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Preliminary communication

SKELETAL REARRANGEMENT IN THE METHOXYMERCURATION OF 2-METHYL-3-ARYLBUT-1-ENE-3-OLS

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Summary

Skeletal rearrangement in solvomercuration of olefins has been found to be dependent on the polarity of the Hg—X bond.

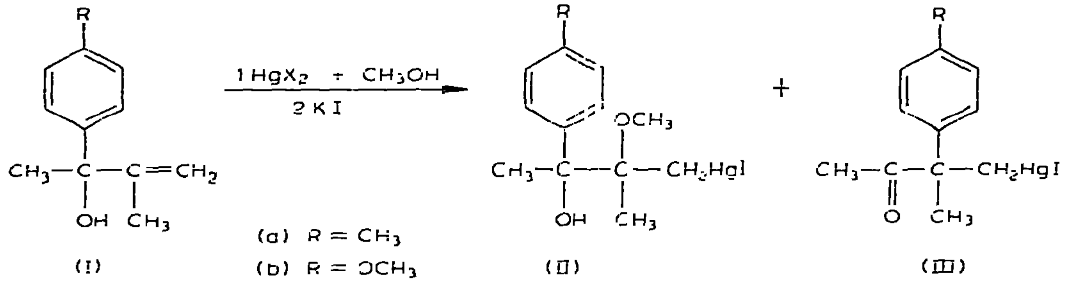
Electrophilic addition of mercuric salts to olefins has been the subject of a large number of investigations [1-5]. The usual products of this reaction are the 1,2-solvomercurials, and skeletal rearrangements are extremely rare [6, 7]. Even the methoxymercuration of norbornene proceeds substantially without the rearrangement taking place [4, 5].

However one important question may be put forward: does the occurrence of a rearrangement depend on the polarity of the Hg—X bond in the electrophilic agent? There is no answer to this question although many investigations have been devoted to the study of the utilization of different mercuric salts in the solvomercuration reaction. It is only known that both the rate of oxymercuration [1] and the rate of solvolytic decomposition of oxymercurials [8] increase with increasing ionic character of the Hg—X bond. Usually either mercuric acetate, trifluoroacetate or aqueous perchlorate has been used for the oxymercuration, each giving approximately the same result. For methoxymercuration mercuric acetate has been used almost exclusively: however, Bach [9] observed that a stereoselectivity of ethoxymercuration of 1,2-cyclononadiene was dependent on the mercuric salt used.

Our interest in electrophilic addition [10-12] and rearrangements [13-17] led us to investigate the problem of the skeletal rearrangement in the solvomercuration using 2-methyl-3-arylbut-1-ene-3-ols (I) as a model compound. In previous papers we have shown that these models are extremely suitable for investigation of the rearrangement [13, 14, 17].

We have employed the standard procedure which involved mixing alkenols I with the mercuric salt in methanol at room temperature.

The starting concentrations of the reagents were 0.1 mol/l. Mercurials were precipitated by the addition of an aqueous solution of potassium iodide. Products were identified by their IR and NMR spectra. Ketones III were additionally characterised by their dinitrophenylhydrazine (DNPH) derivatives (DNPH of IIIa m.p. 193°; DNPH of IIIb m.p. 162°). For all compounds acceptable analytical data were obtained.



Reaction of mercuric acetate with Ia gives only methoxymercurial IIa (94% yield, m.p. 112°). Only unrearranged product IIb (35% yield, m.p. 102°) was obtained in the reaction of mercuric acetate with Ib. However, the reactions of alkenols I with mercuric nitrate (IV) and mercuric perchlorate (V) in methanol occurred in a completely different manner, and produced ketones III via a 1,2-aryl shift. Ketone IIIa (m.p. 107°) was prepared in 35 and 40% yields from the reactions between alkenol Ia and mercuric salts IV and V, respectively. Analogously, addition of IV and V to the alkenol Ib produced ketone IIIb (m.p. 91°) in 78 and 80% yields respectively.

Two important conclusions may be drawn from the above data. Skeletal rearrangement in solvomercuration of olefins should decrease with (i) decreasing polarity of the Hg—X bond ($Hg-ClO_4 \geqslant Hg-NO_3 \gg Hg-OAc$) and (ii) decreasing nucleophilicity of the migrating group ($CH_3OC_6H_4 > CH_3C_6H_4$).

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