Tetrahedron Letters, Vol.22, No.23, pp 2239 - 2240, 1981
Printed in Great Britain

0040-4039/81/232239-02$02.00/0

MERCURY(II) OXIDE/TETRAFLUOROBORIC ACID.[1] AN UNUSUAL BEHAVIOR IN THE OXIDATION OF ALKENES. SYNTHESIS OF *trans*-CINNAMYLETHERS

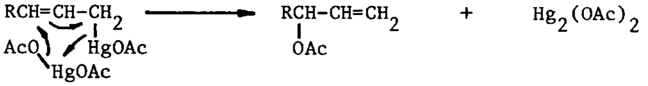
José Barluenga*, Luisa Alonso-Cires and Gregorio Asensio

Departamento de Química Orgánica. Facultad de Ciencias,
Universidad de Oviedo. Oviedo, Spain

Abstract: The synthesis of *trans*-cinnamylethers by oxidation of allylbenzene is described. The reaction cannot be explained by formation of an allylic mercurial. A new type of mechanism in the oxidation of alkenes by mercury(II) salts is proposed.

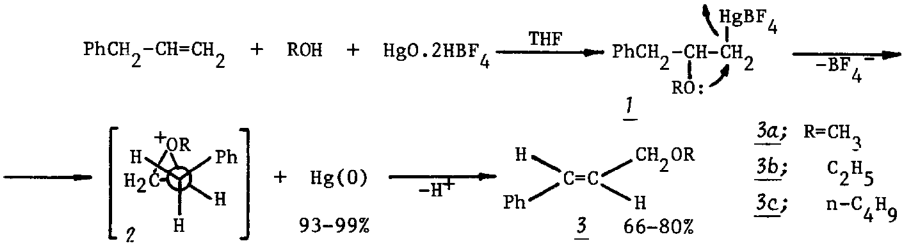
Oxidation of olefins with mercuric salts, usually sulfate, nitrate and acetate, has been extensively studied and is the subject of several recent review articles.[2] Typical oxidations are the Denigès[2b] and the Treibs[3] reactions in which alkenes are converted into α,β-unsaturated carbonyl compounds or allylic esters respectively.

A large number of reactions take place with these oxidants and the nature of the products depends on factors such as the structure of the alkene, the reaction media, the reaction time[4] and the type of acid from which the mercuric salt derives. Kinetic studies by Rappoport et al.[4] demonstrate that the allylic mercuric acetates are the most plausible intermediates in the allylic oxidation by mercuric acetate. Results of the oxidation of ^{13}C-labelled propene with mercuric sulfate in aqueous media are also consistent with a mechanism which involves an intermediate allylic mercurial.[2b,5]



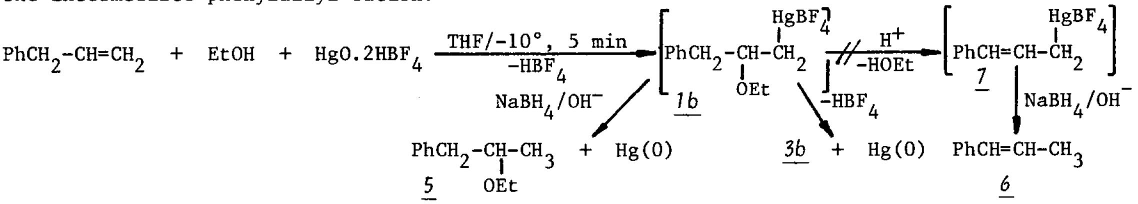
$$\underset{\mathrm{AcO}\quad \mathrm{HgOAc}\quad \mathrm{HgOAc}}{\mathrm{RCH{=}CH{-}CH_2}} \longrightarrow \underset{\mathrm{OAc}}{\mathrm{RCH{-}CH{=}CH_2}} + \mathrm{Hg_2(OAc)_2}$$

We have found that allylbenzene reacts with mercury(II) oxide/tetrafluoroboric acid[6] and alcohols in THF to give exclusively *trans*-cinnamylethers 3. The reaction may be explained through the intramolecular displacement of the mercury by the alkoxy group in an intermediate oxymercurial 1 followed by the loss of a benzylic proton in 2.



3a;	R=CH$_3$	3d;	n-C$_5$H$_{11}$
3b;	C$_2$H$_5$	3e;	i-C$_3$H$_7$
3c;	n-C$_4$H$_9$	3f;	i-C$_4$H$_9$
		3g;	C$_6$H$_{11}$

The presence of 3-alkoxy-3-phenylpropene *4* could not be detected in the reaction mixture in any case independently of the reaction time or temperature. This fact, as well as the stereospecific nature of the process can hardly be explained by a mechanism involving an intermediate allylic mercurial. Moreover, when the mercuration with ethanol is carried out at -10°C and the reaction mixture "*in situ*" reduced after 5 min upon treatment with a solution of sodium borohydride in potassium hidroxide, affords a mixture of *3b* and 2-ethoxy-1-phenylpropane *5* but the presence of 1-phenylpropene *6* is not detected. It clearly shows the rapid formation of an intermediate 2-alkoxy-3-phenylpropylmercury(II) tetrafluoroborate *1b* which decomposes even at -10°C but not through the formation of an allylic mercurial *7*. This could results from the acid promoted loss of ethanol and would lead to 1-phenylpropene *6* or allylbenzene by reduction. At this low temperature and short reaction time the possibility of a total isomerization of *4b* to *3b* should, at first, be discarded. This is also supported by the lack of rearranged products from the intermediate phenylallyl cation.[7]



The mechanism suggested by us is in good agreement with the *trans*-stereospecific character of the oxyamination of alkenes promoted by mercury(II) oxide/tetrafluoroboric acid.[1] On the other hand, the mercuration-demercuration of allylbenzene in the presence of stronger nucleophiles, i.e. aromatic amines, does not afford monoamination compounds, but 1,2-diamino-3-phenylpropane derivatives.[6]

Preparation of *3a*. Typical Experimental Procedure

To a solution of allylbenzene (4.7 g, 40 mmol) and methanol (1.9 g, 60 mmol) in THF (40 mL) was added $HgO.2HBF_4$ (7.5 g, 20 mmol). The reaction was stirred under reflux for 2 h and then cooled. The mercury(0) precipitated was filtered off (3.7 g, 93%) and the solution hydrolyzed with 3N aqueous potassium hydroxide (15 mL) and extracted with ether (3 x 20 mL) and dried. Solvents are removed and the residue distilled under vacuum to yield *3a* (2.1 g, 71%) (b.p. .01torr 65-70°C). I.r. film ν_{max} 1100 (CO); 740, 790, 3020 (arom) cm^{-1}. ^1H N.m.r. ($CDCl_3$) δppm 3.35 (s, 3H), 4.1 (d 6Hz, 2H), 6.2 (d 16Hz, t 6Hz, 1H), 6.6 (d 16Hz, 1H), 7.1-7.6 (m, 5H). ^{13}C N.m.r. ($CDCl_3$) δppm 57.1 (q), 71.9 (t), 125.9 (d, C=C), 131.6 (d, C=C), 125.9 (d), 126.9 (d), 127.9 (d), 136.6 (s).

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(Received in UK 7 April 1981)