Acetoxymercuration of Alkylphenylacetylenes

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Summary Acetoxymercuration of alkylphenylacetylenes proceeds completely in a *trans* fashion to give an isomeric mixture of two vinylmercury(II) compounds, the extent of attack of Hg at the carbon α to alkyl group being increased upon increasing the carbon chain length of the alkyl group.

Although oxymercuration of acetylenes is well known, its stereochemistry has not yet been thoroughly studied.[1] Thus, acetoxymercuration of diphenylacetylene with $Hg(OAc)_2$ gave completely the *cis*-adduct,[2] while dimethylacetylene afforded the *trans*- and *cis*-adducts, their ratios depending on the temperature.[1,3] Furthermore, no data are yet available on the regiospecificity of oxymercuration of unsymmetrical acetylenes. In order to study both the stereo- and the regio-specificity of oxymercuration of acetylenes we carried out acetoxymercuration of alkylphenylacetylenes and found that it proceeds completely in a *trans*-fashion, in sharp contrast to the *cis*-acetoxymercuration of diphenylacetylene;[2] attack of Hg at the carbon α to alkyl group is increased markedly by increasing the length of the carbon chain of the alkyl group.

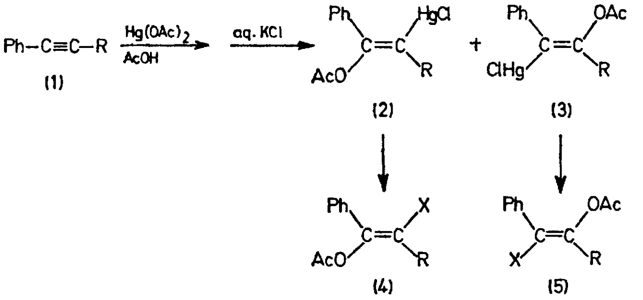
Reaction of the alkylphenylacetylene (**1**) with $Hg(OAc)_2$ [(**1**)$:Hg(OAc)_2 = 2:1$] in acetic acid at 55—60° for 5 h, followed by treatment of the resulting mixture with aqueous KCl, produced an isomeric mixture of (**2**) and (**3**) in 44—96% yield. Under these conditions formation of oxidation products such as ketone and ester was negligible. Although the yields of (**2**) + (**3**) were somewhat lower for (**1**) when R = Pr^{n} and Bu^{n}, the reactions were incomplete in these cases and the unchanged $Hg(OAc)_2$ could be recovered. Here, the yield increased with longer reaction times at the same temperature without affecting the ratio of (**2**) : (**3**) [*e.g.*, 55% yield of (**2**) + (**3**) (R = Bu^{n}) after 7 h].

Table. Acetoxymercuration of (**1**). Yield and isomer ratio of the products.

(**1**) R	Yield[a]/% (**2**) + (**3**)	(**2**)/(**3**)[b]	M.p./°C[c]
Me	96	3·0	104—108
Et	88	5·0	95—98
Pr^{n}	74	11·0	100—104
Bu^{n}	44	16·5	94—97

[a] Based on $Hg(OAc)_2$ charged. All the mixtures of (**2**) and (**3**) gave satisfactory analytical data. [b] Determined by n.m.r. spectroscopy by comparison of the intensity of the acetoxymethyl protons. [c] M.p. of the mixture.

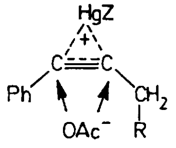
The reaction proceeded even at 20° for (**1**) (R = Me), the isomer ratio (**2**) : (**3**) remaining 3·0. Compounds (**2**; R=Me) and (**3**; R = Me) were each isolated by recrystallization from ethanol: (**2**; R = Me), m.p. 120°; i.r. (Nujol and hexachlorobutadiene mulls) 1740 (ν_{CO}) and 1640 ($\nu_{C=C}$) cm^{-1}; δ ($CDCl_3$) 2·01 [s, 3H, MeC=, J(^{199}Hg–Me) 190 Hz], 2·19 (s, 3H, AcO), and 7·2—7·6 (m, 5H, Ph); (**3**; R = Me), m.p. 155—157°; i.r. 1740 (ν_{CO}) and 1640 ($\nu_{C=C}$) cm^{-1}; δ ($CDCl_3$) 1·88 (s, 3H, AcO), 2·24 [s, 3H, MeC=, J (^{199}Hg–Me) 26 Hz], and 7·1—7·5 (m, 5H, Ph). Similar treatment of phenylacetylene at 20° resulted in quantitative formation of bis(phenylethynyl)mercury.



Scheme

When a 3:1 mixture of (**2**; R = Me) and (**3**; R = Me) was heated under reflux in acetic acid for 2 h, protodemercuration occurred almost quantitatively to give a 3:1 mixture of the corresponding esters, (**4**) and (**5**) (X = H). Similarly halogenodemercuration with I_2–MeOH or Br_2–pyridine at 15—20° gave the corresponding derivatives, (**4**) and (**5**) (X = I or Br). Since the structures of (**4**) and (**5**) (X = H, I, or Br) have already been established[4] and these demetallations are known to proceed generally with retention of configuration,[4,5] this finding shows that both (**2**) and (**3**) have the structures shown in the Scheme; namely, acetoxymercuration occurred completely in a *trans* fashion. A coupling constant J (^{199}Hg–Me) of 26 Hz in (**3**) is smaller than the observed value in propenylmercury derivatives, but agrees well the calculated value.[6]

Contrary to the acetoxythallation of (**1**) where the ratio (**2**):(**3**) = 2·5—1·9 for the n-alkyl groups R = Me—Bu^n,[4] the isomer ratio (**2**):(**3**) increased markedly on increasing the carbon chain length in the alkyl group in this case (see Table). Although alkyl groups having unbranched chains would not normally be expected to produce such steric differences at the site of reaction, this finding may be explained by assuming a bridged mercurinium ion intermediate in which phenyl and alkyl groups are not on a straight line, but are bent toward the attacking side of acetate anion as shown in structure (A). Since back-side attack of acetate anion on this intermediate (*trans*-acetoxymercuration) should occur in the same plane containing phenyl, alkyl, and C=C groups, increased carbon chain length of the alkyl groups may increase the steric interaction even in the unbranched alkyl groups. Thus, the isomer ratio may be determined in the last step. In acetoxythallation, on the other hand, the step involving $Tl(OAc)_2^+$ attack on acetylenes seems to play an important role for determining the isomer ratio, but more work is necessary to clarify the mechanistic difference between both reactions.



(A)

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