

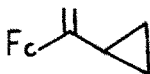
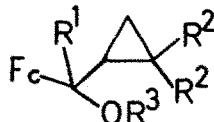
STEREOSPECIFICITY IN THE RING-OPENING OF  
FERROCENYL-CYCLOPROPYL CARBINOLS

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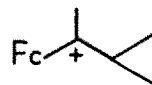
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Dehydration of the alcohol (1a) to the olefin (2, 60%) by a sulphuric acid-benzene system is accompanied by considerable decomposition of the starting material. A milder, more efficient dehydration was achieved by subjecting the same alcohol (1a), as a concentrated ethereal solution, to chromatography on silica gel made up in petroleum ether. Under these conditions the mixture heats up as it is adsorbed onto the substrate. Continued elution with ether yields the olefin (2, 80%). The formation of the olefin probably results from the deprotonation of an intermediate  $\alpha$ -ferrocenyl carbonium ion (3). The formation of  $\alpha$ -ferrocenyl carbonium ions under such a system has support from the conversion of the alcohol (1b) into the ether (1c) by reflux of the alcohol in methanol with added silica gel.

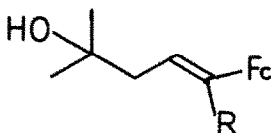


(2)



(3)

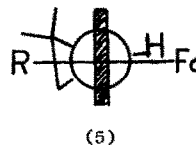
- (1) a.  $R^1 = \text{Me}, R^2 = \text{H} = R^3$   
 b.  $R^1 = R^2 = \text{H} = R^3$   
 c.  $R^1 = R^2 = \text{H}, R^3 = \text{Me}$   
 d.  $R^1 = R^2 = \text{Me}, R^3 = \text{H}$   
 e.  $R^1 = R^3 = \text{H}, R^2 = \text{Me}$



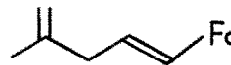
(a)  $R = \text{Me}$

(b)  $R = \text{H}$

(4)



(5)



(6)

Surprisingly, there was no evidence in the above experiments for ring-opening of the cyclopropyl ring. Ring-opening of cyclopropylcarbinyl carbonium ions has been observed in a variety of systems.<sup>2</sup> In all of these previous examples the ring-opening of the cyclopropyl system is both highly efficient and highly stereospecific. The absence of ring-opening in the ferrocenylcyclopropyl ion could be due to the powerful stabilising

influence of the ferrocenyl group resulting in considerable charge localisation at the  $\alpha$ -site. Whether the introduction of substituents into the cyclopropyl ring would influence this situation was tested by the use of the alcohols (1d and 1e).

Alcohol (1d) upon chromatography on silica gel, under conditions which dehydrated alcohol (1a), gave a single product which was identified as the olefinic carbinol (4a), which results from ring-opening of the cyclopropyl moiety. On the basis of the bisected conformation for the cyclopropylferrocenyl carbonium ion (5), which is preferred by 9-26 kcal (37.7-108.9kJ) over other possible forms in simpler cyclopropylcarbinyl systems,<sup>3</sup> the product is anticipated to have the trans-(E)-geometry shown in (4a). The n.m.r. spectrum of this molecule shows allylic coupling ( $J = 1.6$  Hz) between the vinyl hydrogen and the allylic methyl group. This, however, cannot be used as confirmation of trans-coupling in the absence of information about the cis-isomer, since there is uncertainty about the magnitude of such couplings.<sup>4</sup> Ring opening of the alcohol (1e) under the same conditions gave the diene (6, 35%) and the ene-ol (4b, 28%) as well as unchanged starting material. The n.m.r. of both these products exhibits a coupling constant of 15.5 Hz for the double bond adjacent to the ferrocene clearly showing it to be of trans-configuration.

Both of the ring-opening reactions are thus highly stereospecific and show that the likely conformation of the carbonium ion intermediate is as shown in (5).

Examination of molecular models of alcohols (1d and e) clearly shows that the dramatic change in reaction path does not arise from steric factors introduced by the cyclopropylmethyl groups. Thus it is likely that electronic factors must be dominant and although methyl groups are only poor electron donors their relatively weak effect is sufficient to tip the balance in favour of ring-opening.

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#### References

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