohexene oxide (**5**) which was studied in some detail, the ratio of these isomers (**9** and **10**) was influenced by the dielectric constant of the solvent and the halogen used. If one considers this reaction to be analogous to the tertiary phosphine-alcohol reaction then only *cis* vicinal dihalides are to be expected from *cis* fused epoxides. We consider the origin of the *trans* dihalide produced to be due to participation of the initially introduced halogen as shown in Scheme I (Path A).

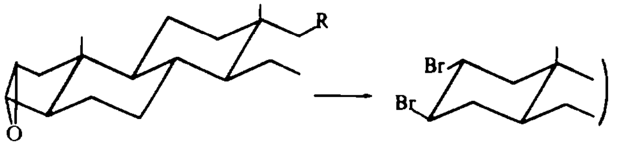
Support for the involvement of the alkoxyphosphonium salt, **7**, was obtained from the production of the same *cis-trans* ratio of 1,2-dibromocyclohexanes (**9**:**10**) from the reaction of either cyclohexene oxide (5) or *trans*-2-bromocyclohexanol (6) with triphenylphosphine dibromide. The relative amount of *trans* dihalo product from 5 is increased upon changing from Ph_3PCl_2 to Ph_3PBr_2 or from Ph_3PCl_2 to $[(CH_3)_2N]_3PCl_2$ as well as by increasing the dielectric constant of the reaction solvent.*

SCHEME I

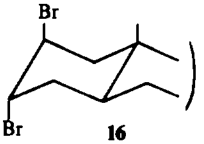


All of these observations are compatible with neighboring halogen participation (i.e. reaction *via* **8** as the origin of the *trans* product (**10**). Alkene formation was noted to be a low yield side reaction in the reaction of Ph_3PCl_2 with cyclohexene oxide (5). Presumably the products of this reaction are $Ph_3P{=}O$, Cl_2 and alkene. Conducting this reaction in the presence of cyclopentene gave no 1,2-dichlorocyclopentane. Furthermore, Ph_3PCl_2 did not react with cyclopentene under the usual reaction conditions used for the conversion of epoxide to dichlorides. Thus the formation of *trans*-1,2-dichloro products from *cis* epoxides does not appear to involve initial deoxygenation of the epoxide to the alkene followed by chlorination.

In an attempt to determine if the *cis* vicinal dihalide products were formed by inversions at both epoxide carbons, we investigated the reaction of steroidal epoxides.



14 **15**



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* The reaction of epoxides with tertiary phosphine dihalides is evidently limited since $Ph_3\overset{\oplus}{P}CN\ \overset{\ominus}{Br}$, $Ph^3\overset{\oplus}{P}CN\ Cl^{\ominus}$ and $Ph_3\overset{\oplus}{P}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}Ph\ Br^{\ominus}$ did not react (even at 80°) with cyclohexene oxide in MeCN.

TABLE 1. REACTION OF TERTIARY PHOSPHINE DIHALIDES WITH EPOXIDES

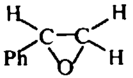
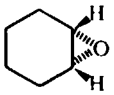
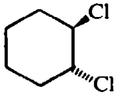
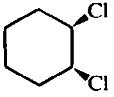
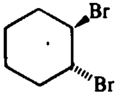
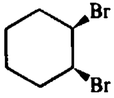
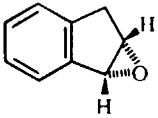
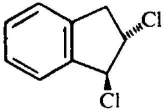
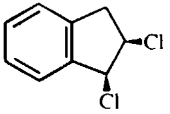
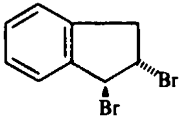
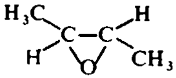
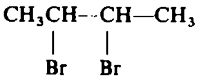
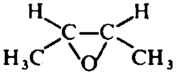
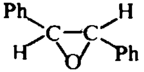
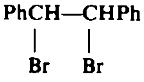
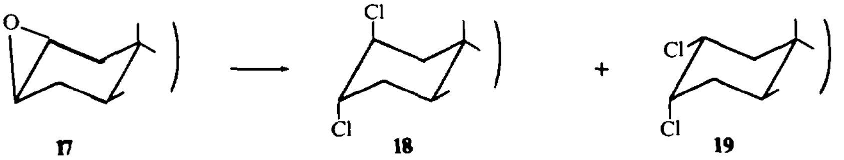
Phosphorus Reagent	Epoxide	Solvent	Products	Total Yield (analysis method)
Ph_3PCl_2	 **1**	$CH_3C{\equiv}N$	$PhCHCl{-}CH_2Cl$ **2**	86% (isolation
Ph_3PBr_2	**1**	$CH_3C{\equiv}N$	$PhCHBr{-}CH_2Br$	32% (isolation)
Ph_3PCl_2	 **5**	$CH_3C{\equiv}N$	  *trans* : *cis* 50 : 50	68% (isolation) (12%) cyclohexene formed
Ph_3PCl_2	**5**	C_6H_6	only *cis*	71% (isolation)
Ph_3P in CCl_4	**5**	CCl_4	*trans* : *cis* 50 : 50	50% (isolation)
$[(CH_3)_2N]_3PCl_2$	**5**	$CHCl_3$	*trans* : *cis* 95 : 5	75% (isolation)
Ph_3PBr_2	**5**	C_6H_6	  *trans* : *cis* 35 65	73% (g.l.p.c.)
Ph_3PBr_2	**5**	$CH_3C{\equiv}N$	*trans* : *cis* 58 42	70% (g.l.p.c.)

TABLE 1—*continued*

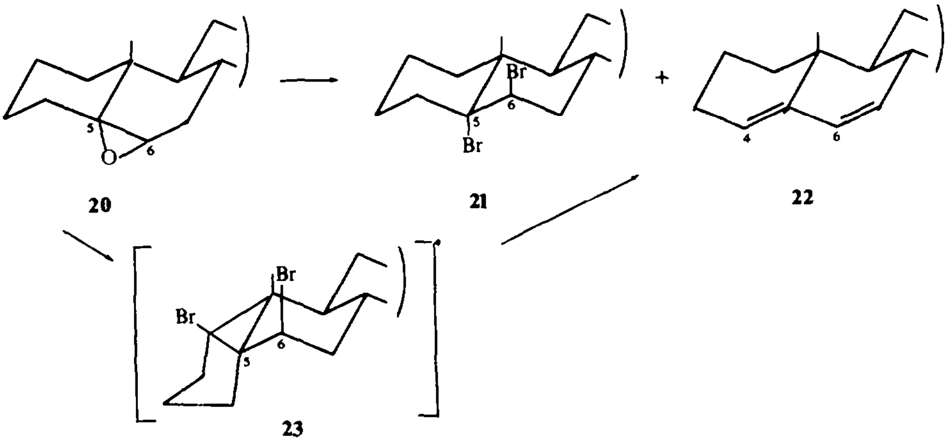
Phosphorus Reagent	Epoxide	Solvent	Products			Total Yield (analysis method)
Ph_3PCl_2		$CH_3C{\equiv}N$	 *trans* 25	:	 *cis* 75	50% (isolation)
Ph_3PBr_2	**11**	$CH_3C{\equiv}N$	 only			50% (g.l.p.c.)
Ph_3PBr_2	 **12**	C_6H_6	 $CH_3\underset{Br}{CH}{-}\underset{Br}{CH}{-}CH_3$ *meso* 40	:	*dl* 60	74% (g.l.p.c.)
Ph_3PBr_2	**12**	$CH_3C{\equiv}N$	*meso* 40	:	*dl* 60	70% (g.l.p.c.)
Ph_3PBr_2		$CH_3C{\equiv}N$	*meso* 44	:	*dl* 56	62% (g.l.p.c.)
Ph_3PBr_2		$CH_3C{\equiv}N$	 $Ph\underset{Br}{CH}{-}\underset{Br}{CH}Ph$ *meso* only			60% (isolation)

However, 2α,3α-cholestene oxide, **14**, reacted with triphenylphosphine dibromide in dimethyl formamide (DMF) to give only 2α,3β-dibromocholestane, **15**, and 2β,3α-dibromochloestane **16**. The reaction of **14** with triphenylphosphine dichloride gave, quite unexpectedly, only Δ^2-cholestene.

The reaction of 2β,3β-cholestene epoxide **17** with triphenylphosphine dichloride in DMF gave 2β,3α-dichlorocholestane (**18**) and 2α,3α-dichlorocholestane (**19**) in a 1:4 ratio.



The reaction of 5α,6α-cholestene oxide, **20**, with triphenylphosphine dibromide in DMF gave 5α,6β-dibromocholestene, **21**, and $\Delta^{4,6}$-cholestaidene, **22**. The latter product presumably arises from diaxial dehydrobromination of 5β,6β-dibromocholestane, **23**, during work up. The absence of 5β,6α-dibromocholestane is significant since it is the major component of the equilibrium mixture obtained when it or **21** is refluxed in $CHCl_3$.[7] The presence of only the 5α,6β-dibromo isomer, **21**, is consistent with S_{N_1} cleavage of the 5α bond of **20** in the initial epoxide ring opening reaction.



EXPERIMENTAL

M.p's were determined using a Fisher–Johns apparatus and are uncorrected. NMR spectra were recorded on a Varian Model A56/60 spectrometer using TMS as internal standard. Mass spectra were recorded on a Hitachi Perkin–Elmer RU-6 mass spectrometer. G.l.p.c. was performed on a Varian Aerograph Autoprep A-705 unit using a 6′ × ¼″ 15% Carbowax 20M on 60/80 mesh Chromasorb W. Yields were determined using decalin as an internal standard and are accurate to ±2%.

Preparation of epoxides. Styrene oxide used was obtained from Matheson Coleman and Bell, Norwood, Ohio and distilled prior to use.

The epoxides of cyclohexene, indene, *cis* and *trans*-2-butenes and *trans*-stilbene were prepared by reaction of the alkenes with peracetic acid (40%) in CH_2Cl_2* containing excess Na_2CO_3. The epoxides were isolated in (70–80%) by distillation or crystallization and were determined to be pure by g.l.p.c. and NMR. *Trans*-2-bromocyclohexanol was prepared by reaction of aqueous HBr with cyclohexene oxide.

The 2α,3α-cholestene oxide (**14**) was prepared by reaction of Δ^2-cholestene[4j] with perbenzoic acid in C_6H_6. After usual workup **14** was isolated (70%) m.p., 103–104°C (lit[8a] 103–105°C).

The 2β,3β-cholestene oxide **17** was prepared from Δ^2-cholestene.[4j] The epoxide was isolated in 20% yield m.p., 89–90°C (lit[8b] m.p., 89–90°).

The 5α,6α-cholestene oxide (**20**) was prepared by reaction of Δ^5-cholestene[9a] (8·1 g) with perbenzoic acid in C_6H_6. After the usual workup and five recrystallizations from acetone **20** (2 g) was isolated m.p., 64–65°C (lit m.p.,[9b] 74–75°C).

Reaction of triphenylphosphine dihalides with styrene oxide. To a solution of triphenylphosphine (10 g) in 100 ml MeCN under N_2 was added an equimolar amount of Br_2 at such a rate that the temperature of the reaction did not exceed 5°C. After stirring at room temperature for 30 min styrene oxide (3 g) was added slowly The reaction was stirred at 50°C overnight and solvent stripped *in vacuo*. The residue was extracted with ether, concentrated and filtered through a short column of neutral alumina (activity I).. The ether eluent was concentrated and the concentrate crystallized from petroleum ether (30–60°C) to give 2·1 g (32%) of 1,2-dibromophenylethane m.p. 74–75°C (lit[10] m.p. 74–75·5). This procedure was repeated using chlorine gas. Chromatography of the reaction mixture gave 1,2-dichlorophenylethane which was identical with a sample prepared by chlorination of styrene.

Reaction of triphenylphosphine dichloride with cyclohexene oxide. The reaction of triphenylphosphine dichloride with cyclohexene oxide was carried out as described above in MeCN and C_6H_6 on a 0·03 M scale. After stirring overnight the solvent was removed *in vacuo*. Treatment of this distillate with chlorine followed by concentration *in vacuo* gave a 10% yield of *trans*-1,2-dichlorocyclohexane. The residue was extracted with three 100 ml portions of petroleum ether (30–60°C) to separate the dichloride from the triphenylphosphine oxide which precipitated in 73% yield. The petroleum ether extract was fractionally distilled at reduced pressure (50–60°/10 mm) to give a mixture or dichlorides (63%). Analysis of this distillate by g.l.p.c. revealed two major compounds which were identified as *cis* and *trans*-1,2-dichlorocyclohexanes as described below. Chromatography of the dichloride mixture of neutral alumina gave upon elution with petroleum ether (30–60°C) *trans*-1,2-dichlorocyclohexane (31%) 50°/10 mm (lit.[12] 186–90/760 mm). Elution with C_6H_6 gave the *cis*-1,2-dichloro isomer (32%) 50°/10 mm (lit.[12] 114·4–114·5/50 mm). The NMR spectra of the *cis* and *trans*-1,2-dichlorocyclohexanes were identical in the δ2–δ5 region with those published.[13] The *trans*-1,2-dichlorocyclohexane was identical to a sample prepared by chlorination of cyclohexene.

Reaction of triphenylphosphine dichloride with cyclohexene oxide in the presence of cyclopentene. To a solution of 8·3 g of triphenylphosphine dichloride (6·6 g Ph_3P and 1·7 g Cl_2) in MeCN (50 ml) was added cyclohexene oxide (1 g) and 1 g cyclopentene (1 g). The solution was stirred overnight and the solvent slowly removed *in vacuo*. The semisolid residue was distilled (50–60°/10 mm) to give 1·0 g (66%) of *cis* and *trans*-1,2-dichlorocyclohexanes (1:1 g.l.p.c.) No *trans*-1,2-dichlorocyclopentane was detected by g.l.p.c. In an independent experiment it was determined that Ph_3PCl_2 did not react with cyclopentene in MeCN solution at r.t for 24 hr.

Reaction of triphenylphosphine with cyclohexene oxide in carbon tetrachloride. To a solution of cyclohexene oxide (3 g) in 50 ml CCl_4 was slowly added triphenylphosphine (10 g). After stirring 1 hr the solvent was stripped *in vacuo* and the residue was extracted with petroleum ether (30–60°C). The petroleum ether extract was fractionally distilled (50–60°/10 mm) to yield a mixture (composition reported in Table I) of dichlorides (45%) identified by g.l.p.c. comparisons with the samples isolated above.

Reaction of hexamethylphosphorous triamide dichloride with cyclohexene oxide. A solution of hexamethylphosphorous triamide[14] (4 g) in C_6H_6 (40 ml) under N_2 was treated with Cl_2 (1·7 g). The solution was allowed to stir for 1 hr then cyclohexene oxide (3 g) added. The reaction was stirred overnight then treated with 0·05 N HClaq. The organic layer was separated dried over anhydrous $MgSO_4$ and fractionally distilled to give a mixture of *cis* and *trans*-1,2-dichlorocyclohexanes (75%) which were identified by g.l.p.c. comparisons with samples described above.

Reaction of triphenylphosphine dibromide with cyclohexene oxide and trans-2-bromocyclohexanol. The reaction of triphenylphosphine dibromide with cyclohexene oxide and *trans*-2- bromocyclohexanol was carried out in C_6H_6 and MeCN on a 0·03 molar scale in the fashion described above for the triphenylphosphine dichloride reaction. Analysis of the reaction mixtures by g.l.p.c. followed by separation by column

* Toluene solvent was used in the preparation of the butene oxides.

chromatography on neutral alumina gave *trans*-1,2-dibromocyclohexane 95–97°/15 mm (lit[12] 101°/14 mm) and *cis*-1,2-dibromocyclohexane 95–97°/15 mm (lit[12] 115°/14 mm). The NMR and mass spectra of both compounds are consistent with the structures proposed.

Reaction of the triphenylphosphine dihalides with indene oxide. Reaction of triphenylphosphine dichloride with indene oxide (2·5 g) in the usual manner gave, after workup, a mixture of two compounds. Chromatography of the reaction mixture on neutral alumina gave (1·5 g) *cis*-1,2-dichloroindane 50°/1 mm, Calc. for: $C_9H_8Cl_2$:226(M +). Found: 226(M +). Elution with C_6H_6 gave 1·5 g *trans*-1,2-dichloroindane 50°/1 mm (lit[15] 108°/15 mm). The NMR of this isomer was identical to the published spectrum.[15]

Reaction of triphenylphosphine dibromide with indene oxide in the usual manner gave, after workup and chromatography only *trans*-1,2-dibromoindane 120°/5 mm (lit[15] m.p. 32°C). This sample gave NMR and mass spectra identical with a sample prepared by the bromination of indene. Neither sample could be induced to crystallize.

Reaction of triphenylphosphine dichloride with cis *and* trans-*2-butene oxides.* The reaction of triphenylphosphine dichloride with *cis*-2-butene oxide in the usual manner gave *meso* and *d,l*-2,3-dichlorobutanes. The *meso* dichlorobutane was identical by g.l.p.c. with a sample prepared by chlorination of *trans*-2-butene. The *d,l*-dichlorobutane was identical by g.l.p.c. with a sample prepared by chlorination of *cis*-2-butene.

The reaction of triphenylphosphine dibromide with *trans*-2-butene oxide in the usual manner gave *meso* and *d,l*-2,3-dibromobutanes. The *meso*-dibromobutane was identical by g.l.p.c. with a sample prepared by bromination of *trans*-2-butene. The *d,l*-dibromobutane was identical by g.l.p.c. to a sample prepared by bromination of *cis*-2-butene.

Reaction of triphenylphosphine dichloride with 2β,3β-*cholestene oxide.* To a soln of triphenylphosphine (1 g) in 50 ml dry MeCN under N_2 was added 0·3 g Cl_2. The soln was stirred at 0° for ½ hr then 2β,3β-cholestene oxide[8] (0·18 g) was added. The soln was stirred at 40° for 18 hr then diluted with water and extracted with three 100 ml portions ether. The ether extract was washed with $NaHCO_3$ aq, dried over $MgSO_4$,-and concentrated *in vacuo*. The concentrate was triturated with 100 ml light petroleum (30–60°) and the triphenylphosphine oxide ppt which formed was removed by filtration. The filterate was evaporated to give an oil which was chromatographed on 5 g basic alumina (activity III). Elution with benzene gave **18**, (0·02 g) mp 110–112°, (lit[7] mp 110–112°. (Found: mass spec 435 (M +); Calcd. for: $C_{27}H_{46}Cl_2$: 435 (M +); (CCl_4): δ 0·650 (s, 3, $C^{18}H_3$ calcd.[16] 0·684) 1·06 (s, 3, $C^{19}H_3$, calcd.[16] 1·03) and 4·53 (2, m, C_2H, C_3H). Elution with benzene–chloroform (1:1) gave **19** (0·08 g) mp 134–135°, $[\alpha]_D^{25}$ +57·3° (*c* = 0·34, hexane). (Found: mass spec 435 (M +); NMR. Calcd. for: $C_{27}H_{46}Cl_2$: 435 (M +); (CCl_4): δ 0·650 (s, 3, $C^{18}H_3$, calcd.[16] 0·684), 0·834 (s, 3, $C^{19}H_3$, calcd.[16] 0·815) and 4·05 (2, m, C_2H, C_3H). It was independently determined that a 3α-chloro group shifted the $C^{18}H_3$ by δ 0·006 and the $C^{19}H_3$ by δ 0·038 upfield.

From the data of Cohen *et al.*[16] for the effect of the 6β-Cl and 2β-Br the effect of a 2β-Cl was estimated to be a downfield shift of δ 0·30 on the $C^{19}H_3$ and δ 0·0 on the $C^{18}H_3$.

Reaction of triphenylphosphine dichloride with 2α,3α-cholestene oxide. The reaction of Ph_3PCl_2 with 2α,3α-cholestene oxide was carried out as described above. Analyses of the reaction mixture by thin layer silica gel and NMR revealed only triphenylphosphine oxide and 2-cholestene which were identified by comparison with the authentic samples.

Reaction of triphenylphosphine dibromide with 2α,3α-chloestene oxide. To a solution of triphenylphosphine (20 g) in 100 ml dry DMF under N_2 was added 12 g Br_2. The solution was stirred at 0° for ½ hr then 2α,3α-cholestene oxide[7] (3 g) in 200 ml of dry DMF added. The solution was stirred for 18 hr at r.t. diluted with water and extracted with three 100 ml portions of ether. The ether extract was washed with $NaHCO_3$ aq, dried over anhydrous $MgSO_4$, and concentrated *in vacuuo*. The concentrate was triturated with 100 ml of petroleum ether (30–60°C) and the triphenylphosphine oxide precipitate which formed removed by filtration. The filterate was evaporated to give an oil (2 g) which was chromatographed on 100 g of basic alumina (activity III). Elution with petroleum ether (30–60°C) gave 2α,3β-dibromocholestane (**15**) (19%) m.p. 142–144°C, $[\alpha]_D^{25}$ −26° (C = 0·5, hexane) (lit[8] m.p. 144–145°C, $[\alpha]_D^{25}$ −27°C). Calc. for: $C_{27}H_{46}Br$: 528 (M +). Found: mass spec 528 (M +); NMR (CCl_4); δ 0·828 (s, 3, $C^{18}H_3$ calcd.[16] 0·73), δ 0·917 (s, 3, $C^{19}H_3$ calcd.[16] 0·90) and 4·40 2, m, C_2H, C_3H). Elution with C_6H_6 gave 2β,3γ-dibromocholestane (**16**, 24%) m.p. 123–124 C, $[\alpha]_D^{25}$ +75·2° (C = 0·6, hexane) (lit[8] m.p. 122–124°C, $[\alpha_D^{25}$ +76°). Calcd. for: $C_{27}H_{46}Br_2$: 528(M +). Found: mass spec 528(M +); NMR ($CDCl_3$): δ 0·903 (s, 3, $C^{19}H_3$, calcd.[16] 0·97), 0·645 (s, 3, $C^{18}H_3$, calcd.[16] 0·692) and 4·66 (2, m, C^2H, C^3H).

Reaction of triphenylphosphine dibromide with 5α,6α-cholestene oxide. The reaction of triphenylphosphine dibromide (0·05 m) with 5α,6α-chloestene oxide (2 g, 0·05 m) was carried out in DMF as described above. Chromatography of the dibromide fraction on basic alumina (act. III) gave 0·6 g of $\Delta^{4,6}$-cholestadiene, m.p. 72·5–74·0°C (lit[17] m.p. 84–85°C). Elution with C_6H_6 gave 1 g of 5α,6β-dibromocholestane, m.p. 110–111°C (lit[17] m.p. 110–111°C); NMR ($CDCl_3$): δ 1·39 (s, 3, $C^{19}H_3$, calcd.[16] 1·329), 0·703 (s, 3, $C^{18}H_3$, calcd.[16] 0·742), and 4·8 (1, m, C^6H).

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