

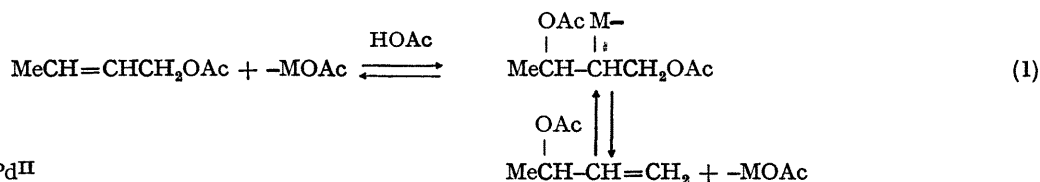
A Novel Palladium(II) Catalysed Allylic Isomerization

By P. M. HENRY

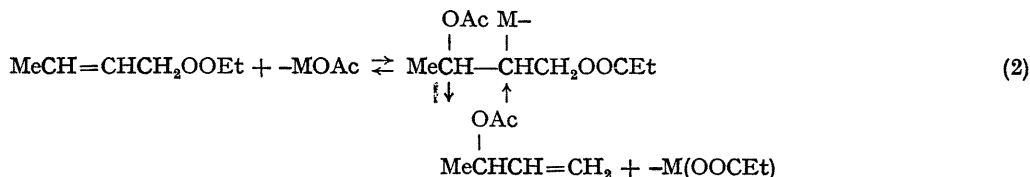
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Summary A palladium(II) catalysed allylic isomerization which apparently proceeds *via* a 1,3-acetoxonium ion type intermediate is reported.

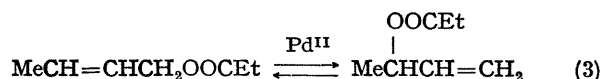
It has been reported that Hg^{II} ¹ and Pd^{II} ^{2,3} salts in acetic acid catalyse the isomerization of one allylic acetate into another, with the suggestion^{1,2} that the isomerization involves an acetoxymetallation-deacetoxymetallation mechanism. By this scheme but-2-enyl acetate should isomerize to but-1-en-3-ol acetate as in reaction (1).



To test this mechanism the propionate esters of but-2-enyl alcohol and but-1-en-3-ol were isomerized in acetic acid containing various metal salts. If the acetoxymetallation-deacetoxymetallation mechanism is operative, exchange should occur when, and only when, there is isomerization.



In the case of palladium(II) acetate or chloride salts, it was found that two reactions actually take place. One reaction is that shown by equation (2). The other is isomerization without exchange—equation (3). ¹⁸O labelling experiments showed that the alcohol oxygen of but-2-enyl propionate becomes the carbonyl oxygen of but-1-en-3-ol



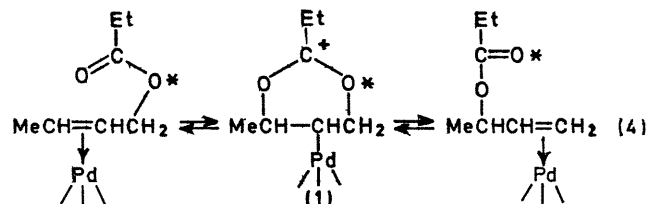
propionate after isomerization [equation (4)]. This result is consistent with a mechanism involving a Pd^{II} σ -bonded 1,3-acetoxonium ion type intermediate.^{4†} As this mechanism involves nucleophilic attack of the carbonyl oxygen, electron-withdrawing groups in the acid fraction of the ester predictably would retard the isomerization. It was

found that trifluoroacetate esters underwent the reaction much more slowly than propionate esters. If the ester carbon-oxygen bond cleavage to give an allylic carbonium ion-carboxylate anion type of intermediate were occurring, the opposite result would be expected.⁵

$\text{Hg}(\text{OAc})_2$, with or without added strong acid, in acetic acid gave almost exclusively exchange, apparently *via* equation (2). Little, if any, isomerization *via* equation (3) was observed. The Hg^{II} system, however, is complicated by the formation of stable acetoxymercuration adducts and

was not studied in detail. To avoid the acetoxymercuration problem, HgF_2 was used in MeCN. Again, no reaction *via* equation (3) was observed. $\text{Hg}(\text{OCCF}_3)_2$ in MeCN gave some isomerization of but-1-en-2-ol propionate to but-2-enyl propionate. However, the corresponding trifluoroacetate esters were also formed, *via* equation (2), and

but-2-enyl propionate could have been formed from but-1-en-2-ol trifluoroacetate by re-exchange.



Other noble metal salts, such as PtCl_2 , IrCl_3 , RuCl_3 , OsCl_3 , and RhCl_3 , gave the isomerization, although much more slowly than Pd^{II} . AuCl_3 , $\text{Tl}(\text{OAc})_3$, and $\text{Pb}(\text{OAc})_4$ gave oxidation of the allylic ester almost exclusively. AgOAc gave no reaction.

It thus appears that only those metal salts (*i.e.*, noble metal salts) which can activate the double bond by forming

† All of the other mechanisms which seem reasonable for the isomerization would predict either ¹⁸O retention in the ester oxygen or scrambling of the label.

stable π -complexes are capable of catalysing the isomerization. On the other hand, they must be capable of undergoing the acetoxymetallation reaction. AgOAc apparently was ineffective because of its inability to undergo this reaction.

To our knowledge, this is the first example of an oxy-

metallation reaction giving an unstable bridged intermediate such as (1).[‡] This reaction is likely to be general. Thus, under the correct conditions, 1,2-acetoxonium, phenonium, or oxonium ions may be formed as intermediates.

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[‡] A related reaction is the ready hydroxymercuration⁶ and hydroxythallation⁷ reactions which occur with olefins containing hydroxyl groups to give cyclic ethers. However, these adducts are stable compounds unlike (1).

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⁴ 1,3-Acetoxonium ions have been previously suggested in solvolysis reactions. See e.g. L. J. Dolby and M. T. Schwartz, *J. Org. Chem.*, 1965, **30**, 3581; O. Kovacs, G. Schneider, and L. K. Lang, *Proc. Chem. Soc.*, 1963, 374; L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwartz, *J. Amer. Chem. Soc.*, 1963, **85**, 47.

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⁶ R. Adams, F. L. Roman, and W. N. Sperry, *J. Amer. Chem. Soc.*, 1922, **44**, 1781; L. S. Mills and R. Adams, *ibid.*, 1923, **45**, 1842; J. Halpern and H. B. Tinker, *ibid.*, 1967, **89**, 6427.

⁷ H. J. Kabbe, *Annalen*, 1962, **656**, 204.