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CHEMISTRY OF TRIVALENT IODINE: PART I
IODONIUM YLIDES FROM PHENOLS[+]

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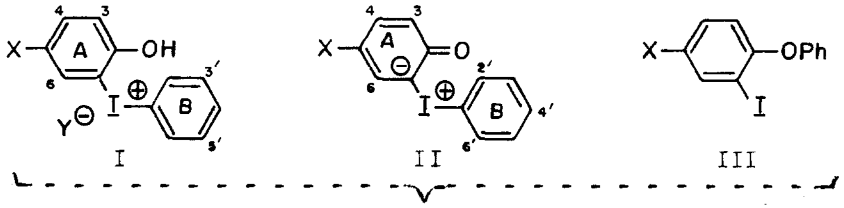
In a study of the reaction of phenyl iodosoacetate with phenols having electron withdrawing substituents, Fox and Pausacker[1] obtained an amorphous compound from the reaction of p-nitrophenol in AcOH solution. It was suggested that this product was most probably 2-hydroxy-5-nitrodiphenyliodonium acetate (Ia, Y = OAc) and it was found to yield 2-iodo-4-nitrodiphenyl ether on heating. All the other phenols of the same type, which were studied, gave only iododiphenyl ethers as reaction products. We have re-examined this reaction and have been able to isolate iodonium ylides in pure form in a couple of cases. There seem to be only two other reports so far on the isolation of iodonium ylides. Potassium salts of cyclopentadienes having three or four electron withdrawing substituents have been found to react with phenyliodosoacetate to give iodonium ylides[2]. An iodine-nitrogen ylide[3] has been obtained from p-toluenesulphonamide by reaction with the same reagent under alkaline conditions. Earlier, halonium ylides were proposed as intermediates in the formation of 3,5,3',5'-tetra-t-butyl-diphenoquinone in the photolysis of 3,5-di-t-butyl-4-diazo-2,5-cyclohexadien-1-one[4,5] in the presence of halogen compounds like isopropyl bromide and iodobenzene.

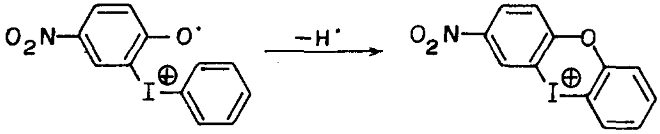
When equimolecular amounts (20 m.moles each) of p-nitrophenol and phenyl iodosoacetate were dissolved in glacial acetic acid (100 ml) and left at r.t. for 24 hrs, a light yellow amorphous precipitate was obtained in high yield (≃ 4.98 g) in agreement with the earlier report. After separation and washing with pet. ether and CCl_4, the 60 MHz PMR spectrum of the product in trifluoroacetic acid (TFA) was examined. The aromatic region of the spectrum was fairly well resolved and the signals appeared to correspond well with those that may be expected for a 2-hydroxy-5-nitrodiphenyliodonium salt. [δ (ppm): 7.35 (3-H, d, J = 9.2 Hz), 8.40 (4-H, q, J = 9.2,2.4 Hz), 8.67 (6-H, d, J = 2.4 Hz), 8.05 (2',6'-H's, m), 7.52 - 7.87 (3',4',5'-H's, m)]. However, the acetate signal was of too low an intensity (about 15% of what was expected) for the material to be a pure sample of Ia (Y = OAc). It appeared likely that the larger part of the iodonium acetate formed in the reaction had lost the elements of AcOH and that the powder could be a mixture of Ia (Y = OAc) and the ylide IIa. A

PMR spectrum of the material obtained in DMSO showed clearly that this was indeed the case. While the absorptions of the B-ring protons were not significantly affected, those of the A-ring protons were shifted markedly upfield in comparison with those obtained in TFA. The shifts were 1.04, 0.50 and 0.47 ppm for the 3-, 4- and 6-protons, respectively, and they suggested the presence of a negative charge on ring-A and the substituents attached to it. The ylide was presumably in the protonated form in TFA solution. The powder could be conveniently converted completely into the ylide by dissolution in pyridine and reprecipitation with pet. ether after filtration. One repetition of the procedure gave the pure acetate-free ylide (m.p. 133°, microcrystalline needles). PMR spectral data for the pure material in the two solvents are shown in Table 1. In addition to the differences between the two sets of chemical shifts for the ylide and the iodonium salt, the data also showed that ring-A protons are somewhat more strongly coupled in the former than in the latter. The ylide character of the material was confirmed by elemental analysis and mass spectral molecular weight (341). A remarkable feature of the mass spectrum was that the (M-1) peak was the strongest, suggesting facile loss of a hydrogen atom from the molecular ion (IV) by intramolecular reaction to give the iodonium ion, V. The ylide rearranged to 2-iodo-4-nitrodiphenyl ether (IIIa) rapidly on heating in solution or on melting. At r.t. in DMSO solution, the isomerization which could be readily monitored by PMR spectra, was about 45% in two days. The ether could also be isolated as a product from the reaction mixture after separation of the yellow powder and subsequent work up.



I II III

	(a)	(b)	(c)	(d)
X:	NO_2	COOEt	CHO	COMe



IV V

TABLE 1

Comp.	Solv.	Chemical shifts (δ) and coupling constants				
		3-H	4-H	6-H	2',6'-H's	3',4',5'-H's
IIa	DMSO	6.35 (d, J=9.4 Hz)	7.97 (q, J=9.4, 2.8 Hz)	8.28 (d, J=2.8 Hz)	8.10 (m)	7.30 - 7.73 (m)
Ia $Y=CF_3COO$	TFA	7.46 (d, J=9.2 Hz)	8.52 (q, J=9.2, 2.4 Hz)	8.79 (d, J=2.4 Hz)	8.23 (m)	7.63 - 7.93 (m)
IIb	DMSO	6.30	8.00	7.53	8.00 (m)	7.23 - 7.73 (m)
Ib $Y=CF_3COO$	TFA	7.40 (d, J=8.16 Hz)	8.37 (q, J=8.2, 1.8 Hz)	8.60 (d, J=1.8 Hz)	8.17 (m)	7.57 - 7.93 (m)

Three other substrates, ethyl p-hydroxybenzoate, p-hydroxybenzaldehyde and p-hydroxyacetophenone were tried instead of p-nitrophenol in the reaction under the same conditions. The behaviour of the benzoate closely paralleled that of p-nitrophenol, although in this case the ylide (IIb, m.p.128-28.5°) was a little more soluble in AcOH and also more labile. Most of the ylide formed in the reaction could be precipitated out by concentration of the reaction mixture in the temperature range 35 to 40°, and, as in the previous case, it was admixed with the corresponding hydroxyiodonium acetate. The total yield was quite good (≃61%) and the pure ylide was obtained from the mixture in the same manner as before. PMR spectral data (Table 1), elemental analysis and mass spectral mol. wt. agreed with the ylide structure, IIb. The ether ester, IIIb, obtained by rearrangement of the ylide was hydrolyzed to the corresponding acid (m.p. 158-59°; lit. m.p. 160°).

With p-hydroxybenzaldehyde and p-hydroxyacetophenone, the ylides (IIc and IIId) could not be isolated although their presence in the product mixtures could be detected by the characteristic position of the 3-proton absorptions. They could be isomerized to the corresponding diphenyl ethers (IIIc and IIId) thermally and the ethers could be separated by column chromatography.

Solutions of IIa and IIb in TFA, in which they were converted into iodonium salts (Ia and Ib, Y = CF_3COO), were found to be quite stable at r.t., and, even on heating at 100° for over 1 hr, formation of diphenyl ethers was not perceptible. This behaviour is in contrast with that obtained in AcOH, and it suggests that iodonium ylides of type II are the true intermediates through which diphenyl ethers are formed in the reaction under consideration. It further implies that the base strengths of the ylides (IIa and IIb) are intermediate between those of the acetate and trifluoroacetate ions.

The implications of these findings are under further study.

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