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# CYCLOBUTYL EDGE PARTICIPATION IN THE THERMAL ELIMINATION OF CARBON MONOXIDE FROM POLYALICYCLIC KETONES

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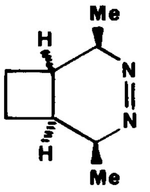
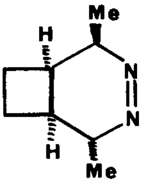
The rate of thermal elimination of carbon monoxide is dramatically increased in systems containing a proximate cyclopropyl group[1] which is geometrically aligned to allow favourable overlap of the Walsh orbitals of the cyclopropyl with the σ-bonds originally attached to the carbonyl group (i.e., the ones breaking in the transition state). Similar rate increases have been observed in related systems where the departing group is nitrogen[2]. Edge participation of a cyclobutyl group has also been recorded in solvolysis reactions[4] where rate increases $(10^{4.3})$ were observed. This of course is only a fraction of the anchimeric assistance afforded by the *endo*-cyclopropyl group $(10^{14})$. In an elegant series of reactions Berson and his co-workers[3] have recently demonstrated the bent bond contribution of a cyclobutyl ring in effecting elimination of nitrogen from the compounds (1) and (2). These occur with complete stereochemical integrity as required by a concerted process. A number of cases of carbon monoxide elimination from systems containing a proximate cyclobutyl or cyclobutenyl group have been reported[4,5]. The mild conditions required to effect elimination and the fact that the *endo* isomer eliminates at a lower temperature (~60°) than the related *exo* isomer is consistent with σ-bond participation, but no serious study of this reaction has yet appeared. The following work bears on this problem.



(1)



(2)

In the reaction of the dienone (3) with 3,4-dichlorocyclobutene in refluxing chloroform solution two 1:1 adducts, (4) and (6), are formed.[6] The structure of the major isomer (4) has been discussed in a previous communication[6] and the structure of the *endo*-adduct* follows from

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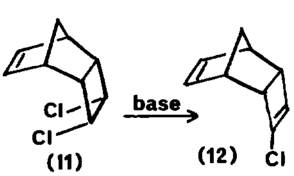
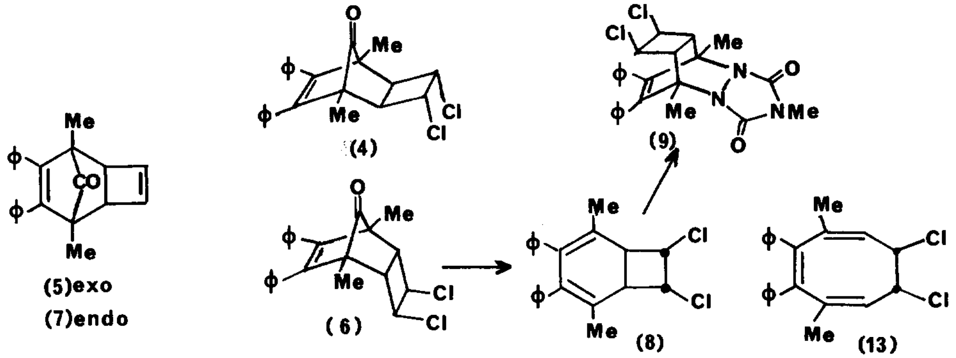
*The *endo-syn* structure is rejected since the dechlorination proceeds smoothly, in contrast to the cyclopentadiene adduct (11)[7] which resists dechlorination by this method. Similarly the dehydrochlorination (11→12) which occurs readily with (11) is not observed with (6).



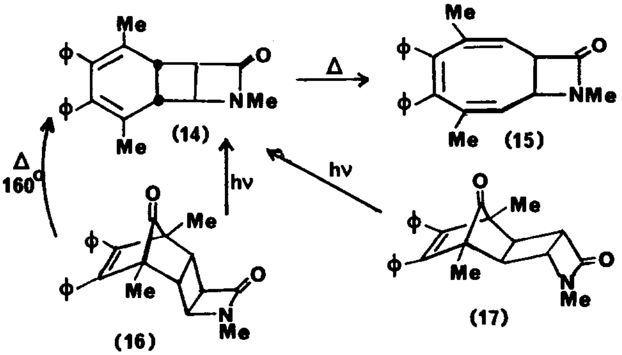
its conversion to the cyclobutene (7), m.p. 142° [p.m.r., CDCl$_3$, δ p.p.m.: 1.30 (s, 6H, CH$_3$); 3.01 (s, 2H, H$_{2,5}$), 6.11 (s, 2H, H$_{3,4}$), 6.8-7.4 (m, 10H, aromatic). $\nu_{max}$ (Nujol) 1766 cm$^{-1}$ (CO)] which differs from the *exo*-cyclobutene (5)[6]

Scheme I



The thermal stabilities of (4) and (6) to cheletropic loss of CO are markedly different - for example, in refluxing xylene solution (6) is smoothly decarbonylated to give (8) whereas (4) remains unchanged. The decarbonylated product is assigned the bicyclic structure (8), m.p. 110°, on the basis of its p.m.r. spectrum [CDCl$_3$, δ p.p.m.: 1.59 (s, 6H, CH$_3$), 3.55 (m, 2H, H$_{1,6}$), 4.90 (m, 2H, H$_{7,8}$), 6.65-3.22 (m, 10H, aromatic)] and its rapid conversion to a $[{}_{\pi}4_{s} + {}_{\pi}2_{s}]$ adduct (9), m.p. 267-8° with *N*-methyl triazolinedione (9) or the related adduct (10) with dimethyl acetylene dicarboxylate. Clearly this observation is consistent with anchimeric assistance from the geometrically aligned cyclobutyl sigma-bond in (6), as it most certainly cannot be explained in terms of steric compression effects.[8] Does the assistance provided by the σ-bond result in only small but reversible distortion of the bond [which results in the initial formation of the diene (8)] or does the loss of CO involve concommitant rupture of the σ-bond [which results in the initial formation of the triene (13)]? Unfortunately our result that (8) is formed exclusively cannot be taken as unequivocal evidence in support of the first alternative because studies by Huisgen and his coworkers[9] on related compounds and our own variable temperature pmr studies on (8) imply strongly that (8) is thermodynamically more stable than (13) and that the equilibration of the isomers would be rapid under our conditions. However in related work (scheme II) we have found that the analogous pair of

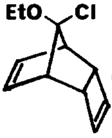
Scheme II



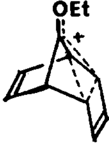
isomers (14) and (15) are stable to interconversion under the conditions which are necessary to effect the cheletropic loss of CO from (16)[10]. Thus, whereas (17)[10] was stable to loss of CO in DMSO at 160°, (16) underwent smooth decarbonylation to give exclusively (14) under these conditions. The structure of the diene (14) follows from its spectral characteristics

Separate studies on the diene (14) at 160° revealed formation of the triene (15) which was slow compared with the decomposition of (16)[10] and that (15) is thermodynamically more stable than (14). The triene structure also follows from its spectral characteristics [p.m.r.[13] singlet $CH_3$ $\delta$ 1.52, singlet *N*-$CH_3$ $\delta$ 2.96 and absence of signals in the $\delta$ 4.5-6.5 region; i.r. CO 1750 $cm^{-1}$] and its rapid formation of an adduct with *N*-phenyl triazoline dione [m.p. 272° (dec.)]. The triene structure also follows from his spectral properties [p.m.r.[13] 1.87 (dd, 3H, $C_6$-$CH_3$), 1.99 (dd, 3H, $C_3$-$CH_3$), 2.86 (s, 3H, $CH_3$), 4.30 (m, 1H, $H_1$), 4.53 (m, 1H, $H_8$), 5.52, 5.68 (m, m, 2H, $H_{2,7}$), 7.0-7.4 (m, 10H, aromatic); i.r. CO 1746 $cm^{-1}$]. We also noted that (14) was exclusively formed from the photochemical decarbonylation[11] of both (16) and (17) although at this stage the photochemical differential reactivities of (16) and (17) have not been investigated.[12]

It is clear, then, that the *endo*-isomer (16)promotes elimination of CO but it *does not involve breakage of the σ-bond.* In relation to our conclusion we draw attention to the recent report[14] concerning edge participation of an *endo*-cyclobutyl system in the solvolysis of (18a) which involves the tricyclic carbonium ion (18). Although appreciable anchimeric assistance to the generation of the carbonium ion (18) was provided by the cyclobutenyl σ-bond it also remained unbroken in the final product.



(18a)



(18)

## References and explanatory notes

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