A Novel Facile Procedure for the Preparation of Vicinal Phenoxyiodoalkanes from Alkenes by means of Mercury(II) Sulfate and Iodine

C. Georgoulis*, E. Paillasseur, J. M. Valery

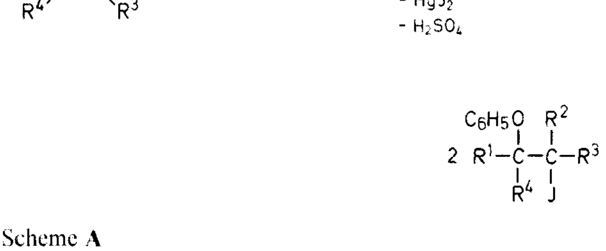
Laboratoire de Cinétique et Mécanismes de Réactions Organiques, C.N.R.S. ER 84, Université Pierre et Marie Curie, 4 Place Jussieu, F-75230 Paris Cedex 05, France

In view of the high yields obtained in the preparation of vicinal alkoxyiodoalkanes by the iododemercuration reaction[1], we undertook to extend the applicability of the method to reagents other than alcohols. We report hereby our results with phenol.

*Intra*molecular phenoxymercuration of 2-allylphenols is well known[2], but phenol itself gives poor results if used in the usual *inter*molecular mercuration procedure. Furthermore, reactions involving olefins, mercury(II) salts, iodine, and nucleophiles used in nearly stoichiometric amount, were shown to lead to difficultly purifiable mixtures. Owing to its specific nucleophilicity, the anion of the mercury(II) salt interferes, even when mercury(II) trifluoroacetate or nitrate are used[3]. Surprisingly, mercury(II) sulfate gives better results, although this reagent is rather employed as a catalyst for effecting additions to acetylenes than for actual mercuration reactions[4].

Moreover, chromatographic monitoring of the reaction progress (T.L.C. over silica gel type H; elution with ether/pentane 1:4) reveals the formation of the 1,2-diiodo derivative followed by its slow disappearance together with the precipitation of mercury(II) iodide. Therefore, it seems unlikely that the reaction proceeds through an organomercury(II) intermediate. It is more probable that the mercury(II) sulfate acts essentially by trapping iodide ions generated by a reversible attack of iodine on the double bond, just as does copper(II) acetate in the previously described alkoxyiodination reaction[5].

The best yields are obtained if mercury(II) sulfate and phenol are used in reasonable excess with reference to alkene and iodine, that is to say according to Scheme A.



Scheme A

As shown in the Table, the transformation leads to good yields with 1,2-disubstituted olefins. Mono- and 1,1-disubstituted alkenes give lower but still interesting yields. The reaction failed with trisubstituted alkenes (e.g. 1-methylcyclohexene) and enol ethers (e.g. dihydropyran). Nevertheless, the method offers a new facile preparation of some vicinal iodophenoxy compounds from common starting materials.

Commercial inorganic and alkenic reagents were used without any further purification, except for cyclohexene which was distillated before use as was chloroform. Vicinal iodo-phenoxy compounds are relatively unstable (decomposition at ~ 180–190°) particularly as "crude" products. So, purification was performed by liquid chromatography (see typical procedure below) rather than by distillation at reduced pressure.

Phenoxyiodination of Cyclohexene; Typical Procedure:

Finely powdered iodine (1.27 g, 5 mmol) is added to a suspension of mercury(II) sulfate (1.05 g, 3.75 mmol) in a mixture of chloroform (15 ml), phenol (0.95 g, 10 mmol), and cyclohexene (0.5 ml, 5 mmol). After 2 h at room temperature under vigorous stirring the precipitate of mercury(II) iodide is filtered off together with excess of mercury(II) sulfate. The filtrate is diluted with chloroform (25 ml) and poured into 2 molar aqueous sodium hydroxide (50 ml) containing potassium tetrahydridoborate (0.5 g, 10 mmol). After 1 h under vigorous stirring, the organic layer is decanted and the above treatment repeated once more. Then, the organic solution is washed twice with water (2 × 50 ml) and dried over sodium sulfate. After evaporation of the chloroform under reduced pressure an oily residue is obtained; yield 1.3 g (85 %). Further purification by column chromatography (Florisil 60/100, elution by ether:

0039-7881/79/0132-0067 $ 03.00

Table. Phenoxyiodinations of Alkenes

Alkene R^1	R^2	R^3	R^4	Yield[a] [%]	m.p. or b.p./torr	Reaction time at r.t.[b]	Molecular formula[c]
C_2H_5	H	H	H	48	106°/0.75	45 min	$C_{10}H_{13}JO$ (276.1)
n-C_3H_7	H	H	H	53	111°/1	90 min	$C_{11}H_{15}JO$ (290.1)
CH_3	H	H	CH_3	40	97°/1	45 min	$C_{10}H_{13}JO$ (276.1)
CH_3	CH_3	H	H	79	98°/1.5	120 min	$C_{10}H_{13}JO$ (276.1)
CH_3	H	CH_3	H	90	103°/1.5	120 min	$C_{10}H_{13}JO$ (276.1)
—$(CH_2)_4$—		H	H	70	40° (7% aqueous methanol)	120 min	$C_{12}H_{15}JO$ (302.1)

[a] Yield of isolated product based on iodine and alkene charged.

[b] Shortened reaction times lead to mixtures containing the 1,2-diiodo derivatives; complex side reactions occur at longer reaction times.

[c] All products gave satisfactory microanalyses (C ±0.35, H ±0.24, J ±0.39).

pentane with the amount of ether being progressively increased from 0 to 10%) affords pure 2-phenoxy-1-iodocyclohexane: yields: 1.05 g (70%); m.p. 40–41° (7% aqueous methanol).

$C_{12}H_{15}JO$	calc.	C 47.70	H 5.01	J 42.03
(302.1)	found	47.57	4.96	42.10

I.R. (KBr): $\nu_{max} = 3040, 1600, 1590, 1235, 755, 695\ cm^{-1}$.

^{1}H-N.M.R. (CCl_4): $\delta = 7.15$ (m, 2H_{atom}); 6.8 (m, 3H_{arom}); 4.3 (m, 2H, C$\underline{H}$J, C$\underline{H}$—O—); 2.5–1.1 ppm [m, 8H, —$(C\underline{H}_2)_4$].

When gaseous substrates are used, the appropriate amount of olefin is bubbled into the phenolic solution before mercury(II) sulfate and iodine are added.

Received: July 24, 1978

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