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# ALLYLIC ACETOXYLATION BY MERCURIC ACETATE. I. ORGANIC CHEMICAL AND ISOTOPIC LABELLING EXPERIMENTS

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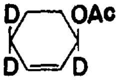
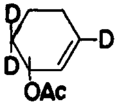
Oxymercuration is a well known and well understood reaction of mercuric salts with olefins which involves addition to the double bond via a cyclic mercurinium ion (1). A variant of oxymercuration which has received relatively little mechanistic attention until recently is the Treibs reaction, allylic acetoxylation by mercuric acetate, which is observed when the medium is hot acetic acid (2a) or the substrate itself (2b). Two groups of workers (3,4) have now suggested that the Treibs reaction proceeds by rearrangement of a mercurinium ion to an allyl organomercurial which then undergoes a solvolytic demercuration to give the allylic acetate.

We have also investigated this reaction (5) but although we have evidence for the intervention of a mercurinium ion, we do not believe that this is a product-determining intermediate.

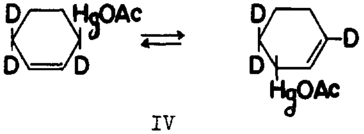
Treatment of cyclohexene with mercuric acetate in acetic acid at 70° resulted in the rapid and quantitative formation of a trans-acetoxymercuriacetate adduct (5a). The adduct was stable for at least 24 hours at this temperature. Heating to 100° in a sealed tube for an additional 24 hours gave 3-acetoxycyclohexene (55%) (6) and regenerated cyclohexene, along with two minor products ( $<$ 2% yield) (7). Under the same conditions, cyclohexene-3,3,6,6-$d_4$ (I) gave a 3-acetoxycyclohexene which on the basis of its n.m.r. spectrum was clearly a mixture of II and III. Acetate II showed the vinyl protons as a quartet centred at $\tau$ 4.3. Acetate III showed the vinyl proton as a broad peak at $\tau$ 4.4, and the allyl proton as a broad peak at $\tau$ 4.8. The vinyl to allyl ratio was 3:1. Therefore, II and III were formed in equal amounts. This result requires the intervention of a symmetrical intermediate but gives no information about the nature of this intermediate (8). It is clear however, that the symmetrical intermediate is not IV because the cyclohexene recovered from the oxidation of I was identical with I and the olefin recovered from an oxidation of ordinary cyclohexene in AcOD showed no incorporation of deuterium (4,9).



II



III

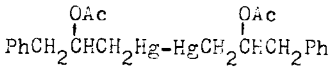


IV

In the oxidations of allylbenzene, 1-hexene, 2-hexene, 1-octene, 2-octene and cyclooctene, there was in each case rapid, reversible formation of an adduct followed by a slower formation of allylic acetate. Mixtures of primary and secondary acetates were obtained from all of the acyclic olefins. The product from cyclooctene was 3-acetoxycyclooctene; no product of a transannular reaction could be detected (11).

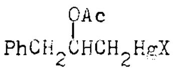
The oxidation of allylbenzene (V) was examined in some detail. Mercuric acetate dissolved rapidly when stirred at room temperature with a solution of allylbenzene in acetic acid to give, successively, VI and then VIIa, the latter compound being analyzed as the crystalline acetoxymercuric chloride, VIIb, m.p. 63-4°. The dimer VI could be isolated from acetic acid at room temperature in 70-80% yield as soon as the dissolution of mercuric acetate was complete (less than two minutes with efficient stirring); taking into account the unreacted olefin present at this point the conversion of allylbenzene to the dimer appeared to be greater than 95%. The dimer could also be prepared by stirring mercuric acetate at room temperature with a solution of allylbenzene in pure chloroform; when the compound was made in this way, acetic acid and mercurous acetate were also products.

The dimer shows C, 34.88%; H, 3.21% and a molecular weight of 768 (average of two cryoscopic and two osmometric determinations). Its infrared spectrum shows a peak for carbon-bound acetate at 5.7$\mu$ ; the adduct VIIa shows peaks for carbon-bound acetate at 5.7$\mu$ and mercury-bound acetate at 6.2 $\mu$. The n.m.r. spectrum of the dimer shows one acetate peak at $\tau$ 8.12; the adduct VIIa shows two acetate peaks, at $\tau$ 8.03 and $\tau$ 8.16.



$$PhCH_2\overset{OAc}{\overset{|}{C}}HCH_2Hg\text{-}HgCH_2\overset{OAc}{\overset{|}{C}}HCH_2Ph$$

VI



$$PhCH_2\overset{OAc}{\overset{|}{C}}HCH_2HgX$$

VII

(a) X = OAc

(b) X = Cl

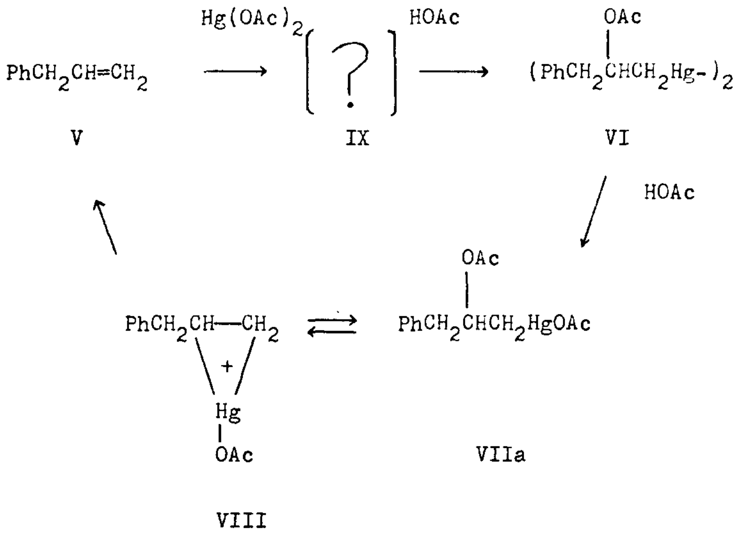
Stirring VI in acetic acid for 60 minutes at room temperature or 15 minutes at 70° led to the formation of VIIa and a gas. This gas does not contain $CO_2$. Mass spectrometric investigation of the gas is underway.

Thus, the conversion of V to VIIa appears to be the result of two one-electron transfers. The preparation of VI with mercuric acetate in $CD_3COOD$ or perdeuteromercuric acetate in $CH_3COOH$ revealed that the acetate groups of this compound are derived from the solvent. Since the acetate groups of mercuric acetate were found not to undergo exchange with $CD_3COOD$ in the tin required for the conversion of V to VI (12), VI must be formed frc an intermediate which can capture acetate from the solvent.

Heating VIIa or VIIb in refluxing acetic acid gave mercury (98%), trans-cinnamyl acetate (91%), cinnamaldehyde (1%), 3-acetoxy-3-phenylpropene ( $<$ 2%; 13) and allylbenzene (6%). 1-Phenylpropene could not be detected among the products. The same products were obtained but in slightly different amounts at lower temperatures.

At temperatures greater than 70°, VIIa underwent stepwise exchange of acetate with the solvent. Reisolation of acetate labelled VIIa after various times from hot $CH_3COOH$, conversion to VIIb and integration of the n.m.r. spectra of the two compounds revealed that the carbon-bound acetate of VIIa exchanged more rapi than the mercury-bound acetate. This result is best interpreted i terms of a rapid equilibration of VIIa with a mercurinium ion, VII under the conditions of formation of the allylic acetate.

When VIIa and p-methylallylbenzene were heated in acetic acid, the reaction mixture contained, after precipitation of mercury was complete, allylbenzene, p-methylallylbenzene, both adducts and both cinnamyl acetates. This result demonstrates the reversibility of the overall olefin $\rightleftarrows$ adduct reaction and permits the following description of the various processes which occur under the conditions of the Treibs reaction:



Since all of these reactions are much faster than allylic acetoxylation, any (or none) of V, VI, VIIa, VIII or IX could conceivably be the product-determining species.

The most reasonable sequence from the mercurinium ion VIII to trans-cinnamyl acetate would involve rearrangement to cinnamylmercuric acetate (X), followed by solvolysis. The case for this sequence of reactions does not appear compelling at this stage in view of our failure to demonstrate the presence in the reaction product of rearranged olefin or more than traces of the isomeric acetate (13). Difficulties also arise when attempts are made to formulate a mechanism starting with V, VI or VIIa.

In fact, on the basis of the purely chemical studies reported so far, it is not yet possible to favour any single mechanism or particular combination of mechanisms. A kinetic study of the reaction is clearly needed before the mechanism can be further discussed. The results of such a study are to be presented in an accompanying communication (14).

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## REFERENCES

1. T. G. Traylor and A. W. Baker, J. Am. Chem. Soc. 85, 2746 (196
2. (a) W. Treibs, G. Lucius, H. Kogler and H. Breslauer, Ann. 581, 59 (1953); (b) W. Treibs and H. Bast, ibid. 561, 165 (1949).
3. K. B. Wiberg and S. D. Nielsen, J. Org. Chem. 29, 3353 (1964).
4. Z. Rappoport, P. D. Sleezer, S. Winstein and W. G. Young, Tetrahedron Letters, No. 42, 3719 (1965).
5. (a) S. Wolfe and P. G. C. Campbell, Can. J. Chem. 43, 1184 (1965); (b) S. Wolfe and G. E. Palmer, Abstracts of the 48th Canadian Chemical Conference, Montreal, June 1965, p. 61; (c) S. Wolfe, P. G. C. Campbell and G. E. Palmer, Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p. 12.
6. Previous workers (2a,3) report yields between 10 and 20%. The increased yield in the present work is the result of a higher temperature, and a longer reaction time, together with the use of a closed system to prevent loss of olefin.
7. One of these appears to be cyclohexyl acetate; the other has not yet been identified.
8. Wiberg and Nielsen (3) reached the same conclusions by degradation of the cyclohexenyl acetate derived from cyclohexene-1,2-C$^{13}$.
9. This conclusion would be invalidated should it be subsequently found that cyclohexenyl mercuric acetate does not afford significant amounts of cyclohexene upon treatment with hot acetic acid. All of our attempts to prepare this compound have so far been unsuccessful. The work of Sleezer et al (10) however, has demonstrated that demercuration to olefin represents one of the reaction paths followed by allylic organomercurials in neutral acetic acid.
10. P. D. Sleezer, S. Winstein and W. G. Young, J. Am. Chem. Soc. 85, 1890 (1963).
11. The oxidation of cyclooctene has been previously reported by A. C. Cope, M. R. Kintner and R. T. Keller, J. Am. Chem. Soc. 76, 2757 (1954).

12. This result, which has some bearing on the structure of mercuric acetate in acetic acid, may be contrasted with the recent work of K. Heusler, H. Labhart and H. Loeliger, Tetrahedron Letters, No. 32, 2847 (1965) on the structure of lead (IV) carboxylates.

13. The amount of this product was the same both in the early stages and in the later stages of the reaction and was never greater than 2%; 3-acetoxy-3-phenylpropene is converted to cinnamyl acetate upon heating in acetic acid (G. E. Palmer, unpublished work) but this reaction is relatively slow. It seems clear, therefore, that cinnamyl acetate is not formed to any significant extent in the Treibs reaction by the rearrangement of initially-formed 3-acetoxy-3-phenylpropene.

14. S. Wolfe, B. Wojciechowski and G. E. Palmer, Manuscript in preparation.