

Preliminary communication

**PEROXYMERCURATION WITHOUT ACCOMPANYING  
 ACYLOXYMERCURATION**

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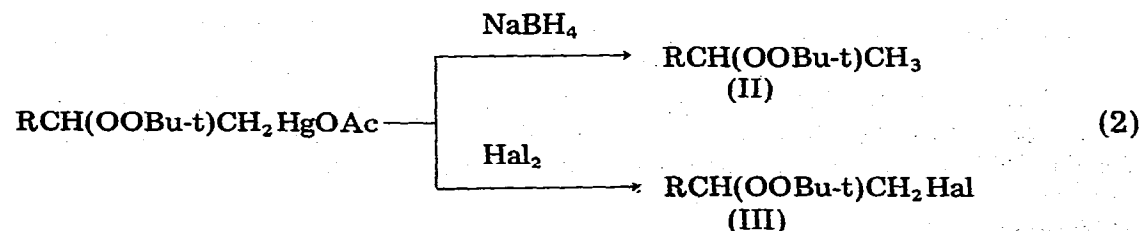
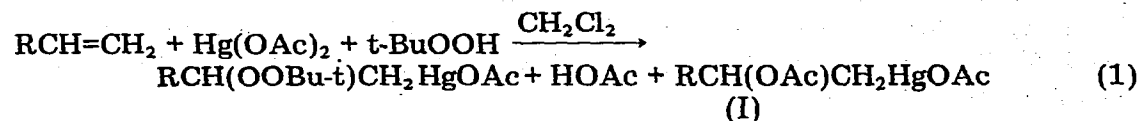
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Summary

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

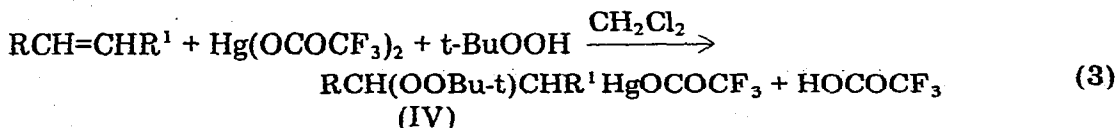
The reaction of mercuric acetate and t-butyl hydroperoxide with mono-substituted ethylenes in dichloromethane (eqn.1) was recently developed to provide the basis of an improved route to sec-alkyl-t-butyl peroxides [1,2]. The reaction proceeds rapidly and in high yield at room temperature, but even using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



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-butoxy-

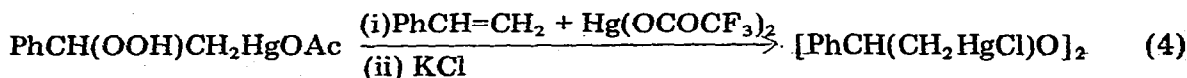
mercuration products [3]. We now wish to report that, by a similar replacement, peroxymercuration can be carried out under the usual conditions [4] without accompanying acyloxymercuration (eqn.3); this greatly enhances the synthetic value of peroxymercuration.



Reaction (3) has been carried out with ethylene, propene and styrene ( $\text{R}^1 = \text{H}$ ), with *cis*- and *trans*-2-butene and *trans*-3-hexene and with cyclohexene and norbornene ( $\text{R}^1 = \text{R}$ ) 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  $^1\text{H}$  NMR spectroscopy.

The absence of the trifluoroacetoxymercurial [ $\text{RCH}(\text{OCOCF}_3)\text{CHR}^1\text{HgOCOCF}_3$ ] in the crude products was apparent from their high gain  $^1\text{H}$  NMR spectra which showed no  $\text{CHOCOCF}_3$  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.



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  $^1\text{H}$  NMR spectroscopy that these reactions are stereospecific.

## References

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- 3 H.C. Brown and M.-H. Rei, J. Amer. Chem. Soc., 91 (1969) 5646.
- 4 A.J. Bloodworth and G.S. Bylina, J. Chem. Soc. Perkin I, (1972) 2433.
- 5 E. Schmitz, A. Reiche and O. Brede, J. Prakt. Chem., 312 (1970) 30.
- 6 A.J. Bloodworth and M.E. Loveitt, unpublished work.

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