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Alkoxyl Radicals from Alcohols.[1] Spectroscopic Detection of Intermediate Alkyl and Acyl Hypoiodites In The Suárez and Beebe Reactions.

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Abstract: Acetyl hypoiodite and a number of alkyl hypoiodites have been characterized as intermediates in the conversion of alcohols into alkoxyl radicals under Suárez (photostimulated iodosobenzenediactetate/iodine reagent) and Beebe (photolysed acetyl hypoiodite/alcohol) conditions.

Alkoxyl radicals are of importance in synthetic, biological and environmental chemistry.[2] Recently Suárez and co-workers introduced the photostimulated iodobenzenediacetate (IBDA)/iodine reagent (Suárez reagent[3]) that reliably converts hydroxyl-containing substrates (alcohols,[3] carboxylic acids,[4] carbohydrates,[5] lactols[6]) into products derived from intermediate oxygen-centred free radicals. Unlike many older reagent combinations, conversions using this reagent do not, so far, appear to be complicated by consumption of first-formed products, a problem demonstrated, for example,[1] in the reaction of cyclopentanol with the mercury II oxide/iodine reagent (Equation 1).


Formate, lactone, acetal
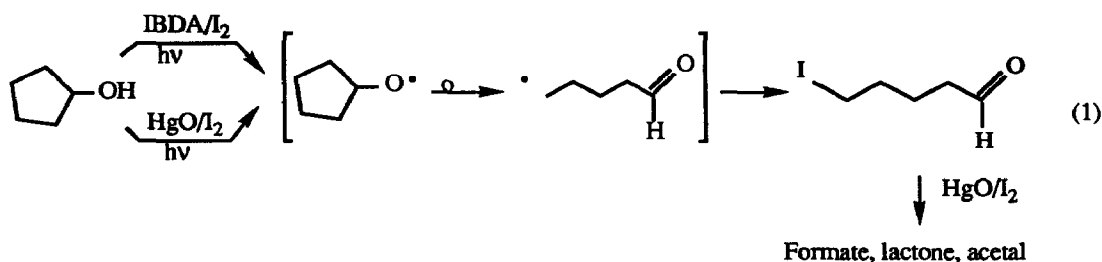
This latter reagent (introduced by Akhtar and Barton[7] and used extensively by Suginome,[8] Macdonald[9] and others[2a]) bears similarity not only to other metal oxidant/halogen combinations for the conversion of alcohols,[10] but also to that introduced by Prévost for reactions of silver carboxylates and iodine with alkenes[11] and with the Cristol modification of the Hunsdiecker Reaction (conversions of carboxylic acids using HgO/I_2).[12]

By analogy to Walling's hypochlorite studies,[13] these reactions, for alcohols, have been assumed to develop via intermediate hypohalites. It is the case, however, that for these reactions, the intermediacy of hypohalite such intermediates has not, hitherto, been demonstrated. Accordingly, we describe details of experiments which show that the sequence using the Suárez reagent is as depicted in Equation 2 (Δ = ambient temperature reaction in dark; hv = photoreaction) and give characterization data for the intermediate organic hypoiodites.

(2)
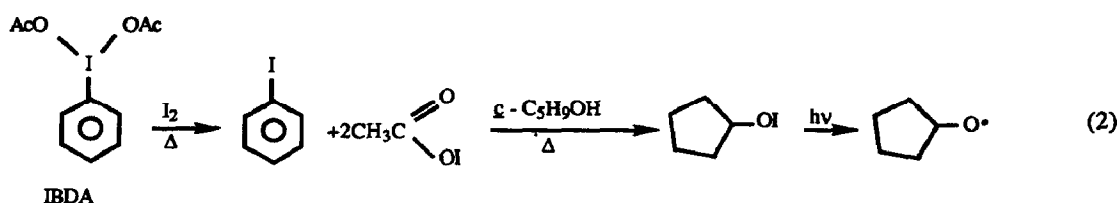
Examination, by ^{1}H NMR, of the reaction of IBDA and iodine in deuteriochloroform at ambient temperature showed conversion of IBDA into iodobenzene and an acetyl-containing product [δ_H = 2.19ppm, cf.δ_H(AcOH) = 2.10 and δ_H(IBDA) =1.99]. This absorption is ascribed to that of acetyl hypoiodite since its chemical shift is the same as that of the principal signal observable in the spectrum of the filtered solution obtained in the Prévost reaction by treating silver acetate with iodine in deuteriochloroform (a reaction shown previously by wet chemical analysis to form acetyl hypoiodite:[11] Equation 3).[14]

(3)
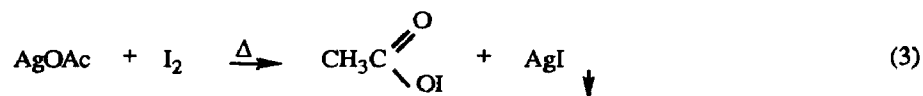
GC/MS analysis of these solutions failed to conclusively demonstrate the formation of acetyl hypoiodite, although under limiting iodine concentration (when, for example, the iodine was incompletely dissolved) methyl acetate was detected. This product is consistent with the intermediacy of acetyl hypoiodite (the Simonini Reaction:[11] Equation 4).

(4)
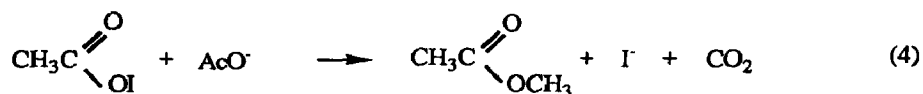
Reaction of either of these solutions with cyclopentanol, in the dark, resulted in conversion of the alcohol into an unstable intermediate and of the acetyl hypoiodite into acetic acid. The intermediate was assigned as cyclopentyl hypoiodite, on the basis of the following data. NMR spectra of the reaction solutions showed signals characteristic of an intact cyclopentyl moiety, with absorptions observable at δ_H4.75 ppm ($\Delta \delta$ = -0.52 ppm, versus cyclopentanol, with appropriate integral ratios both internally and with respect to the acetic acid co-product) and δ_C = 87.12, 35.01 and 23.26ppm (cf. δ_C(c-C_5H_9OH) = 73.6,35.3 and 23.7 ppm). The intermediate was unstable both to hydrolysis (addition of deuterium oxide reformed cyclopentanol, behaviour which parallels that of tert-butyl hypobromite[15]) and towards standing (cyclopentanone was formed at ambient temperature overnight in the dark).

In accord with the sequence shown in Equation 2, prompt photolysis of the intermediate resulted in rapid conversion of the intermediate into 5-iodovaleraldehyde,[1] the product expected on the known ß-cleavage behaviour of the cyclopentyloxyl radical[16] and rapid trapping[17] of the resultant 5-oxovaleryl radical by iodine.

Extension of these studies to the reactions of acetyl hypoiodite (from IBDA and iodine) with methanol, ethanol, 1-pentanol, cyclohexanol and 2-propanol similarly resulted in the observation of signals ascribed to the corresponding alkylhypoiodites (δ (αH) = 3.96, 4.35, 4.16, 4.17 and 4.37ppm respectively, i.e. $\Delta \delta$ = -0.50, -0.68, -0.55, -0.47 and -0.37ppm, when compared to the ^{1}H NMR signals for the corresponding alcohols).

The only characterizations of alkyl hypoiodites of which we are aware are the ethyl[18] and tert-butyl[19] cases. For the former, the reported data [δ_H (CH_3 CH_2 OI) = 4.37ppm (from EtOCl/I_2 or EtOCl/MeI] accords well with the spectrum which we obtain from the dark reaction of ethanol with IBDA [vide supra]. The latter species was investigated in considerable detail by Tanner and co-workers.[19] They concluded that different species were formed under different conditions. Our data for reaction of tert-butanol with either IBDA/I_2 or AgOAc/I_2 suggest that these two reactions generate identical tert-butyl hypoiodite [δ_H = 1.30, 1.29ppm; δ_C (methyl) = 30.30, 30.78ppm, respectively for each route, which agrees with Tanner's data for tert-butyl hypoiodite].

While the intermediacy of alkyl and acyl hypoiodites has been repeatedly inferred in reactions of this type, we believe that our observations not only demonstrate the formation of these classes of compounds but also serve to define the mechanistic sequence of events for the Suárez and related reactions.[20] Finally, we note the relationship between the Suárez reaction and an earlier procedure of Beebe et al[21] in which alcohols were reacted, under photolysis, with a solution of acetyl hypoiodite in acetic acid (prepared by reaction of iodine and silver acetate). Consistent with this is our finding that, under the Suárez conditions, 1-pentanol is converted into the same product, 2-methyltetrahydrofuran (yield 89%), as that reported by Beebe et al (yield 80%) under their conditions.

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20. We note that alternative, ionic pathways are open to the reactions of IBDA, particularly in the absence of iodine: see, for example, the reactions with 1,2-glycols (Pausacker K. M., J. Chem. Soc., 1953, 107). Control experiments failed to show corresponding reactions of cyclopentanol under our conditions.

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