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SYNTHESIS OF BENZYL HALIDES FROM ALDEHYDES PROMOTED BY HALOSILANES AND 1,1,3,3-TETRAMETHYLDISILOXANE (TMDS)[1].

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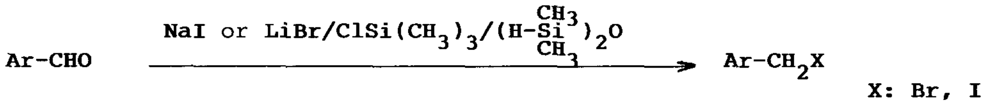
Summary: Direct synthesis of monoalkyl halides from aldehydes by a new reductive halogenation method is briefly described.

The use of halotrimethylsilane reagents became significant during recent years in organic synthesis[2]. We describe in this paper a new application of these reagents for the direct synthesis of alkyl halides from aldehydes and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agent.



$$\text{Ar-CHO} \xrightarrow{\text{NaI or LiBr/ClSi(CH}_3\text{)}_3\text{/(H-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}\text{)}_2\text{O}} \text{Ar-CH}_2\text{X}$$

X: Br, I

The experimental procedure is exemplified by the reductive iodination of benzaldehyde: a mixture of benzaldehyde (1.02ml, 10mmol), trimethylchlorosilane (1.92ml, 15mmol) and sodium iodide (2.25g, 15mmol) in anhydrous acetonitrile (5ml) is stirred at room temperature for 10min and them cooled at 0ºC. Immediately after, 1,1,3,3-tetramethyldisiloxane (1.79ml, 10mmol) is dropwise added giving an exothermic reaction. Stirring is maintained for 30min again, after which, two organic phases are formed. The upper siloxane layer is separated, and the lower is taken up in dichloromethane (20ml) to precipitate inorganic salts which are filtered off. Evaporation of the solvent yields crude benzyl iodide, which is purified by reduced pressure distillation (1.99g, 91%). b.p: 60-62ºC/0.3torr (lit. m.p: 24ºC)[3]. ^{1}H-NMR (CCl_4) δppm: 4.19 (s, 2H, CH_2), 7.03 (s, 5H, arom.).

We have tested the method with a number of aromatic aldehydes and the results obtained are summarized in the table. The wide utility of this new reductive halogenation method is also exemplified by the direct conversion of aldehydes into bromides[4]. The halide formation can be explained by the reduction of an O-silylated halohydrin intermediate[2] or by the cleavage of an "in situ" generated symmetrical ether. Since, aldehydes give gem-dihalides by the literature procedures[5], our method represents a high efficient direct synthesis of monoalkyl halides from aldehydes. To our knowledge, this is an unusual transformation. We are continuing to explore the scope[6] of the method and will report the results in due course from synthetic and mechanistic points of view.

Table. Preparation of aryl halides.

Ar	X	T (ºC)	time (min)	Yield[a] (%)	m.p. or b.p./torr
C_6H_5-	I	0	30	91[b]	23-24
	Br	80	30	94	198/760
4-CH_3O-C_6H_5-	I	15	30	89[b]	32-34
	Br	80	15	84	145-148/30
2-Cl-C_6H_4-	I	25	45	86	—
	Br	80	15	64	95-98/0.4
4-Cl-C_6H_4-	I	0	5	95	59-61
	Br	80	20	90	48-50
3-NO_2-C_6H_4-	I	80	30	48[c]	72-75

a) Yield of isolated pure products, the purity as determined by glc and tlc analysis was ⩾97%. b) Some benzyl iodides were unestable compounds, which decompose during storage. c) 30% of symmetrical ether was obtained. Isolation of products was achieved by column chromatography. (Silica gel; eluent: n-hexane/AcOEt, 3:1).

REFERENCES AND NOTES

1.- Considered as Reagents and Synthetic Methods 37. This work was supported by the Hezkuntza Saila of Eusko Jaurlaritza (Basque Government) and Wacker-Chemie GMBH (München,Germany) with gifts of chlorotrimethylsilane and 1,1,3,3-tetramethylsiloxane reagents.

2.- G.A. Olah, S.C. Narang. Tetrahedron, 38, 2225 (1982).

3.- Z. Rappoport, "Organic Compounds Identification", 3rd Edn. C.R.C. press, Cleveland, 1977. p. 137.

4.- Chlorotrimethylsilane was not useful to obtain the corresponding benzyl chlorides. Benzaldehyde was recovered unchanged after 1h under reflux with chlorotrimethylsilane and 1,1,3,3-tetramethyldisiloxane.

5.- a) C.A. Buehler, D.E. Pearson, "Survey of Organic Synthesis", Wiley--Interscience, New York, Vol. 1, p. 335 (1970) and vol.2, p.350(1977). b) M.S. Newman, P.K. Sujeeth, J.Org.Chem., 43, 4367 (1978); c) S.D. Saraf, Synth. Commun., 13, 7 (1983).

6.- From aliphatic aldehydes we have found in a preliminary experience that symmetrical ethers are formed instead of the corresponding halides. Thus, under the conditions used in the reductive halogenation of benzaldehyde, n-pentanal gives the symmetrical ether in 80% yield.

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