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OXIDATION OF α-PHENYLETHYL CHLORIDE BY METAL OXIDES. NEW SYNTHETIC METHOD OF BIS(α-PHENYLETHYL) ETHER

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Oxidation of α-phenylethyl chloride by metal oxides were investigated. When benzene or carbon tetrachloride solution of α-phenylethyl chloride was refluxed in the presence of various metal oxides, formation of bis(α-phenylethyl) ether was observed only in the cases of three metal oxides, i.e., mercuric oxide, lead dioxide, and thallium(III) oxide in considerable yields.

Williamson synthesis of ethers and dehydration of alcohol have been widely used for the purpose of synthesis of ethers.[1] Senderens has reported dehydration of α-phenylethyl alcohol.[2] Present author thinks that formation of ethers in the reactions of alkyl halides with metal oxides has not yet been reported.

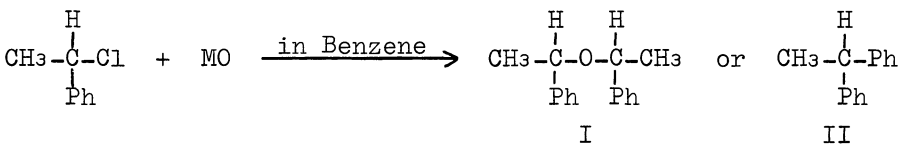
When benzene or carbon tetrachloride solution of α-phenylethyl chloride was refluxed in the presence of mercuric oxide or lead dioxide or thallium(III) oxide, the formation of bis(α-phenylethyl) ether was observed. When benzene solution of α-phenylethyl chloride was refluxed in the presence of cupric oxide, this ether was not formed but alkylation product was formed in low yield. When this solution was refluxed in the presence of aluminum oxide or barium oxide, only trace amount of alkylation product was formed. When carbon tetrachloride solution of α-phenylethyl chloride was refluxed in the presence of mercuric oxide or lead dioxide or thallium (III) oxide, bis(α-phenylethyl) ether was obtained. On the other hand, the carbon tetrachloride solution refluxed in the presence of aluminum oxide or cupric oxide or barium oxide did not give this ether. Yields of these reactions are listed in Table I. Products were identified by g.l.c. and n.m.r. spectroscopy. Although the reaction velocities were not measured, it would be qualitatively said that the reactivities of these metal oxides are in the order Tl>Hg>Pb.

Although the reactions of metal oxides with many organic substances have been reported to give carbonyl compounds,[3,4] in the reactions of α-phenylethyl chloride with lead dioxide, mercuric oxide, and thallium(III) oxide acetophenone was obtained in only trace amount.

It has been reported that mercuric salts, lead salts, and thallium salts have excellent ability in oxymetalation reaction.[5~8] It is interesting that only these three metal oxides of various metal oxides used in the present study can react with α-phenylethyl chloride to give bis(α-phenylethyl) ether.

No corresponding ether formation from benzyl chloride was observed. The mechanism and applications of this reaction are now being investigated.

Table I. Oxidation of α-phenylethyl chloride[a)]



I II

Metal oxide	Condition[b)] Solvent(ml)		Reaction time(hr)	Product	Yield(%)[c)]
Tl_2O_3	Carbon tetrachloride	15	0.5	I	57
HgO	Benzene	5	1	I	68
HgO	Benzene	5	0.5	I	45
PbO_2	Benzene	5	4	I	63
CuO	Benzene	5	6	II	24
Al_2O_3	Benzene	5	6	II	trace
BaO	Benzene	5	6	II	trace

a) The experimental conditions are not necessarily optimum.
b) 0.01 mol of α-phenylethyl chloride and metal oxide were used.
c) Yields of ether are shown as (mol of product/mol of chloride used) X 100 X 2. Yield of II is shown as (mol of product/mol of chloride used) X 100.

References

1) D. J. Cram and G. S. Hammond, "Organic Chemistry", 2nd ed, Mcgraw-Hill, New York, 1964, p 75 and 250.
2) J. B. Senderens, Compt. Rend., 182, 614 (1926).
3) R. L. Augustine, "Oxidation", vol. 1, Marcel Dekker, New York, 1969, Chapter 1 and 2.
4) T. Mukaiyama, K. Narasaka, and M. Furusato, J. Amer. Chem. Soc., 94, 8641 (1972).
5) K. B. Wiberg and S. D. Nielsen, J. Org. Chem., 29, 3353 (1964).
6) Z. Rappoport, P. D. Sleezef, S. Winstein, and W. G. Young, Tetrahedron Lett., 1965, 3719.
7) J. B. Lee and M. J. Price, Tetrahedron, 20, 1017 (1964).
8) H. Arzoumanian and J. Metzger, Synthesis, 1971, 527.

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