Mechanistic Studies on the Isomerisation of Methyl-substituted 5-Oxabicyclo[2.1.0]pent-2-enes (Dewar Furans) to Acetylcyclopropenes

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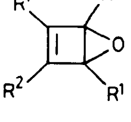
Deuterium labelling and ^{2}H n.m.r. studies have been used to establish the mechanism of the title rearrangement.

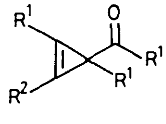
The isomerisation of Dewar furans to acylcyclopropenes was first reported in 1982 in association with a study of the tetrakistrifluoromethyl derivative (**1d**).[1] Subsequently we have shown that this is a general reaction of Dewar furans.[2,3] The facility with which this reaction can occur is well illustrated in the case of the parent member (**1a**) which yields cyclopropene-2-carbaldehyde (**2a**) even at −65 °C.[2]

This unusual rearrangement, unique amongst the five-membered Dewar heterocycles,[4] was reported by Wirth and Lemal to proceed *via* a vinylcarbene intermediate, *e.g.* (**3d**).[1] Support for this proposal was provided by calculations carried out by them on the parent system (**3a**). Interpretation of the selectivity observed in the rearrangement of the trimethyl Dewar furan (**1c**), *i.e.* exclusive formation of (**2c**), and our inability to trap (**3b**),[2] led us to question the role of vinylcarbene intermediates in these isomerisation reactions.[5] We now present experimental evidence which indicates that alkyl-substituted Dewar furans rearrange *via* a mechanism involving C–O bond cleavage of the oxirane ring as the first step, rather than one involving a vinylcarbene.

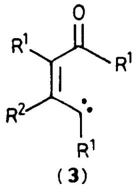
Irradiation of (**6c**), prepared from the previously described (**4a**)[6] as shown in Scheme 1, generates the selectively deuteriated Dewar furan (**7**), which undergoes ring contraction under the reaction conditions (254 nm; acetone; −80 °C) to its acetylcyclopropene isomers. Analysis of the deuterium-labelling pattern in these acetylcyclopropenes allows a distinction to be made between the various reaction pathways. Ring contraction of the labelled Dewer furan (**7**) *via* the vinyl carbene (**8**), would lead to the two labelled methyl groups (see Scheme 2) being directed specifically into the acetyl and vinylic methyl positions of the resultant acetylcyclopropene (**9**). In contrast a mechanism involving a simple C–O bond cleavage of the epoxide ring leads to a dipolar intermediate (**10**) or (**11**), the symmetry of which dictates the formation of a mixture of isomers (**9**) and (**12**). Thus a labelled methyl group is directed to the acetyl position in each case whilst the other could appear with equal probability at either the vinylic positions [to form (**9**)] or the allylic position [to form (**12**)]. This latter labelling pattern is supported by the ^{2}H n.m.r.



(**1**)

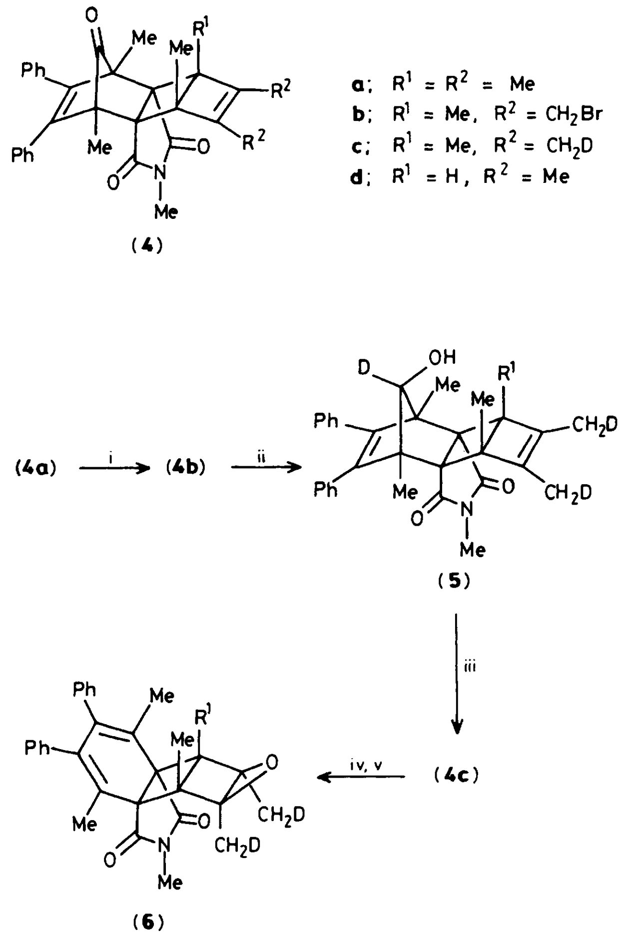


(**2**)

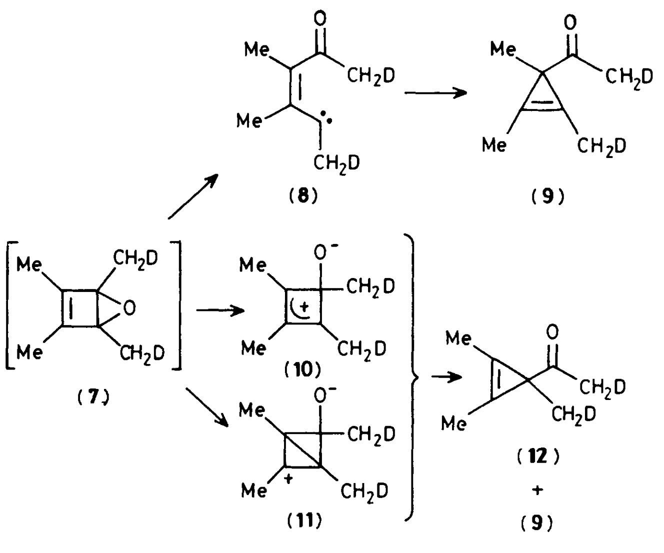


(**3**)

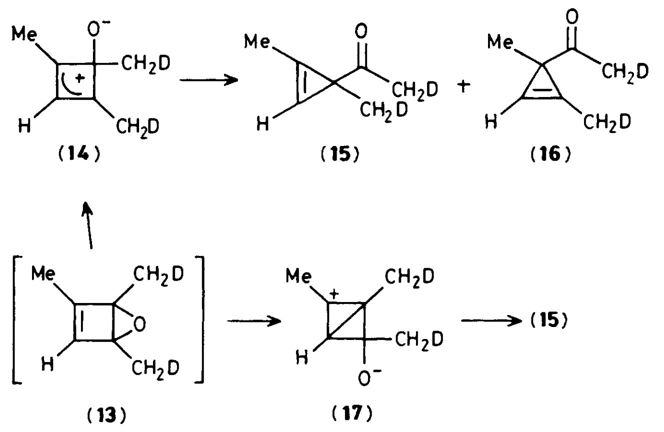
a; $R^1 = R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = Me, R^2 = H$
d; $R^1 = R^2 = CF_3$



Scheme 1. *Reagents:* i, *N*-bromosuccinimide, CCl_4, reflux; ii, $NaBD_4$, Me_2SO, 100 °C; iii, Jones' reagent, 0 °C; iv, 3-chloroperbenzoic acid, CH_2Cl_2; v, $(MeOCH_2CH_2)_2O$, reflux.



Scheme 2



Scheme 3

spectrum† of the labelled acetylcyclopropene obtained from the low temperature photolysis of (**6c**), and thus the C–O bond cleavage mechanism is indicated.

To gain further insight into the role of the π-bond in the ring contraction of alkylated Dewar furans, we have investigated the isomerisation of the trimethyl derivative (**1c**), which affords a single ring-contracted product (**2c**). We have argued previously that this is more likely to arise *via* a cyclobutenyl rather than a bicyclobutyl intermediate,[5] and now provide supporting evidence. Thus photolysis of the labelled precursor (**6d**), prepared as described for (**6c**), afforded a 1 : 1 mixture of isomers (**15**) and (**16**), differing only in their deuterium distribution. Any contribution from the bicyclobutyl intermediate (**17**) would favour the formation of isomer (**15**). Thus we conclude that these acetylcyclopropenes are derived exclusively from the cyclobutenyl intermediate (**14**).

These results clearly show that a vinylcarbene intermediate is not involved in the isomerisation of alkyl Dewar furans in solution and by analogy question the involvement of such an intermediate in the rearrangement of the parent molecule.

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† δ 1.12(CH_2D), 1.74 ($COCH_2D$), and 1.96 (vinylic CH_2D) (1 : 2 : 1). ^2H N.m.r. spectra were recorded at 50 MHz and are referenced to $CDCl_3$ (δ 7.25). Solutions of acetylcyclopropenes were prepared in $CDCl_3$ containing 5% pyridine in order to prevent acid-catalysed rearrangement.