Cleavage of Benzyl Ethers with [Bis(trifluoroacetoxy)iodo]benzene

By SPYROS SPYROUDIS and ANASTASIOS VARVOGLIS
(Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece)

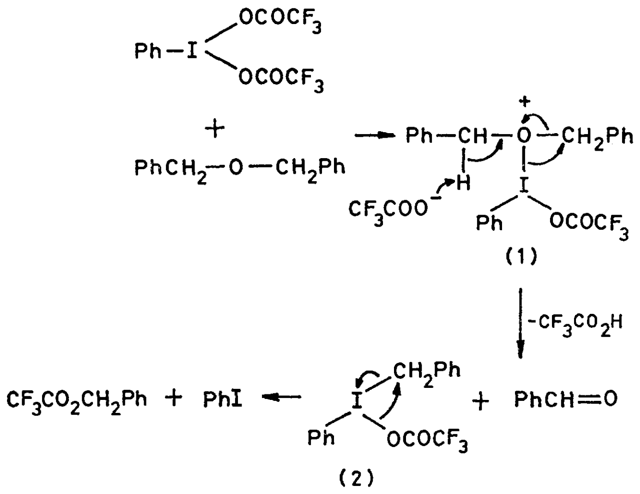
Summary A new reaction of [bis(trifluoroacetoxy)iodo]benzene is described, involving the oxidative cleavage of various benzyl ethers into carbonyl compounds and benzyl (or alkyl) trifluoroacetates.

THE oxidative cleavage of ethers has recently received considerable attention and several oxidants, including trityl tetrafluoroborate,[1] uranium hexafluoride,[2] nitronium tetrafluoroborate,[3] and the cation radical of tris-(*p*-bromophenyl)amine,[4] have been shown to be effective in producing carbonyl compounds and alcohols from, mainly, benzyl ethers.

As part of a study of the oxidative properties of [bis(trifluoroacetoxy)iodo]benzene[5] (TIB) we have found that it cleaves dibenzyl ether smoothly and quantitatively (24—48 h at ambient temperature) into an equimolecular mixture of benzaldehyde and benzyl trifluoroacetate. The reaction occurred in various solvents (CH_2Cl_2, $CHCl_3$, *etc.*) using a slight excess of TIB and the products were separated by column chromatography (SiO_2).

We suggest that the reaction proceeds *via* initial formation of an oxonium complex (**1**), which forms benzaldehyde and a trivalent iodine intermediate (**2**), which is finally split into iodobenzene and benzyl trifluoroacetate (Scheme).

N.m.r. spectroscopy showed that benzaldehyde appeared first and that only at the end were the two products present in equimolecular quantities. During the reaction a peak at δ 4·87 (in $CDCl_3$) is present, which finally disappears and is attributed to (**2**). Compounds analogous to (**2**) are reasonably stable and we have isolated and characterised several of them[6] [*e.g.* (**3**)] from TIB and benzyl aryl ethers in a normal aromatic electrophilic substitution.



SCHEME

p-$PhCH_2OC_6H_4I(Ph)OCOCF_3$

(**3**)

Benzyl alkyl ethers are cleaved by TIB to give benzaldehyde and alkyl trifluoroacetates (see Table), with $CHCl_3$–CF_3CO_2H or neat CF_3CO_2H being the best solvents. Since alkyl trifluoroacetates are easily hydrolysed, oxidative removal of the benzyl group, which is a common protecting group for alcohols, could well prove to be a suitable method when the substrate contains a reducible function.

TABLE. Reaction of TIB with various benzyl ethers

Ether	Products (% yield of isolated products)
$(PhCH_2)_2O$	PhCHO (56) + $CF_3CO_2CH_2Ph$ (42)
$PhCH_2OEt$	PhCHO (100) + CF_3CO_2Et (100)[a]
$PhCH_2OC_8H_{17}$	PhCHO (80) + $CF_3CO_2C_8H_{17}$ (72)[b]
$PhCH_2OCPh_3$	PhCHO (49) + $HOCPh_3$ (51)
$PhCH_2OPh$	p-$(PhCH_2O)C_6H_4I(Ph)OCOCF_3$ (56)

[a] Products estimated by n.m.r. spectroscopy. [b] Isolated as n-octyl 3,5-dinitrobenzoate.

Benzyl trityl ether reacts quickly with TIB to give benzaldehyde and trityl alcohol. The latter is obtained directly during the chromatographic work-up, as has been observed with other trifluoroacetates.[7] This reaction might be of use for the selective oxidation of benzylic alcohols under mild conditions (see Table). It should be noted that benzyl benzhydryl ether, as well as asymmetrically ring-substituted dibenzyl ethers, gives mixtures of two carbonyl compounds and two trifluoroacetates with TIB.

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