

RING-OPENING REACTIONS OF FERROCENYL-DIHALOCYCLOPROPANES<sup>1</sup> -

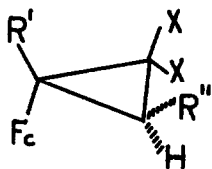
BUTADIENE AND OLEFIN FORMATION.

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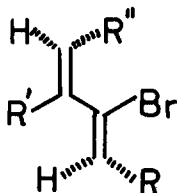
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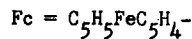
Current interest in the ring-opening reactions of arylcyclopropanes (3) prompts us to report our observations in the ferrocene series. The comparative ease of synthesis of the ferrocenyl-dihalocyclopropanes (4) from alkenyl ferrocenes (5) has allowed the study of several ring compounds.



- I a. R' = Me, R'' = H, X = Br  
 b. R' = Et, R'' = H, X = Br  
 c. R' = H, R'' = Me, X = Br  
 d. R' = R'' = H, X = Br



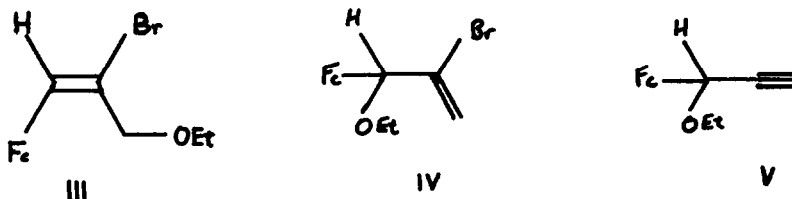
- II a. R = R'' = H, R' = Fc  
 b. R = H, R'' = Me, R' = Fc  
 c. R' = R'' = H, R = Fc



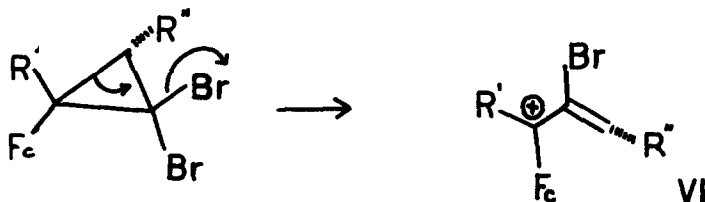
Reflux of 1-alkyl substituted 1-ferrocenyl-2,2-dihalocyclopropanes (I<sub>a,b</sub>) in acetonitrile<sup>†</sup> produced 2-bromo-3-ferrocenylbuta-1,3-diene<sup>†</sup> [II<sub>a</sub>, 63%, n.m.r. (T): 4.04s (1);

4.34s (1); 4.48s, 4.52s (2); 5.64m, 5.80m, 5.94s (9)] and 2-bromo-3-ferrocenylpenta-1,3-diene [II<sub>b</sub>, 40%, n.m.r. ( $\tau$ ): 4.30q ( $J = 6.9$  c/s); 4.38, 4.54s (3); 5.85m, 6.11s (9); 8.34d ( $J = 6.9$  c/s) (3)] respectively. 1-Ferrocenyl-2-methyl-3,3-dibromocyclopropane, (I<sub>c</sub>) similarly yields a butadiene [II<sub>c</sub>, 54%, n.m.r. ( $\tau$ ): 3.35-3.80 (4 lines), 4.32-4.90 (4 lines) ( $J_{AX} = 10$  c/s,  $J_{AY} = 15$  c/s,  $J_{XY} < 0.5$  c/s) the eight lines making up a deceptively simple AX<sub>2</sub> spectrum (6); 3.32s (1); 5.22m (2); 5.64m (2) and 5.68s (5)].

On reflux in ethanol<sup>†</sup> the simple cyclopropane (I<sub>d</sub>) produced only one isolable product identified as 2-bromo-3-ethoxy-1-ferrocenylprop-1-ene [III, 68%, n.m.r. ( $\tau$ ): 3.50s (1); 5.48m (2); 5.95m, 6.08s, 6.10s (9); 6.65q ( $J = 6.9$  c/s) (2); 8.84t ( $J = 6.9$  c/s) (3)]. Treatment of I<sub>d</sub> with sodium ethoxide/ethanol gave two products 3-ethoxy-3-ferrocenyl-2-bromoprop-1-ene [IV, 24%, n.m.r. ( $\tau$ ): 4.26s (1); 4.46s (1); 5.70m, 5.90s (9); 6.45q ( $J = 6.9$  c/s) (2); 8.75t ( $J = 6.9$  c/s) (3)] and the acetylene (V), derived from (IV) by dehydrobromination. [27%, n.m.r. ( $\tau$ ): 5.05bs (1); 5.65m, 5.89s (9); 6.45q ( $J = 6.9$  c/s) (2); 7.45bs (1); 8.80t ( $J = 6.9$  c/s) (3)]. T.L.C. examination of the ethanol solvolysis of I<sub>d</sub> indicated that during the reaction the  $\alpha$ -ether (IV) was formed initially and was quantitatively isomerised to (III), the  $\gamma$ -ether. The dependence of this isomerisation on the presence of HBr was shown by the conversion of IV to III, in 48% yield in ethanol with a trace of HBr. Schlögl and Mohar (7) have reported a similar although less efficient acid isomerisation of ferrocenyl allyl alcohols.



These ring-openings can be interpreted as involving carbonium ions and in this respect are similar to other *gem*-dihalo cyclopropanes where current theory indicates ionisation of a carbon-halogen bond as the initial process (8,9,10). Thus elimination of bromide ion and collapse of the cyclopropyl carbonium ion gives rise to an  $\alpha$ -ferrocenyl carbonium ion (VI) (11).



Insolvents of high dielectric constant proton loss from R' (Me or Et) or from R'' (Me) gives II<sub>a</sub>, b and c. If R' and R'' are hydrogen, solvolysis in ethanol gives the  $\alpha$ -ether (IV), a product of kinetic control. Further studies regarding mechanistic details and stereochemistry of the products is under investigation.

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1. Part VI of a series - ref. 5 is part V.
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† Addition of sodium carbonate to neutral solutions was found to be necessary. The heterogeneous system prevents build up of high HX concentrations which degrade the products.

‡ All new compounds reported gave satisfactory elemental analyses.