Reaction of Methylenecyclopropanes with Lead Tetra-acetate

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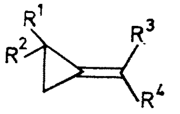
Summary The title reaction involves a fission of the C-2–C-3 bond of the cyclopropane ring, and gives 2-methylenepropane-1,3-diol diacetates selectively.

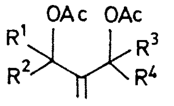
In connection with our studies of the reaction of methylenecyclopropanes with metallic compounds,[1] we have examined the reaction with lead tetra-acetate and observed a clean 1,3-addition reaction.

A mixture of methylenecyclopropane (Ia) (7 mmol) and lead tetra-acetate (4 mmol) in anhydrous acetic acid (16 ml) was maintained at 35° for 10 h in a sealed tube, to give 2-methylenepropane-1,3-diol diacetate (IIa)[2] in 60% yield (based on lead tetra-acetate). 2-Phenylmethylenecyclopropane (Ib),[3] on treatment with lead tetra-acetate at 20°, afforded (IIb)† (70%) together with a small quantity of the isomer, 2-benzylidenepropane-1,3-diol diacetate (3%), whereas benzylidenecyclopropane (Ic) gave exclusively (IIb) (67%). Similarly, the 2,2-dimethyl derivative (Id) yielded (IIc) (55%) and 2-acetoxymethyl-3-methylbuta-1,3-diene[4] (6%). The isomer, isopropylidenecyclopropane (Ie), gave the same products in 62 and 3% yields, respectively. Control experiments showed that the monoacetate could be derived from the primary product (IIc) during the reaction or the work-up. Feist's ester was found to be inert to the reaction conditions.



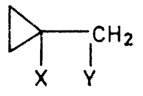
(I)

(a) $R^1 = R^2 = R^3 = R^4 = H$
(b) $R^1 = Ph, R^2 = R^3 = R^4 = H$
(c) $R^1 = R^2 = R^3 = H, R^4 = Ph$
(d) $R^1 = R^2 = Me, R^3 = R^4 = H$
(e) $R^1 = R^2 = H, R^3 = R^4 = Me$



(II)

(a) $R^1 = R^2 = R^3 = R^4 = H$
(b) $R^1 = Ph, R^2 = R^3 = R^4 = H$
(c) $R^1 = R^2 = Me, R^3 = R^4 = H$



(III) X = Br
Y = Br, H, OH

Treatment of methylenecyclopropane with electrophilic reagents such as bromine, hydrogen bromide, and hypobromous acid *etc.* has been recorded to give corresponding simple addition products (III),[5] while lead tetra-acetate oxidation like oxymercuration[6] affords the ring-opened, allylic compounds. The mechanism must involve an electrophilic attack of lead tetra-acetate or some derived species such as $Pb(OAc)_3^+$ on the double bond followed by a cleavage of the C-2–C-3 bond of cyclopropane ring forming the allylic cation (IV). The present reaction gives rise to predominantly kinetically-controlled acetates; this should

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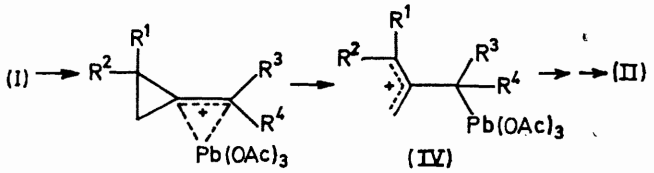
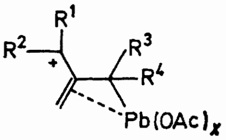
† All new compounds had satisfactory elemental analyses and i.r., n.m.r., u.v., and mass spectra consistent with the structures assigned.

be contrasted with the fact that the acetolysis of cyclopropyl or allylic halides occurring by S_N1 mechanism usually gives thermodynamically stable acetates as the major products.[7] This can be simply explained by assuming the intermediacy of the metal ion-stabilized allylic cation (V) in which the Pb atom exerts its influence by interacting with the less substituted C=C bond.





(V)

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