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PROTONATED CYCLOPROPANES -- I

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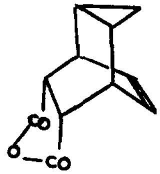
Recently[1], the acid-catalysed ring-opening of the cyclopropane derivative (1) has been studied, and observed to yield as the major product, the anti-Markownikoff adduct (2). This finding has been rationalised in terms of steric interference to solvent approach during the ring-opening of the protonated cyclopropane (σ-protonium complex) (3). The status of this species, as an intermediate, or merely as a point on the free-energy surface leading to a carbonium ion intermediate, is left as an open question[1].

In this communication we present, in a preliminary form, some of our own results, bearing on the behaviour of the closely related species (4) and (5). These results suggest that the phenomena observed by the American workers are not of general occurrence in this ring-system, and are not adequately accounted for by an argument based upon steric considerations.



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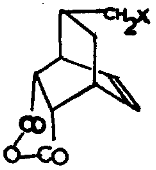

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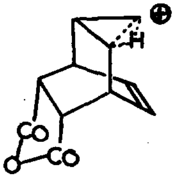

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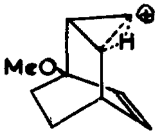

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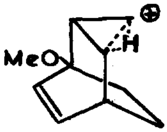

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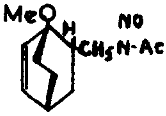

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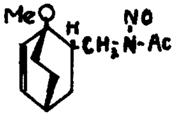

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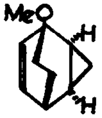

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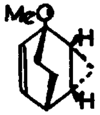

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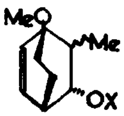

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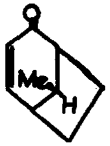
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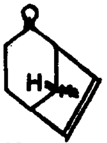
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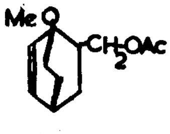
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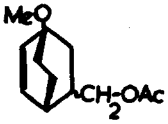
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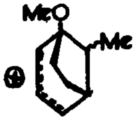
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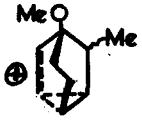
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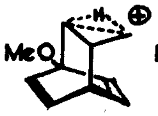
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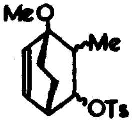
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In connection with our studies on the chemistry of methoxyl-substituted carbonium ions[2], we had occasion to pyrolyse, in an aqueous/1,2-dimethoxyethane medium, the N-nitrosoamides (6) and (7)[3]. The greater number of the complex mixture of products (~70% of the total reaction mixture) were formally derivable from the ions (8), or from the related delocalised ions (22). The most acceptable route to such ions would appear to be via the protonated cyclopropanes (4) and (5)[cf.4], an hypothesis supported by the production of the cyclopropanes (9) and (10) in the same reactions. As a further test of this hypothesis, (9) and (10) were separately treated with p-toluenesulphonic acid in acetic acid. The major products of the four reactions are listed in Table 1.

Table 1.

Product	Pyrolysis of (6)	(10) + TsOH/AcOH*	Pyrolysis of (7)	9 + TsOH/AcOH*
(11)	< 0.5%	5.6%	70.8%	70%
(12)			8.5%	~ 5%
(13)	> 0.3%		> 0.6%	
(14)	30.4%	56.5%	13.7%	
(15)	37.3%	5.5%	> 0.7%	~ 2%
(16)	31.6%	6.0%	1.6%	
(17)			3.0%	~ 10%

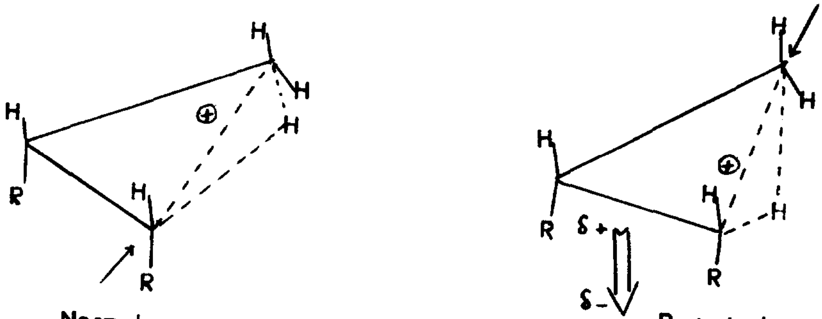
*The products are interconvertible under the protonation conditions, the ultimate product in both cases (9 & 10) being the ketone (11). The figures in this table refer to the products of 10% reaction.

While we wish to defer detailed discussion of these results to another occasion, certain points can be made here: (i) The protonation experiments lead to little if any of the primary acetates (19) (< 0.5%, *exo-* ; < 3%, *endo-*). The isomeric acetates (20) are not known compounds, but in any case could not have been formed in greater than 5% yield. Further, we have evidence (see below) which strongly suggests that the cyclopropanes protonate to give preferentially the intermediates (4) and (5), rather than the isomeric species (23) and (24) which might produce (20). This conclusion is in accord with normal structure reactivity considerations, based on the inductive effect of the methoxyl group.

(ii) Ring-opening of the initially formed protonated cyclopropanes occurs in a normal, Markownikoff fashion to give (formally) the ions (8) which are then involved in extensive rearrangement leading to products derivable either from the allylic ion (21) or the delocalised ion (22). A similar partition between these ions is observed both in the pyrolysis and protonation experiments. That the American workers[1] observed no similar rearrangement is not surprising in view of the known resistance to migration of anhydride-bearing substituents[5].

(iii) In both the deamination reactions, and in the protonation of (9), products of type (12) and (13) are observed in yields which make it clear that the reactions leading to their formation are at least competitive with reactions leading to the primary products (19) and (20).

It is clear therefore that the anti-Markownikoff addition observed by the American workers is not typical of the chemistry of this ring-system and further, that the steric argument advanced by them to account for their results, while necessarily being qualitatively correct, is quantitatively inadequate for this purpose. We would like to suggest that their results are interpretable in terms of the inductive or field effect of the anhydride group, operating so as to reverse the normal polarisation of the σ-protonium complex. The situation is represented schematically in Fig.1. It is perhaps worth noting that, even in the absence of a perturbing group, the two states of polarisation would be expected to differ in energy by a much smaller factor than, say, a primary and secondary carbonium ion. The small arrows indicate the direction of attack by nucleophile on these species.



Normal.

Perturbed.

Fig. 1.

There are some further points in connection with our results which are worth noting at this time: (a). The protonated cyclopropanes (4) and (5) undergo ring-opening reactions with a high degree of specificity, the products of backside attack by the migrating group predominating. Thus (4) leads in 70% yield to the products of rearrangement of the ion (21), while (5) leads in 99% yield to the products derivable from the delocalised ion (22), or from an equivalent set of equilibrating, less extensively delocalised ions. There is little leakage, under the kinetically controlled conditions of the deamination, from (22) to (21) via the ions (8).

(b). The production of (17) from the pyrolysis of (7) and from the protonation of (9) suggests the intermediacy of the isomeric σ-protonium complex (23), and further suggests that this is less stable than its isomer (4). The absence of this product from the other two reaction mixtures (coupled with the probable presence of (18)) supports this hypothesis, and suggests the intermediacy of the epimeric species (24). Since the pyrolysis medium is non-acidic, it follows that (4) and (23) must be directly interconvertible. The solvolysis of the tosylates (25)^{6} produces no trace of (17) or (18), a result which would appear to rule out ions of the type (8) as intermediates between (4) and (23). (Note: the solvolysis of at least two of the tosylates (25) proceeds without concerted migration to give, in the first instance, ion-pairs related to the localised ions (8)^{6}.). It would seem to follow then that (4) and (23) are intermediates, which have lifetimes in aqueous solution, long enough to permit partial or complete equilibration$^{\text{cf.}4}$.

The detailed structures of the intermediates involved in these and related reactions will be fully discussed elsewhere.

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