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The Formation of Monobromides in the Reaction between Bromohydrins and Phosphorus Tribromide

By G. BELLUCCI, F. MARIONI, A. MARSILI, P. L. BARILI, and G. BERTI*

(Istituti di Chimica Organica e Chimica Farmaceutica, Università, 56100 Pisa, Italy)

Summary Substantial amounts of monobromides are formed, in addition to the dibromides, when *trans*-cyclohexene bromohydrins and 2-bromobutan-1-ol react with phosphorus tribromide.

WHILE alcohols can usually be converted in good yield into alkyl bromides by phosphorus tribromide, the analogous transformation of bromohydrins into dibromides often gives much less satisfactory results. For instance, Weinstein¹ obtained only 41% of the *trans*-dibromide from *trans*-2-bromocyclohexanol, while about 30% of an unidentified lower-boiling compound, assumed to be an elimination product, was also formed; we have now found that this compound is simply bromocyclohexane. Table 1 summarizes the g.l.c. analytical results obtained when the bromohydrin and the tribromide reacted for different times in a 3:2 molar ratio in sealed vessels at room temperature. The ratio of mono- to di-bromocyclohexane did not change appreciably in going from a 1:1 to a 3:1 ratio of bromohydrin to phosphorus tribromide. *cis*-2-Bromocyclohexanol did not yield any monobromide under the same reaction conditions.

TABLE 1

Reaction of trans-2-bromocyclohexanol with phosphorus tribromide

Time (hr.)	Bromocyclohexane	Yield (mole %) <i>trans</i> -1,2-Dibromocyclohexane	Total
2	20.1	18.1	38.2
8	33.2	22.0	55.2
48	35.5	39.0	74.5

The reaction of 2-bromobutan-1-ol with phosphorus tribromide gave the results shown in Table 2. The production of mono- and di-bromide was much slower than in the case of *trans*-2-bromocyclohexanol, and only 7.5% of 2-bromobutane was formed after 12 days. 1-Bromobutan-2-ol produced the dibromide more rapidly and in

better yield (up to 70%), but no 1-bromobutane, and at most a trace of 2-bromobutane, could be detected in the gas chromatogram.

TABLE 2

Reaction of 2-bromobutan-1-ol with phosphorus tribromide

Time (hr.)	2-Bromobutane	Yield (mole %) 1,2-Dibromobutane	Total
5.5	4.3	14.6	18.9
150.0	6.7	47.8	54.5
288.0	7.5	54.9	62.4

Several facts indicate that the formation of the monobromide does not proceed through direct reduction of the hydroxy-group, but rather through conversion into alkene, followed by addition of the hydrogen bromide formed in the first step, which undoubtedly involves an esterification of the bromohydrin by the tribromide.

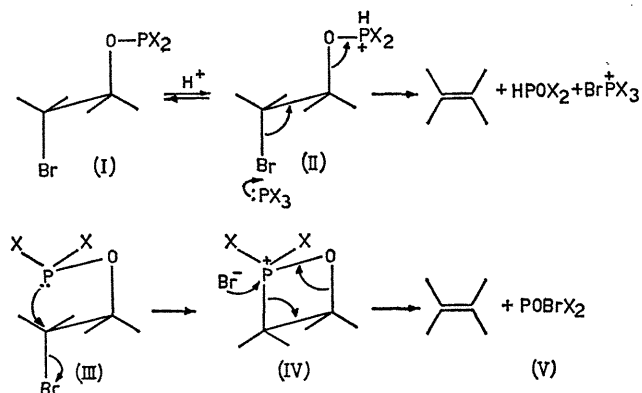
(i) The reaction of *trans*-2-bromo-*cis*-4-*t*-butylcyclohexanol with phosphorus tribromide gave, besides the corresponding *trans*-dibromides, a mixture of *cis*-4-*t*-butyl- and *trans*-3-*t*-butyl-1-bromocyclohexane and minor amounts of *trans*-4-*t*-butyl- and *cis*-3-*t*-butyl-1-bromocyclohexane, the composition of which was very similar to that of the reaction product of 4-*t*-butylcyclohexane with hydrogen bromide in ether.

(ii) When the reaction of *trans*-2-bromocyclohexanol with phosphorus tribromide was carried out in the presence of 4-*t*-butylcyclohexene, which competed with cyclohexene for the hydrogen bromide, some cyclohexene was detected in the product (molar ratio of cyclohexene to bromocyclohexane, 1:10).

(iii) About 3% of cyclohexene was formed when cyclohexene oxide reacted with phosphorus tribromide in a molar ratio of 3:1, *i.e.* under conditions which are known to give tris-2-bromoalkyl phosphites.² When hydrogen bromide was bubbled for 1 hr. through the reaction mixture,

bromocyclohexane and *trans*-1,2-dibromocyclohexane were produced in about equal molar yields of 25%. This indicates that hydrogen bromide is essential for the formation of the monobromide; no cyclohexene or monobromide were obtained when the bromohydrin and the tribromide reacted in the presence of pyridine (molar ratios, 3 : 1 : 3).

The available data do not yet provide an explanation for



the conversion of the phosphite ester of type (I; X = Br or 2-bromoalkoxy-, depending on the bromohydrin-tribromide ratio) into the alkene. However, the failure of *cis*-2-bromocyclohexanol to give bromocyclohexane, and the better yields of monobromides obtained from *trans*-cyclic, than from acyclic bromohydrins, imply a mechanism involving some kind of anchimeric assistance or *trans*-elimination. One of several possibilities is represented by (II). Nucleophilic attack of tervalent phosphorus on halogen is well documented for compounds having electron-attracting substituents in the α -position;³ in the present cases a favourable steric situation could well facilitate the elimination.

An alternative mechanism is shown in the sequence (III)—(V), involving the intramolecular displacement of bromine by phosphorus, in an Arbuzov-type reaction,⁴ to give intermediate (IV), followed by a collapse to (V) and the alkene, which is reminiscent of the mechanism suggested to explain the reduction of epoxides to alkenes by triphenylphosphine⁵ or trialkyl phosphites.⁶

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⁴ Ref. 2, Vol. 12/1, p. 433.

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