Tetrahedron Letters No.11, pp. 573-577, 1964. Pergamon Press Ltd.
Printed in Great Britain.

FORMATION AND DECOMPOSITION OF TETRASUBSTITUTED PHOSPHONIUM SALTS

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(Received 30 December 1963)

In a recent report it was suggested that alkoxyphosphonium salts are formed when trisubstituted phosphites and phosphines react with alkyl hypochlorites.[3]

$$R_3P + R'OCl \longrightarrow R_3\overset{+}{P}\text{-}OR' + \overset{-}{Cl}$$

I $R = OCH_2C(CH_3)_3$, $R' = CH_2C(CH_3)_3$; II $R = OCH_3$, $R' = CH_2C(CH_3)_3$

III $R = OC_6H_5$, $R' = CH_2C(CH_3)_3$; IV $R = C_6H_5$, $R' = CH_2C(CH_3)_3$;

V $R = C_6H_5$, $R' = CH_2C(C_6H_5)_3$

From the reaction of triphenylphosphine and bicyclo -[2,2,1]-1-heptyl hypochlorite it was possible to isolate such a salt.

Trineopentyl phosphite reacts vigorously with neopentyl hypochlorite at -78° in methylene chloride to give a solution of what is most certainly tetraneopentyloxyphosphonium chloride (I). The assignment of the formation and structure of this salt rests in the main on the n.m.r. spectrum of the reaction mixture. The n.m.r. spectrum was observed by removing a sample from the cold bath and recording it as rapidly as possible. The spectrum had a doublet centered at 5.69τ (J=4.8 cps) and a single peak at 8.94τ. The peak at 5.69τ is assigned to the methylene protons of I which are split by the phosphorus and the 8.94 τ absorption is due to the methyl protons. These peaks disappeared rapidly and it is estimated that I has a half life of ca. 3 minutes at room temperature. New peaks appeared at 6.32 τ (J=4.8 cps) and 9.03 τ. These are due to trineopentyl phosphate. Peaks at 6.66 τ and 9.00 τ due to neopentyl chloride also appeared. The salt (I) is fairly stable at -78° since the same initial spectrum was obtained after 17 hours. In another experiment neopentyl chloride (75% yield) and trineopentyl phosphate (ca. 100%) were isolated and characterized.

Treatment of triphenyl phosphite with neopentyl hypochlorite at -78° yielded neopentyl chloride and triphenyl phosphate as major products. Phenol was also found. Reaction of neopentyl hypochlorite with trimethyl phosphite under the same conditions afforded a mixture of dimethylneopentyl phosphate, trimethyl phosphate, methyl chloride and neopentyl chloride. Dimethylphosphorochloridate, $(CH_3O)_2POCl$, was also formed. No evidence could be obtained for the formation of II. Exact yield data were not obtained, however integration of the n.m.r. spectrum of the reaction mixture showed that the ratio o trimethyl phosphate to dimethylneopentyl phosphate was 1:3.75.

Treatment of a solution of I with silver p-toluenesulfonate at -78° led to the formation of silver chloride and tetraneopentyloxyphosphonium p-toluenesulfonate. This salt was considerably more stable than the chloride but did decompose at room temperature in methylene chloride with a half life of ca. 180 minutes. The products of the decomposition were trineopentyl phosphate, 2-methyl 1- and 2-butenes and p-toluenesulfonic acid. In a similar experiment silver acetate was allowed to react with the solution of tetraneopentyloxyphosphonium chloride at -78°. Decomposition was rapid at room temperature and was completed in 40 minutes. The major products were neopentyl acetate and trineopentyl phosphate.

Triphenylneopentyloxyphosphonium chloride (IV) and triphenyl-β,β,β-triphenylethoxyphosphonium chloride (V) were prepared by allowing chlorine, the alcohol and triphenylphosphine to react in hexane and methylene chloride respectively.[4] The yields were 85% and 64%. Decomposition of IV at 62° in 1,2-dichloroethane yielded neopentyl chloride, 73%, neopentyl alcohol, 27% and triphenylphosphine oxide, 100%. The half life under these conditions was ca. 23 hours. Decomposition of V was much more rapid under the same conditions, complete in 45 minutes, and yielded triphenylethylene, triphenylphosphine oxide and hydrogen chloride. The half life of this salt in 1,2-dichloroethane at 56° was ca. 10 minutes.

Nucleophilic substitution on a neopentyl group without rearrangement is well known but is in general a very slow process.[8] Decomposition of I is particularly striking because of the lack of rearrangement and the very fast rate. That this is a bimolecular process i.e. S_N2 is indicated by the lack of rearrangement and the finding that rearranged products are formed when chloride is replaced by p-toluenesulfonate ion. The difference between the two anions is their nucleophilicity with chloride being a much more powerful nucleophile. It is also interesting to note that acetate ion, which has nucleophilic power about that of chloride, gave unrearranged product.

Although it is not possible to assess all of the factors which cause these rapid decompositions, it is clear from a comparison of the rates of decomposition of I and III with IV that trialkyl and triaryl phosphate leaving groups are much better than triphenylphosphine oxide which in its own right is quite efficient.[4]

Another interesting feature of these reactions is the finding that II yielded not only methyl chloride but also neopentyl chloride. This indicates that in this system the usual rate difference, ca. 10^6, between methyl and neopentyl has been virtually eliminated.[6] This is reasonable in view of the very fast decomposition rates.

Further work is in progress on the theoretical and synthetic application of these reactions. It seems clear that they provide a means for effecting substitution reactions under conditions which are considerably milder than those previously available.

Acknowledgement. Funds for the purchase of the n.m.r. spectrometer were provided in part by the National Science Foundation.

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