

## Reaction of Phenylcyclopropane with Lead(IV) Diacetate Difluoride

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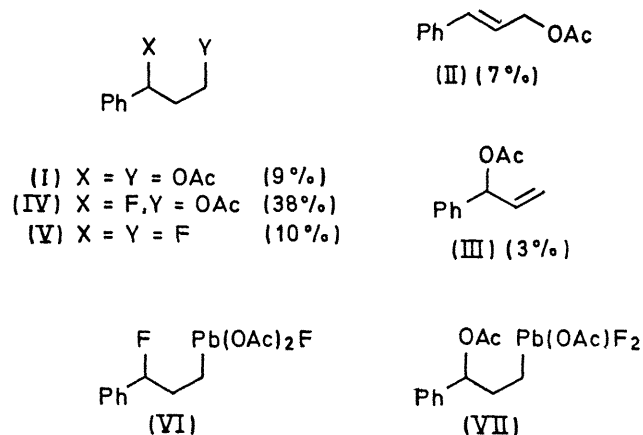
**Summary** The 3-membered ring of phenylcyclopropane is asymmetrically cleaved by lead(IV) diacetate difluoride to give a mixture of products the main components of which are 3-acetoxy-1-fluoro-1-phenylpropane and 1,3-difluoro-1-phenylpropane.

THE recently discovered compound, lead(IV) diacetate difluoride (LDADF)  $\text{Pb}(\text{OAc})_2\text{F}_2$ , has been shown to be highly useful for the fluorination of 1,1-diarylethylenes<sup>1</sup> and ketone arylhydrazones.<sup>2</sup> These initial studies have revealed a distinct similarity in the chemical behaviour of LDADF

and lead tetra-acetate (LTA) which leads us to believe that LDADF will display the same broad range of reactivity as a fluorinating agent as that possessed by LTA as an oxidizing agent. Therefore, we decided to examine other organic substrates known to be reactive toward LTA. We have investigated phenylcyclopropane, which had been shown by Ouellette and his co-workers<sup>3,4</sup> to suffer oxidative cleavage in the presence of LTA to yield 1,3-diacetoxy-1-phenylpropane (I) and *trans*-cinnamyl acetate (II). Herein we present additional evidence of the versatility of LDADF, *viz.* the fluorination of phenylcyclopropane.

Addition at 0° during 30 min of a solution of phenylcyclopropane (81 mmol) in chloroform (15 ml) to a stirred suspension of LDADF (81 mmol) in chloroform (50 ml) followed by stirring of the mixture at room temperature for 24 h afforded compounds (I)–(V) on pouring the mixture into water; no attempt was made to maximize the yields (based on consumed phenylcyclopropane). The structures of (I) and (II) were verified by comparison with authentic samples obtained from oxidation<sup>8</sup> of phenylcyclopropane with LTA. 1-Phenylallyl acetate (III) was also isolated (2%), and found to be identical with both an authentic specimen<sup>5</sup> and the material produced by reaction of the hydrocarbon with LDADF. The structures of the fluorine-containing products (IV) and (V) were established by elemental analysis and spectroscopy. The i.r. spectrum (neat) of (IV) (b.p. 86–87° at 0.4 mmHg,  $n_D^{26}$  1.4852) displayed strong absorption bands at 1740 and 1245  $\text{cm}^{-1}$  (acetate) and its 60 MHz n.m.r. spectrum ( $\text{CCl}_4$ ) showed signals at  $\tau$  8.08 (3H, s, Me), 7.88 (2H, m,  $\text{CH}_2$ ), 5.85 (2H, t,  $J$  7 Hz,  $\text{OCH}_2$ ), 4.50 (1H, m,  $J$  48 Hz, CHF), and 2.74 (5H, s, ArH). When set aside, compound (IV) slowly lost HF; the residue was shown (g.l.c. and i.r.) to be (II). 1,3-Difluoro-1-phenylpropane (V) was similarly unstable, especially in contact with glass, and was best kept in a polyethylene container in the cold;  $\tau$  ( $\text{CCl}_4$ ) 7.78 (2H, m,  $\text{CH}_2$ ), 5.48 (2H, m,  $J$  48 Hz,  $\text{CH}_2\text{F}$ ), 4.45 (1H, m,  $J$  48 Hz, CHF), and 2.73 (5H, s, ArH);  $M^+$ , 156.

On the basis of our earlier studies of LDADF<sup>1,2</sup> and the results of the present investigation it seems likely that the mechanism of the reaction of the fluorinating agent with



phenylcyclopropane is similar to that of the reaction of LTA with this hydrocarbon. It is of note that both reagents cause only asymmetric cleavage of the cyclopropane ring. Accordingly, we suggest that LDADF or some derived species<sup>6</sup> such as  $\text{Pb}(\text{OAc})_2\text{F}^+$  or  $\text{Pb}(\text{OAc})\text{F}_2^+$  reacts with phenylcyclopropane to afford the  $\gamma$ -substituted organolead intermediates (VI) and (VII) which are transformed to the observed products by pathways analogous to those previously proposed<sup>8</sup> to explain the electrophilic cleavage of the hydrocarbon by LTA.

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<sup>4</sup> R. J. Ouellette, R. D. Robins, and A. South, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 1619. See footnote 7 of this reference.

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