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REARRANGEMENT OF 1-CYCLOPROPYL-1-FERROCENYL-2,2-DIBROMOCYCLOPROPANES.(1)

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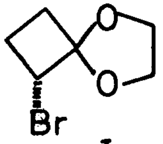
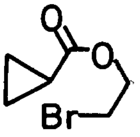
Recent publications (3,4) have reported reactions which are potentially examples of 6-electron processes (5) involving migration of a bromine atom. Thus Salaun and Conia (3) reported the conversion of a bromoketal (I) to a cyclopropane carboxylate (II) and Baldwin and Gano (4) published an account of a related reaction where the attempted ketalisation of 2-bromotropone with ethylene glycol gave 2-bromoethylbenzoate presumed to arise from the rearrangement of a norcaradiene intermediate (III).



I



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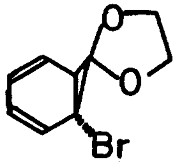
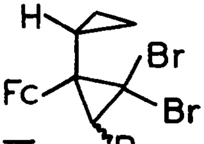
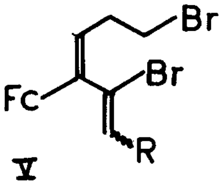


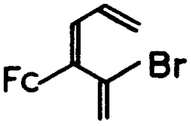
III



IV



V



VI

Fc = ferrocenyl

a. R = H

b. R = CH_3

We wish to report the first examples of this type of bromine migration and rearrangement in a carbocyclic system. Thus 1-cyclopropyl-1-ferrocenyl-2,2-dibromocyclopropane[†] (IVa) undergoes a smooth conversion in refluxing acetonitrile, benzene or cyclohexane[‡] to yield 2,6-dibromo-3-ferrocenyl-hexa-1,3-diene (Va). A similar rearrangement is also encountered in the conversion of (IVb) to (Vb) although in this example the reaction is so facile as to prevent isolation of the dibromocyclopropane (IVb). An experiment to test the "concertedness" of the present rearrangement by a solvolysis of (IVa) in ethane (6) leads to only two products, the isomerised product (Va) and the result of its dehydrobromination (VI). However, such an experiment does not a priori rule out the intermediacy of carbonium ions.

The geometrical arrangement of reaction termini in the dicyclopropanes and the heterospiro systems is similar. It is therefore possible that the rearrangements reported for these systems have a reaction path in common namely a concerted $\sigma_a^2 + \sigma_s^2 + \sigma_a^2$ process. However proof of this must await stereochemical verification.

1. Part VIII of a series. Part VII is W.M. Horspool, R.G. Sutherland and J.R. Sutton, Can.J.Chem. 1969, in press.
2. Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.
3. J. Salaun and J.M. Conia, Tetrahedron Letters 4545, 1968.
4. J.E. Baldwin and J.E. Gano, Tetrahedron Letters, 1101, 1969.
5. Such 6 electron processes first proposed by Baldwin and Gano (4) could well be concerted and if so are covered by the theories relating orbital symmetry to chemical reactivity. see R. Hoffman and R.B. Woodward, Accounts Chem.Res. 1, 17, 1968.
6. Our previous studies on the ring-opening reactions of ferrocenyl-cyclopropanes have shown that solvolysis in ethanol leads to a high percentage incorporation of solvent in the products. W.M. Horspool, R.G. Sutherland and B.J. Thomson, Tetrahedron Letters, 6045, 1968 and unpublished observations.

[†] all new compounds gave satisfactory spectral and analytical data.

[‡] The reaction in cyclohexane was slower than those in benzene and acetonitrile.