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Preliminary communication

PEROXYMERCURATION WITHOUT ACCOMPANYING ACYLOXYMERCURATION

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Summary

With mercuric trifluoroacetate and t-butyl hydroperoxide in dichloromethane, olefins react under peroxymercuration without accompanying acyloxymercuration.

The reaction of mercuric acetate and t-butyl hydroperoxide with monosubstituted ethylenes in dichloromethane (eqn.1) was recently developed to provide the basis of an improved route to sec-alkyl-t-butyl peroxides [1,2]. The reaction proceeds rapidly and in high yield at room temperature, but even using a one-fold excess of hydroperoxide, affords products containing up to 20% of acetoxymercurial (I)

$$\begin{aligned}&\mathrm{RCH{=}CH_2 + Hg(OAc)_2 + t\text{-}BuOOH} \xrightarrow{\mathrm{CH_2Cl_2}} \\ &\qquad \mathrm{RCH(OOBu\text{-}t)CH_2HgOAc + HOAc} + \underset{\textstyle (\mathrm{I})}{\mathrm{RCH(OAc)CH_2HgOAc}}\end{aligned} \qquad (1)$$

$$\mathrm{RCH(OOBu\text{-}t)CH_2HgOAc} \begin{cases} \xrightarrow{\mathrm{NaBH_4}} \underset{\textstyle (\mathrm{II})}{\mathrm{RCH(OOBu\text{-}t)CH_3}} \\[2ex] \xrightarrow{\mathrm{Hal_2}} \underset{\textstyle (\mathrm{III})}{\mathrm{RCH(OOBu\text{-}t)CH_2Hal}} \end{cases} \qquad (2)$$

We have extended reaction (1) to 1,2-disubstituted ethylenes such as 2-butene and cyclohexene, but here competitive acetoxymercuration consumes an even higher proportion of alkene (ca. 30%). For small scale preparations of compounds (II) and (III) the acetoxymercurial (I) has to be removed before the demercurations (eqn.2) are carried out [2]. This is time-consuming and leads to reduced overall yields.

It was shown previously that replacing mercuric acetate by trifluoroacetate in reactions with alkenes in alcohols leads to greatly improved yields of t-butoxymercuration products [3]. We now wish to report that, by a similar replacement, peroxymercuration can be carried out under the usual conditions [4] without accompanying acyloxymercuration (eqn.3); this greatly enhances the synthetic value of peroxymercuration.

$$\mathrm{RCH{=}CHR^1 + Hg(OCOCF_3)_2 + t\text{-}BuOOH \xrightarrow{CH_2Cl_2} \underset{(IV)}{RCH(OOBu\text{-}t)CHR^1HgOCOCF_3} + HOCOCF_3} \tag{3}$$

Reaction (3) has been carried out with ethylene, propene and styrene ($R^1 = H$), with *cis*- and *trans*-2-butene and *trans*-3-hexene and with cyclohexene and norbornene ($R^1 = R$) to give compounds IV (about 85%) which require little or no purification. Treatment of compounds IV with potassium halide gives the corresponding organomercury halides which for the monosubstituted ethylene and cyclohexene[*] derivatives were identified by comparison with authentic samples [2,5]. Peroxymercurials derived from the other alkenes are new and have been characterised either as the trifluoroacetate or as the halides by satisfactory elemental analyses and by ^1H NMR spectroscopy.

The absence of the trifluoroacetoxymercurial [$RCH(OCOCF_3)CHR^1HgOCOCF_3$] in the crude products was apparent from their high gain ^1H NMR spectra which showed no $CHOCOCF_3$ resonances. This held for the *cis*-2-butene derivative even when an excess of only 10% of t-butyl hydroperoxide was used, suggesting that mercuric trifluoroacetate has the added advantage of reducing wastage of hydroperoxide. This conclusion must be regarded with some caution, however, since a reaction with norbornene employing an excess of 5% of t-butyl hydroperoxide afforded a product containing 25% of trifluoroacetoxymercurial.

Another useful contrast with mercuric acetate is that the trifluoroacetate is completely soluble in dichloromethane under the usual working conditions (20 mmol in 30 ml). This has enabled a smooth reaction to be carried out with insoluble hydroperoxides (e.g. eqn.4) [6] and may provide an opportunity to study poorly soluble alkenes.

$$\mathrm{PhCH(OOH)CH_2HgOAc \xrightarrow[(ii)\ KCl]{(i) PhCH{=}CH_2 + Hg(OCOCF_3)_2} [PhCH(CH_2HgCl)O]_2} \tag{4}$$

A final aspect of employing mercuric trifluoroacetate is that the cleanness of the peroxymercuration of *cis*- and *trans*-2-butene permits a clear demonstration by ^1H NMR spectroscopy that these reactions are stereospecific.

References

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[*] Schmitz et al. [5] quote τ 5.1m for the CHOO resonance of the cyclohexene peroxymercurial but we find τ 5.9m for this and τ 5.1m for the CHOAc resonance of the acetoxymercurial.