

THE CHLORINATION OF EPOXIDES BY TRIPHENYLPHOSPHINE IN
CARBON TETRACHLORIDE.

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Triphenylphosphine in carbon tetrachloride has been shown to be a useful and specific reagent for the replacement of certain oxygenated functions by chlorine. Alcohols are converted to alkyl chlorides¹ and enolisable ketones to enyl chlorides or gem dichloromethylene derivatives². We now find that epoxides readily take part in the reaction to give good yields of the corresponding cis-1,2-dichloroalkane, I.

In a typical reaction, epoxide (0.1 mol), triphenylphosphine (0.15 mol) and carbon tetrachloride (50-100 ml) were refluxed together under nitrogen for 1-2 hours. The solution darkened and an oily layer of triphenylphosphine oxide separated and crystallised. After cooling, the products were extracted into petroleum ether and the oxide removed by filtration. In this way, dicyclohexene oxide was converted in good yield to cis-1,2-dichlorocyclohexane, only a trace of the trans isomer being formed. The product was identified by mass spectrometry and by the comparison of the retention times with those of authentic samples of cis- and trans-dichlorocyclohexanes on two glc columns. Other examples of this reaction are given in Table I. The scope of the reaction seems quite general and products are more stereospecific than those obtained by other routes such as additions to olefins. Bromination using carbon tetrabromide also occurs but seems to be less stereospecific. Dextrorotatory propylene oxide was prepared³ and converted to 1,2-dichloropropane which was found to be laevorotatory. From the known relative configurations of these compounds⁴ it is clear that inversion has occurred at C-2 and, since in the cyclic cases a cis-product is obtained, inversion must occur at each carbon. A scheme consistent with these findings is given

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below. β -Elimination of the intermediate II would lead to a chloro-olefin which is sometimes observed as byproduct.

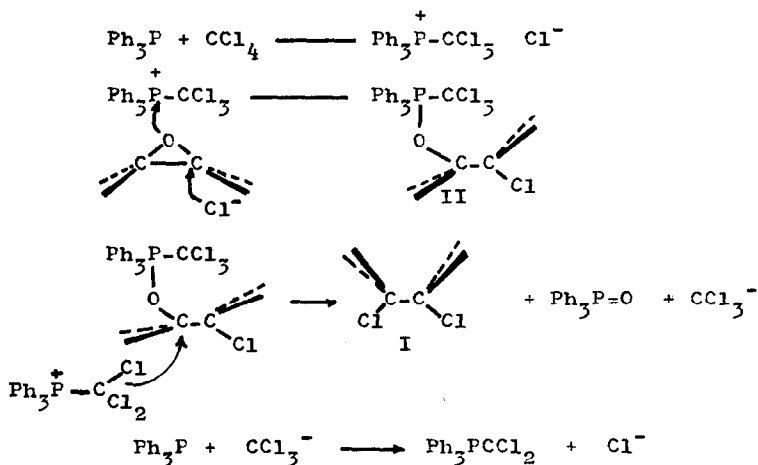


Table I

Epoxide	Product	Yield, %	Byproducts
1,2-epoxy-cyclohexane	<u>cis</u> -1,2-dichloro-cyclohexane	80	<u>trans</u> -1,2-dichloro-cyclohexane, 5%
1,2-epoxy-cyclopentane	<u>cis</u> -1,2-dichloro-cyclopentane	80	
1,2-epoxyoctane	1,2-dichlorooctane	75	1,1-dichloro-2-(1-hexyl)cyclopropane
epichlorohydrin	1,2,3-trichloropropane	60	
epibromohydrin	1-bromo-2,3-dichloro-propane	50	2,3-dichloropropene
exo-2,3-norbornene oxide	dichloronorbornane (structure not established)	poor	

with carbon tetrabromide and triphenylphosphine in benzene solution:

1,2-epoxy-cyclohexane	<u>cis</u> -1,2-dibromo-cyclohexane	60	<u>trans</u> -1,2-dibromo-cyclohexane, 40%.
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References

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