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Preliminary communication

SYMMETRISATION OF β-ALKOXYALKYLMERCURY(II) ACETATES

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Summary

β-Alkoxyalkylmercury(II) acetates have been symmetrised in situ with alkaline sodium stannite to afford good yields of bis(β-alkoxyalkyl)mercurials, $[R^1R^2C(OR)CHR^3]_2Hg$.

Symmetrisation (eq.1) is preparatively important in organomercury chemistry, because although the principal methods for making Hg—C bonds readily

$$2RHgX \rightarrow R_2Hg + [HgX_2] \qquad (1)$$

afford organomercury(II) salts, they are much less successful in providing the di(organo)mercurials [1]. This is particularly so in oxymercuration (eq.2),

$$R^1R^2C{=}CHR^3 + HgX_2 + ROH \rightarrow R^1R^2C(OR)CHR^3HgX + HX \qquad (2)$$

where further uptake of alkene to give the bis(β-oxyalkyl)mercury(II) rarely occurs. Yet reports of the symmetrisation (eq.3) of oxymercurials are sparse.

$$2R^1R^2C(OR)CHR^3HgX \rightarrow [R^1R^2C(OR)CHR^3]_2Hg + [HgX_2] \qquad (3)$$

Those that exist often relate to compounds derived from typical alkenes (e.g. norbornene [2, 3], chalcone [4], and mesityl oxide [4]) and the conditions used vary widely. No general method has been reported, probably because oxymercurials and many of the common symmetrising agents react by alternative pathways. Symmetrisation is usually brought about by the action of reducing agents or of compounds that form strong complexes with mercury(II) salts. Treatment of oxymercurials with such reagents often leads to regeneration of the alkene and/or to hydrogenodemercuration.

We find that sodium stannite can be used under the conditions described below to symmetrise a wide range of β-alkoxyalkylmercury(II) acetates. Considering the established versatility of sodium stannite as a symmetrising agent, it is surprising that its previous use [5, 6] with these compounds is virtually unknown.

The symmetrisations (eq.4) were carried out in situ on freshly prepared organomercury acetates using the following procedure. Mercury(II) acetate (10 mmol) was added to a stirred solution of alkene (10 mmol; excess for a diene or gas) in methanol (30 cm^3). After 5 to 10 min when the methoxymercuration was complete (negative NaOH test for Hg^{2+}), dichloromethane (150 cm^3) and a solution of $SnCl_2 \cdot 2H_2O$ (4 g) and NaOH (8 g) in H_2O (50 cm^3) were added simultaneously over 1—2 min, and the resulting mixture was stirred for 30 minutes. The dichloromethane layer was separated and the aqueous layer extracted with more dichloromethane (70 cm^3). The combined dichloromethane solution was filtered through anhydrous K_2CO_3 and the solvent removed at 12 then 0.1 mmHg to afford the dialkylmercurial.

$$R^1R^2C{=}CHR^3 \xrightarrow[\text{MeOH}]{Hg(OAc)_2} R^1R^2C(OMe)CHR^3HgOAc \xrightarrow[\text{NaOH}]{SnCl_2} [R^1R^2C(OMe)CHR^3]_2Hg \qquad (4)$$

Products were often obtained analytically pure at this stage. Yields varied from 91 to 54% but were usually>75%. In this way bis(β-methoxyalkyl)mercurials have been obtained from the following alkenes: ethene, propene, 2-methylpropene, *cis*-but-2-ene, *trans*-but-2-ene, cyclopentene, hex-1-ene, cyclohexene, 1-methylcyclohexene, styrene, 2-phenylpropene, 1,1-diphenylethene, buta-1,3-diene, penta-1,3-diene, hexa-1,5-diene, methyl vinyl ether, diallyl ether, and 3-oxacyclohexene. The ethoxymercurials, $[R^1CH(OEt)CHR^2]_2Hg$, derived from ethene, *trans*-but-2-ene, cyclohexene and ethyl vinyl ether, and the compound, $(i\text{-}PrOCH_2CH_2)_2Hg$, were prepared in a similar way.

The new dialkylmercurials are colourless oils except for that (m.p. 50—52°C) from styrene, that (m.p. 60—61°C) from 2-phenylpropene, and that (m.p. 126—128°C) from 1,1-diphenylethene which are white solids. The structures were established by a combination of satisfactory elemental analyses, consistent ^1H and proton-decoupled ^{13}C NMR spectra (including the observation of appropriate satellites arising from coupling with naturally occurring ^{199}Hg nuclei), and quantitative conversion to the known organomercury chlorides by reaction with mercury(II) chloride (eq.5).

$$[R^1R^2C(OR)CHR^3]_2Hg + HgCl_2 \rightarrow 2R^1R^2C(OR)CHR^3HgCl \qquad (5)$$

The bis(β-methoxyalkyl)mercurials derived from hex-1-ene and 3-oxacyclohexene and the compound $[(EtO)_2CHCH_2]_2Hg$ were further characterised by mass spectrometry; prominent M^+ and $(M-OR)^+$ ions were observed for each.

Bis(β-alkoxyalkyl)mercurials derived from monosubstituted ethenes ($R^2 = R^3 = H$) and from 2-phenylpropene should be obtained as mixtures of diastereoisomers (*meso* and *dl*), but this could not be detected. However, in the ^{13}C NMR spectra of products derived from the medial alkenes, signals arising from the *dierythro*-, *dithreo*-, and *erythro,threo*-stereoisomers could be distinguished.

We are currently investigating the chemistry of these new dialkylmercurials.

Photolysis (eq.6) of solutions of them in cyclopropane at −40°C provides a convenient method of generating the β-alkoxyalkyl radicals for study by ESR spectroscopy.

$$[R^1R^2C(OR)CHR^3]_2Hg \xrightarrow{h\nu} R^1R^2C(OR)\dot{C}HR^3 \qquad (6)$$

Our main interest is in developing reactions unavailable to the parent organomercury acetates that will extend the synthetic value of oxymercuration.

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