A Convenient Procedure for the Preparation of Vicinal Alkoxyiodoalkanes from Alkenes by means of Copper(II) Acetate and Iodine

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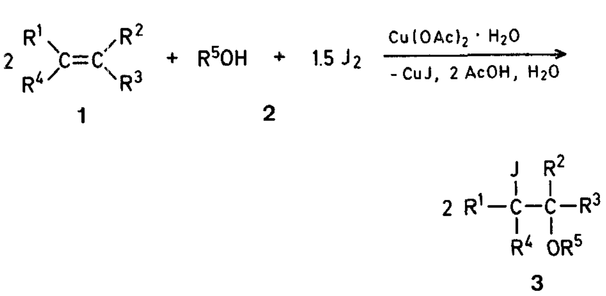
In an earlier publication[1], we reported on the solvomercuration-iododemercuration reaction in the presence of alcohols for conversion of representative alkenes into vicinal alkoxyiodoalkanes in high yields (70–95 %). Although our technique (*in situ* iododemetallation) avoids the necessity for isolation and handling of the organomercury(II) intermediate involved in the procedure, the use of mercury(II) salts may appear as a disadvantage. Thus, we undertook the present work to ascertain whether the same goal could be attained by means of another metallic reagent.

In preliminary experiments, we found that the reaction between cyclohexene and iodine in methanol in the presence of copper(II) acetate monohydrate provided trans-1-iodo-2-methoxycyclohexane in nearly quantitative yield according to Scheme A[2].



Scheme A

The results listed in the Table show that the reaction is of wide applicability. Our technique avoids the use of an excess of any reagent, and, especially in the case of cyclohexene, it appears more efficient than the alkoxyiodination

Table. Alkoxyiodination of Olefins According to Scheme A

Alkene R^1	R^2	R^3	R^4	Solvent R^5—OH	Yield[a] [%]	b.p./torr	Lit. b.p. torr	Molecular formula[b]
—$(CH_2)_4$—		H	H	H_3C—OH	93 (53)[3]	80°/1	100°/20[3]	$C_7H_{13}JO$ (240.1)
—$(CH_2)_4$—		H	H	H_3C—CO—OH	99	91°/1	120°/12[6]	$C_8H_{13}JO_2$ (268.1)
—$(CH_2)_4$—		H	H	C_6H_5—CH_2—OH	90	148°/1	—	$C_{13}H_{17}JO$ (316.2)
—$(CH_2)_4$—		H	H	(*E*)-H_3C—CH═CH—CH_2—OH	29	103°/1	—	$C_{10}H_{17}JO$ (280.2)
—$(CH_2)_4$—		H	H	H_2C═CH—CH(CH_3)—OH	29	96°/1	—	—
—$(CH_2)_3$—		H	H	H_3C—OH	97	65°/1		$C_6H_{11}JO$ (226.1)
—$(CH_2)_3$—		H	H	C_6H_5—CH_2—OH	95	129°/1	—	$C_{12}H_{15}JO$ (302.2)
—$(CH_2)_3$—		H	H	H_2C═CH—CH(CH_3)—OH	30	85°/1 (dec.)	—	$C_9H_{15}JO$ (267.0)
C_6H_5	H	H	H	H_3C—OH	90 (91–94)[3]	91°/1	94.5°/3[3]	—
C_6H_5	H	H	H	H_2C═CH—CH(CH_3)—OH	24[c]	—	—	—
H	H	H	OCH_3	H_3C—OH	72[d]	37°/1	—	$C_4H_{10}JO_2$ (217.0)
H	H	H	OCH_3	C_6H_5—CH_2—OH	40[d]	110°/1	—	$C_{10}H_{13}JO_2$ (292.1)
—$(CH_2)_3$—O—		H	H	H_3C—OH	60	85°/1	—	$C_6H_{11}JO_2$ (242.1)
—$(CH_2)_3$—O—		H	H	H_2C═CH—CH(CH_3)—OH	75	95°/1 (dec.)	—	$C_9H_{15}JO_2$ (282.1)
—$(CH_2)_3$—O—		H	H	(*E*)-H_3C—CH═CH—CH_2—OH	70	105°/1	—	$C_9H_{15}JO_2$ (282.1)

[a] Yield of isolated product based on all reagents charged according to Scheme A.
[b] All products gave satisfactory microanalyses (C ±0.37 %, H ±0.22 %, J ±0.38 %).
[c] Product contains a trace of styrene.
[d] Yield based on iodine charged.

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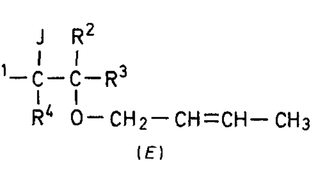
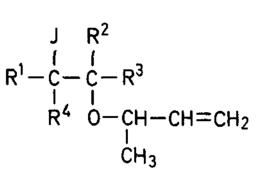
method previously reported by Onoe et al.[3]. The latter reaction is similar to that described by Baird et al.[4] for the preparation of chloroiodoalkanes using copper(II) chloride, metal iodides, and alkenes.

We have previously suggested[2] that, in the alkoxyiodination by means of iodine and copper(II) acetate, the transformation may start by a reversible electrophilic attack of iodine on the double bond. The copper(II) acetate acts essentially by trapping iodide ions, thus allowing exclusive subsequent reaction between the solvent and the iodonium intermediate without formation of the 1,2-diiodo derivative. If this is the case, the reaction may exhibit, owing to the low electrophilic power of iodine, some sensitivity towards the nature of the carbon-carbon double bond. In fact, the transformation can even be conducted successfully in unsaturated solvents such as α,β-unsaturated (allylic) alcohols. The yields obtained in this way are, however, lower than those obtained in methanol except when a very reactive substrate such as dihydropyran is used.

Nevertheless the method offers a facile one pot route from common alkenic materials to vicinal unsaturated alkoxyiodoalkanes of type **A** or **B**.


$R^1-C(J)(R^4)-C(R^2)(R^3)-O-CH_2-CH=CH-CH_3$ (E)

A


$R^1-C(J)(R^4)-C(R^2)(R^3)-O-CH(CH_3)-CH=CH_2$

B

Commercial inorganic reagents and alkenic starting materials were used without any purification, except for cyclohexene which was distillated before use, as were the various solvents. Vicinal iodo alkoxy compounds may be unstable[5]. *Crude* products must not be heated at temperatures higher than 40° in order to avoid decomposition. Therefore purification was accomplished by chromatography (column: Florisil 60/100, eluent: pentane) rather than by distillation at reduced pressure.

Alkoxyiodination of Dihydropyran in (*E*)-2-Buten-1-ol; Typical Procedure:

Finely powdered iodine (1.9 g, 7.5 mmol) is added to a green solution of copper(II) acetate monohydrate (1.0 g, 5 mmol) and dihydropyran (1.1 ml, 10 mmol) in 2-buten-1-ol (10 ml). The mixture is allowed to stand for 15 h at room temperature under vigorous stirring, then the white precipitate of copper(I) iodide (0.9 g, 4.7 mmol) is filtered off. The filtrate is diluted with pentane (100 ml) and washed first with 5% aqueous sodium hydrogen carbonate (25 ml) then twice with water (2 × 25 ml). After drying with calcium chloride and evaporation of the pentane under reduced pressure an oily residue is obtained; yield: 2.87 g (100%). Purification by column chromatography (Florisil 60/100, elution by pentane) affords pure 2-butenyloxy-3-iodotetrahydropyran; yield: 1.95 g (70%)

$C_9H_{15}JO_2$	calc.	C 38.31	H 5.36	J 44.98
(282.1)	found	38.12	5.25	45.17

I.R. (CCl_4): $\nu_{max}=3010, 1670, 1355, 1020, 965\ cm^{-1}$.

^{1}H-N.M.R. (CCl_4): $\delta=5.60$ (m, 2H, CH=CH); 4.65 (d, 1H, O—CH—O, $J=4$ Hz); 4.10–3.30 (m, 5H, O—CH_2—C=C, >CH̲J, CH_2—$C\underline{H}_2$—O); 2.10–1.30 ppm (m, 7H, $C\underline{H}_3$—C=C, $C\underline{H}_2C\underline{H}_2$).

Saturation with potassium carbonate of the combined aqueous extracts and decantation affords 5–7 ml of recovered crude butenol.

When methanol is used instead of an allylic alcohol, the solvent is evaporated under reduced pressure after complete reaction (the reaction time may be reduced to 3 hours at 50°) and separation of copper(I) iodide precipitate by filtration. The green residual oil is triturated with pentane (50–70 ml) in order to eliminate traces of unconsumed copper(II) salt. Further filtration and evaporation gives the methoxyiodo product.

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