Novel Reactions of Iodosobenzene with Various Organic Compounds

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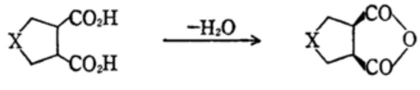
Little attention has so far been paid to the chemistry of iodosobenzene[1] with various organic compounds. When a solution of an alcohol (RCH_2OH, 10 mmol) and iodosobenzene (11 mmol) in dry dioxane (20 m*l*) was refluxed for 12 hr in a stream of nitrogen gas, the corresponding aldehydes (RCHO) were obtained in the following yields[2]: (R, %); (C_6H_5–, 85), (*p*-CH_3-C_6H_4–, 98), (*p*-CH_3O-C_6H_4–, 67), (*p*-Cl-C_6H_4–, 79), (C_6H_5CH=CH–, 88), (CH_2=CH–, 56), (H–, 40)[3], (CH_3–, trace)[3], (*n*-C_3H_7–, trace), and (2-furyl, 31). Glyoxal was obtained from ethylene glycol in a 15% yield. When 20 mmol of iodosobenzene were used to 10 mmol of benzyl alcohol, the yield of benzaldehyde was 86%. This result seems to show that the oxidation of benzaldehyde to benzoic acid does not proceed. In fact, when benzaldehyde was treated with iodosobenzene under similar conditions, benzaldehyde was recovered in a 90% yield.

Compounds other than primary alcohols were also oxidized by iodosobenzene under conditions similar to those described above. The results are summarized in Table 1.

Another interesting reaction of iodosobenzene is the dehydration of the dibasic acid of the *cis*-Ia[4] or Ib[4] type to the corresponding anhydride, IIa[4] or IIc, and that of 1,4-butanediol to tetrahydrofuran (see Table 1):



Ia: X=CH_2
Ib: X=S
Ic: X=SO

IIa: X=CH_2
IIc: X=SO

After the *cis*-Ib (10 mmol) and iodosobenzene (20 mmol) in dioxane (20 m*l*) had been refluxed for 12 hr, the reaction mixture was evaporated to dryness *in vacuo* and the residue was recrystallized from acetone to give IIc in a 78% yield; mp 205—207°C. *trans*-Ib did not afford IIc, but instead the sulfoxide *trans*-Ic was obtained in a 27% yield; mp 170—171°C from ethanol-acetone. Similarly, *cis*-Ia gave the anhydride IIa in a 65% yield, but the use of *trans*-Ia resulted in its recovery in a 70% yield. Under the above reaction conditions, no formation of an anhydride, IIa or IIc, from *cis*-Ia or Ib was observed in the absence of iodosobenzene.

TABLE 1. OXIDATION OF COMPOUNDS OTHER THAN PRIMARY ALCOHOLS*1

A solution of compounds (10 mmol) and iodosobenzene (11 mmol) in dioxane was refluxed in each run.

Compound	Reaction time hr	Product	Method of isolation	Yield, %
$C_6H_5CH_3$	12	C_6H_5CHO	a	17
$C_6H_5CH_2Cl$	12	C_6H_5CHO	a	14
Cyclohexanol	12	Cyclohexanone	a	26
C_6H_5SH	2	$(C_6H_5S–)_2$	b	76
p-NO_2-$C_6H_4NH_2$	6	(*p*-NO_2-C_6H_4N=$)_2$	b	40
$(C_6H_5NH–)_2$	2	$(C_6H_5N=)_2$	b	100
HO-$(CH_2)_4$-OH	2	Tetrahydrofuran	c	40
Hydroquinone	12	Quinhydrone	b	98
Hantsch Ester	6	DLD*2	b	79

a) An acidic solution of 2,4-dinitrophenylhydrazine was added to the reaction mixture, and the precipitate thus obtained was separated, washed with hot water, dried, and then weighed.
b) The reaction mixture was evaporated to dryness, and the residue was purified by recrystallization.
c) The reaction mixture was subjected to distillation to give the liquid product.
*1 Except 1,4-butanediol.
*2 DLD=Diethyl 2,6-lutidine-3,4-dicarboxylate.

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[1] A. H. Ford-Moore (*J. Chem. Soc.*, **1949**, 2126) has reported that iodosobenzene is a reagent for the oxidation of sulfides to sulfoxides without further oxidation to sulfones. For the method of preparation, see H. J. Lucas, E. R. Kennedy and M. W. Formo, "Organic Syntheses," Coll. Vol. III, p. 483 (1955).

[2] The yields were calculated from the weight of the 2, 4-dinitrophenylhydrazone in each run.

[3] The reaction was carried out in the absence of a solvent.

[4] T. Takaya, H. Yoshimoto and E. Imoto, This Bulletin, **40**, 2636, 2844 (1967).