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SYNTHESIS OF β-IODO-*t*-BUTYL AND METHYL ETHERS FROM THE REACTION OF ALKENES WITH *t*-BUTYL AND METHYL HYPOIODITES

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Abstract: *t*-Butyl or methyl hypoiodite, generated from potassium t-butoxide or sodium methoxide and iodine monochloride, react with olefins via a bridged iodonium ion intermediate giving the *trans*-vicinal iodo -*t*-butyl or -methyl ethers.

Recent interest in the olefin addition reactions of alkyl[1,2] and acyl[3,4] hypohalites has prompted us to examine the reaction of *t*-butyl hypoiodite with alkenes. Recent methods for the synthesis of vicinal iodo ethers from alkenes involve either the solvation of a bridged iodonium ion species or alkoxy-metallation followed by reaction with iodide salts. Neither method appears to be suitable for the formation of β-iodo-t-butyl ethers[5,6,7,8]. Walling and Clark have synthesised β-chloro-*t*-butyl ethers by the addition of *t*-butyl hypochlorite to cold olefin-alcohol mixtures containing boron trifluoride etherate[1].

We have found that *t*-butyl hypoiodite can be conveniently prepared by the addition of iodine monochloride to a slight excess of potassium-*t*-butoxide in *t*-butanol or benzene (reaction 1) (carbon tetrachloride may be used as solvent if the order of addition is reversed)[9] and that it reacts both regio- and stereospecifically with a number of olefins in the dark (Table 1).

$$Bu^tOK + ICl \longrightarrow Bu^tOI + KCl \;\ldots\ldots\; 1.$$

Trans addition of *t*-butyl hypoiodite to cyclohexene, cyclopentene[10] and indene was established by n.m.r. spectroscopy and the *trans* adduct (1) from (E)-methyl-*p*-methoxy cinnamate was identified by X-ray crystallography[11]. (Z)-methyl-*p*-methoxycinnamate rapidly isomerises to the (E)-form under the reaction conditions, prior to hypoiodite addition.

Table 1

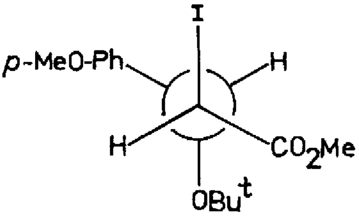
Substrate	Reaction Conditions[a]	Addition Product	Yield % (isolated)
Cyclohexene	t-butanol	trans-2-iodocyclohexyl-t-butyl ether	58
Cyclopentene	t-butanol	trans-2-iodocyclopentyl-t-butyl ether	28
Indene	t-butanol	trans-1-t-butoxy-2-iodoindane	62
Indene	r.t;t-butanol	trans-1-t-butoxy-2-iodoindane	64
Styrene	t-butanol	2-t-butoxy-2-phenyl-ethyl iodide	100
Styrene	r.t;t-butanol	2-t-butoxy-2-phenyl-ethyl iodide	90
Styrene	benzene	2-t-butoxy-2-phenyl-ethyl iodide	45
1-Octadecene	t-butanol	2-t-butoxyoctadecyl iodide 2-iodooctadecyl t-butyl ether	42 17
(E)-methyl-p-methoxycinnamate	t-butanol	erythro[c]-methyl-3-t-butoxy 3-(p-methoxyphenyl)-2-iodo-propionate (m.p. 76-78°)	38 [b]
(Z)-methyl-p-methoxycinnamate	t-butanol	erythro[c]-methyl-3-t-butoxy 3-(p-methoxyphenyl)-2-iodo-propionate	76 [b]
(E)-methylcinnamate	t-butanol	-	-
(E)-Stilbene	t-butanol	-	-

[a] Solvent at reflux temperature unless otherwise stated; Bu^tOI: alkene = 5:1.

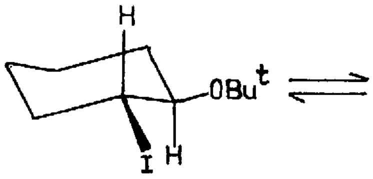
[b] Different reaction times.

[c] The term erythro, although not strictly applicable, is used for clarity.

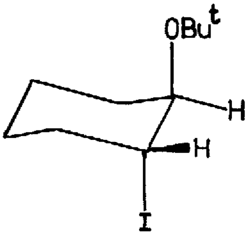
The n.m.r. spectrum of trans-2-iodocyclohexyl-t-butyl ether displayed a well defined 6-spin multiplet (τ5,6 CHI) with an unusually small vicinal coupling, $J_{1,2}$ = 7Hz[5]. This can be ascribed to either a deformation of the ring or an averaging out effect of the diequatorial and diaxial chair conformations (2) and (3). Conformer (3) would relieve both dipolar and steric interaction between the



(1)



(2)



(3)

bulky t-butoxyl and iodine substituents.

The Markovnikov and anti-Markovnikov products from 1-octadecene were identified from their mass spectra since their n.m.r. spectra displayed considerable complexity due to the asymmetric environment of the terminal methylene protons.

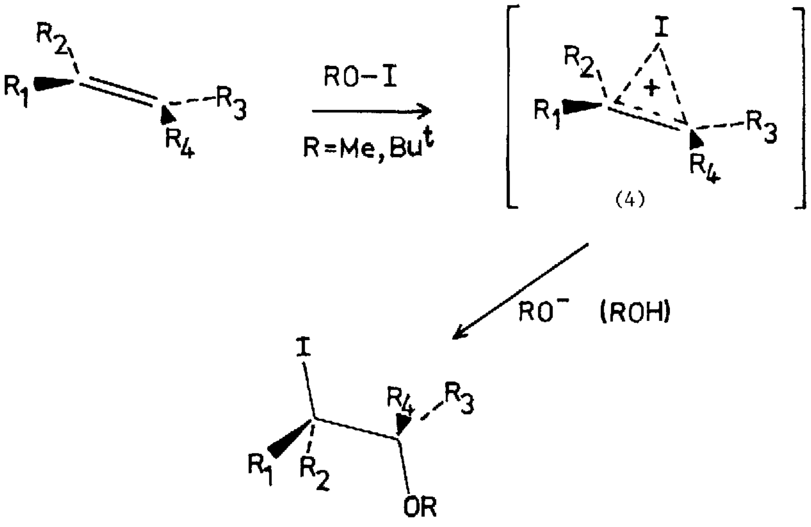
The failure to form adducts from both stilbene and methyl-cinnamate indicates that the reaction is not suitable for deactivated olefins. t-Butyl hypochlorite behaves similarly[1]. The possibility of steric restrictions cannot however be ruled out in the case of stilbene.

Preliminary results show that β-iodo-methyl ethers can be prepared by the reaction of olefins with what we have formally designated as solutions of methyl hypoiodite in methanol (prepared by successive addition of sodium hydride and iodine monochloride) (Table 2).

Table 2

Substrate	Reaction Conditions[a]	Addition Product	Yield % (isolated)
Styrene	MeOH	2-methoxy-2-phenyl ethyl iodide	85
Indene	MeOH	trans-1-methoxy-2-iodo-indane	73
1-Octadecene	MeOH	2-methoxyoctadecyl iodide	45
Cyclohexene	MeOH	trans-2-iodocyclohexyl methyl ether[5]	73

[a] Solvent at reflux temperature; MeOI : alkene = 5:1.



The stereospecific nature of these additions as well as a comparison of the products from t-butyl hypoiodite and methyl hypoiodite with 1-octadecene suggests that the reaction takes place via a bridged iodonium ion species (4).

In the case of octadecene, attack at the 2-position of (4, $R_1 = R_2 = R_3 = H$, $R_4 = C_{16}H_{33}$) is easier for methoxide than t-butoxide, which in addition reacts to some extent at the less hindered terminal carbon.

Acknowledgement

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