Strong Acid Chemistry. 6.[1]
# Direct Reduction of Benzyl Chlorides in Strong Acids

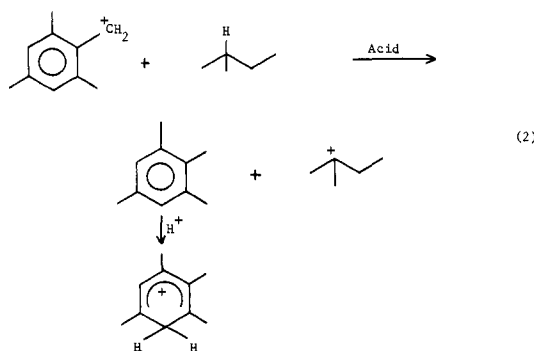## M. Siskin* and R. H. Schlosberg

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Abstract: The reactions of benzyl chlorides with the $HF-TaF_5$, $HBr-AlBr_3$, and HF acid systems have been investigated. In the superacid systems, benzyl chloride and methylated benzyl chlorides undergo a direct reduction reaction to form toluene and methylbenzenes even in the absence of an alkane solvent capable of transferring a hydride. No added contribution toward the formation of the direct reduction product is observed in the presence of isoalkanes. In the weaker proton–acid, HF, no reduction reaction takes place even in the presence of isopentane. These results are consistent with results previously reported for the direct reduction of simple alkyl chlorides to the corresponding alkane in strong acid systems.

We recently reported that direct reduction of C_1–C_3 alkyl chlorides to the corresponding alkanes readily occurs in the $HF-TaF_5$, $HCl-AlCl_3$, and $HBr-AlBr_3$ strong acid systems.[2] The reduction itself involves hydride abstraction from the chloronium ion by another alkyl chloride molecule (eq 1). The
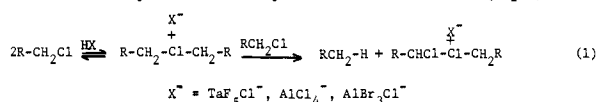
reactions were carried out on the neat alkyl halides so that the alkyl chloride represented the only source of hydride ion available. In the case of methyl chloride, NMR evidence (δ_{CH_3} 4.1, lit.[3] δ 4.2) gave support to a reduction mechanism involving the intermediacy of dialkylchloronium ions.[4] In this paper we wish to report our results on the reaction of benzyl chlorides in the $HF-TaF_5$, $HBr-AlBr_3$, and HF acid systems. Benzyl cations are reported to be good hydride acceptors, capable of oxidizing isoalkanes dissolved in strong protonic acids to alkyl carbenium ions[3] (eq 2). The reduction of the pentamethyl-

benzyl cation to hexamethylbenzene and the reduction of a number of methyl-substituted benzyl cations by hydride-transfer reactions from tertiary alkanes or hydrogen in proton acids such as H_2SO_4, HF, and HSO_3F have been reported.[4-11] The reduction of benzyl chloride to toluene has been observed by Schmerling[12] as a significant side product (27% yield) in the aluminum chloride catalyzed alkylation of methylcyclohexane. Since these benzyl cations were generated from the corresponding benzyl chlorides and since we observed direct reduction with simple alkyl chlorides, we were curious to see whether the direct reduction of the benzyl halides could also be effected on the neat compounds, that is, in the absence of an added hydride source.

Results and Discussion

The first conclusion to be made from the data summarized in Table I is that benzyl chlorides, like simple alkyl chlorides,

can undergo *direct* reduction to form the corresponding methylated benzene reduction products in strong Friedel-Crafts acid systems. The best results are obtained using the $HBr-AlBr_3$ acid system which has a significant hydrocarbon solubility. The results in $HBr-AlBr_3$ clearly indicate that under our reaction conditions the presence of an isoalkane capable of donating a tertiary hydrogen (e.g., isopentane) is not required and yields obtained are in the same range as reported with the simple alkyl chlorides[2] (20–30% conversion to hydrocarbon product in both cases). Comparing the last two entries in Table I for 2,5-dimethylbenzyl chloride shows that there is no advantage in aromatic hydrocarbon yield when isopentane was employed as a solvent.

Mechanistically these results are consistent with the formation of dibenzyl chloronium ions as the source of hydride ions for the reduction of the benzyl chlorides (eq 3). The
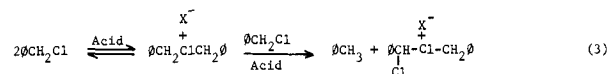
methylated benzenes are present as protonated cyclohexadienyl cations in the acid layer until quenched in water. In these studies the water-quenched reaction mixtures were extracted with pentane in order to free and isolate the product.

The yields of reduced products are sharply reduced in $HF-TaF_5$ systems. This reflects the lower acidity of these systems and the inability to allow the formation of high concentrations of halonium ion precursors. Anhydrous hydrogen fluoride ($-H_0 = 11.03$)[13,14] alone, or in the presence of isopentane, is too weak to bring about the reduction reaction. In the $HF-TaF_5$ system at lower acid:alkyl chloride ratio (lower acidity) there is a conversion to the methylated benzene product.

It is also interesting to note that benzyl fluoride does not react in $HF-TaF_5$ to form toluene. This is probably because fluorine is too electronegative to support the positive charge required for halonium ion formation. In $HBr-AlBr_3$ the benzyl fluoride undergoes a slow conversion to hydrocarbon via initial conversion to benzyl bromide. This conversion is brought about by a slow halogen exchange reaction for which the formation of aluminum fluoride is the presumed driving force (eq 4).[15]
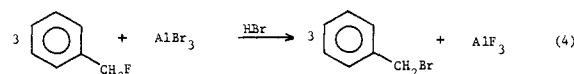
Complete details of the behavior of benzyl fluorides in superacids will be presented in a forthcoming paper.

Summary

Benzyl chlorides and bromides are reduced in good yield to the corresponding aromatic hydrocarbon in strong acids. An

Table I. Summary of Results of Reactions of Benzyl Halides with Strong Acids

Compd (ArCH2Cl)	MXn/ArCH2Cl, mole ratio	Acid	T, min	Temp, °C	% ArCH3 product
C6H5CH2Cl	1.3	30:1 HF–TaF5	15	20	4.7[a]
	2.6	30:1 HF–TaF5	15	20	1.7
	6.5	30:1 HF–TaF5	15	20	0.2
	1.3	TaF5 only	15	20	0.0
	1	AlBr3	3	20	6.5
	1	AlBr3	1	20	24
C6H5CH2Br	1	AlBr3 + n-C5H12	1	20	27
	2	AlBr3 + n-C5H12	1	20	20
C6H5CH2F	3.2[b]	30:1 HF–TaF5	30	20	0.0
	1	AlBr3	1	20	0.0
CH3	1	AlBr3 + n-C5H12	1	20	2.9
C6H5C(CH3)HCl	7	30:1 HF–TaF5	15	20	0.66
2,5-(CH3)2C6H3CH2Cl	3.2	30:1 HF–TaF5	15	20	2.0
	3.2[c]	30:1 HF–TaF5	15	20	4.1
	3.2	HF only	30	20	
	3.2	30:1 HF–TaF5 + i-C5H12	60	20	2.8
	3.2	HF only + i-C5H12	60	20	
	1	AlBr3	1	20	36
	1	AlBr3 + i-C5H12	1	20	25
(CH3)5C6CH2Cl	4	30:1 HF–TaF5	120	20	0.78

[a] Calculated on basis of mole of product/100 mol of benzyl halide charged. [b] Repeated twice. [c] Added to premixed HF–TaF5.

extra source of hydrogen (e.g., from a tertiary isoalkane C–H bond) does not enhance the rate or yield of the reduction reaction. The extent of the reduction reaction is a function of the acidity of the system. Anhydrous HF is too weak an acid to allow the reaction to proceed. Benzyl fluorides are resistant to the reduction reaction and only react via an initial halogen–fluoride exchange reaction.

It is thus clear that, as with alkyl halides, the chemistry of benzyl halides in acid systems is complicated and depends upon the nature of the halide and of the acid system.

Experimental Section

The benzyl halides used were commercial chemicals of the highest available purity and were used without further purification.

General Procedure for HF–TaF5 Catalyzed Reactions. In a 125-cm³ Hastelloy C-276 Parr reactor under a nitrogen atmosphere was placed a Teflon-coated magnetic stirring bar and tantalum pentafluoride (14.0 g, 0.051 mol). The reactor was sealed and a tared 75-cm³ stainless steel cylinder containing hydrogen fluoride (30 g, 1.5 mol), distilled from a copper still at 19.6–29.5 °C, was attached to the reactor and pressured into the reactor with 40 psig of nitrogen. To the catalyst stirring at room temperature benzyl chloride (2.5 g, 0.020 mol) was added as above from a 10-cm³ tared stainless steel cylinder. The reaction mixture was stirred at room temperature for 15 min, after which as much HF as possible was vented before opening the reactor. The mixture was carefully quenched with 50 mL of ice–water, extracted with pentane, and subsequently dried over anhydrous sodium sulfate. The pentane extract to which a known weight of n-propylbenzene was added as an internal standard was analyzed on a Perkin-Elmer Model 910 gas chromatograph with a flame ionization detector using a 10 ft × 1/8 in. 5% DC550 on 80/100 Chromosorb from Supelco at 50 °C for 6 min and programmed to 250 °C at 10°/min.

General Procedure for AlBr3 Catalyzed Reactions. Aluminum bromide (8.6 g, 0.032 mol) was stirred in a 500-cm³ Teflon (FEP) bottle, the benzyl halide was added, and there was usually some brown gas evolved (HBr). A gas sample taken from the C6H5CH2Cl reaction and analyzed by mass spectroscopy contained no hydrocarbons. After addition of the reagents the reaction mixture was mixed for a minute and ice–water was added to quench the reaction. The mixture was then extracted with n-pentane and analyzed as above by GC.

References and Notes

(1) Part 5 in this series: M. Siskin, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) R. H. Schlosberg, M. Siskin, W. P. Kocsi, and F. J. Parker, *J. Am. Chem. Soc.*, **98**, 7723 (1976).
(3) G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc.*, **96**, 884 (1974).
(4) Confirmation of our results with alkyl halide reduction has just been reported by G. A. Olah and J. Kaspi, *J. Org. Chem.*, **42**, 3046 (1977).
(5) (a) H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **89**, 794 (1970), and references cited therein; (b) P. van Pelt and H. M. Buck, *ibid.*, **92**, 1057 (1973).
(6) H. M. Buck, M. J. van der Sluys-van der Vlugt, H. P. J. M. Dekkers, H. H. Brongersma, and L. J. Oosterhoff, *Tetrahedron Lett.*, 2987 (1964).
(7) H. M. Buck, G. Holtrust, L. J. Oosterhoff, and M. J. van der Sluys-van der Vlugt, *Ind. Chim. Belge*, **32** (Vol. III, S. 21), 581 (1967).
(8) H. M. Buck, *Chem. Weekblad*, **63**, 392 (1967).
(9) H. H. Brongersma, H. M. Buck, H. P. J. M. Dekkers, and L. J. Oosterhoff, *J. Catal.*, **10**, 149 (1968).
(10) P. van Pelt and H. M. Buck, *Recueil*, **93**, 206 (1974).
(11) P. van Pelt and H. M. Buck, *J. Am. Chem. Soc.*, **98**, 5864 (1976).
(12) L. Schmerling, *J. Am. Chem. Soc.*, **97**, 6134 (1975).
(13) R. H. Gillespie and T. E. Peel, *Adv. Phys. Org. Chem.*, **No. 9**, 1 (1971).
(14) R. J. Gillespie, personal communication.
(15) N. O. Colloway, *J. Am. Chem. Soc.*, **59**, 1474 (1937). G. A. Olah in "Friedel–Crafts and Related Reactions", Vol. I, G. A. Olah, Ed., Wiley-Interscience, New York, N.Y., 1963, p 869: "... during Friedel–Crafts reactions involving organic-fluorides and aluminum halides a metathetic reaction takes place with the formation of aluminum fluoride ...".