The [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] Cycloaddition of 3-Oxaquadricyclane with Ethenetetracarbonitrile

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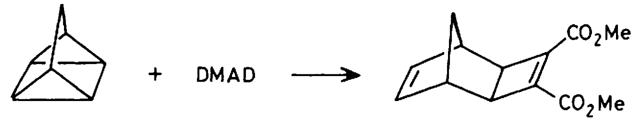
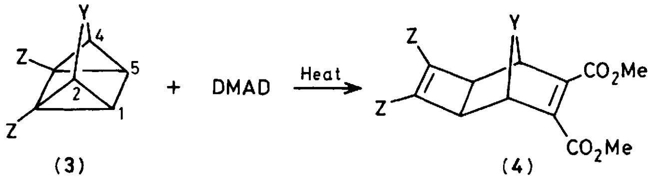
3-Oxaquadricyclane (**3a**) reacted with ethenetetracarbonitrile in a [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] manner to produce (**5**), demonstrating 1,5-attack in the concerted reaction of 3-heteroquadricyclanes, a result expected on the basis of molecular orbital analyses.

Although quadricyclane (**1**) is well known to react with activated olefins, such as dimethyl acetylenedicarboxylate (DMAD) and ethenetetracarbonitrile (TCNE), in a [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] manner to give (**2**),[1] the 3-heteroquadricyclanes (**3a**—**c**) have been shown to take a totally different reaction course (2,4-attack) to produce (**4**). In an extention of their elegant studies on hetero-substituted systems,[2] Prinzbach and Babsch[2f] demonstrated that the reaction of the 3-oxaquadricyclane (**3a**) with DMAD produces (**4a**). The [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] cycloaddition observed in the reactions of (**1**) has been shown to proceed in a concerted fashion,[3,4] whereas the 2,4-cycloaddition observed in the reactions of (**3**) is proposed to take a stepwise pathway involving an intermediate (an ylide or a diradical).[2,4] Haselbach and Martin[4] have discussed this problem in MO terms and have pointed out, on the basis of the shape of the respective HOMO's, that the HOMO–LUMO interaction is effective for 1,5-attack to occur for all systems including (**3**). Now, the favourable 2,4-attack in the heterosystems has been shown to be due to the heteroatom at the 3-position providing a driving force for 'biradical' formation. However, the wider separation between the HOMO of (**3**) and the LUMO of the addend compared to the hydrocarbon system[4] appears in part to make the 1,5-attack somewhat unfavourable in the heterosystems. If this were the case, one would expect that the concerted [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] cycloaddition (1,5-attack) might be observable even in the reactions of heterosystems if the addend had a very low-lying LUMO. We have found that (**3a**) does indeed react with TCNE readily in a [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$] manner.

3-Oxaquadricyclane (**3a**)[2f] reacted with TCNE at room

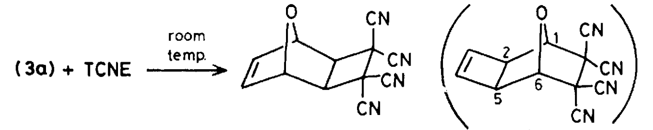


(1) (2)



(3) (4)

a; Y = O, Z = H
b; Y = O, Z = CO_2Me
c; Y = NR, Z = CO_2Me



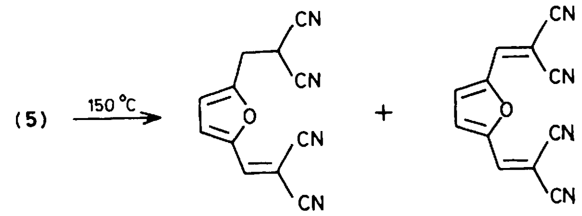
(5) (6)

temperature in acetonitrile to give a crystalline 1 : 1 adduct, m.p. 198—200 °C (decomp.),† in practically quantitative yield. The ^1H n.m.r. spectrum of the adduct showed two apparent triplets (deceptively simple AA′XX′) at δ 5.27 and 6.42 besides a singlet at δ 3.15. Structure (**5**) is compatible with this spectrum, but not (**6**). If the adduct were (**6**), C-1-H (C-6-H) would be expected to resonate as a singlet at δ *ca.* 5.27, since the coupling constant between the hydrogen at the bridged position and the *endo* hydrogen at C-2 (C-5) in the 7-heterobicyclo[2.2.1]heptane ring system is known to be very small.[2]

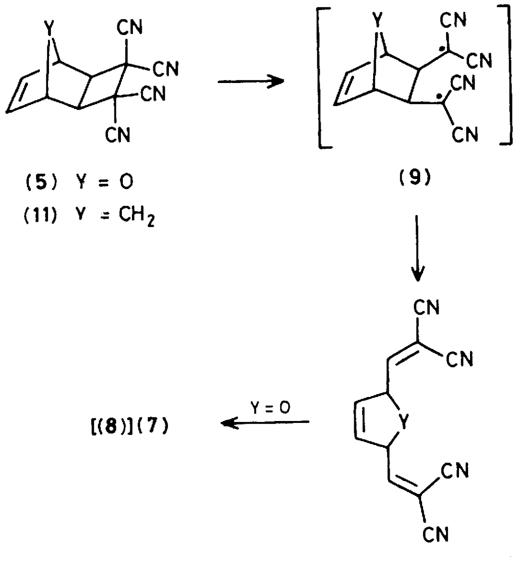
Since elucidation of the structure of the adduct on the basis of spectral examination is not entirely conclusive, we tried to prove the structure of (**5**) by studying its thermal behaviour. We expected that the retro-Diels–Alder reaction would take place, but in fact fragmentation of the four-membered ring in (**5**) was the exclusive process. When (**5**) was heated at 150 °C in 1,2-dichloroethane for 14 h, two products were isolated and characterized as the furans (**7**), m.p. 126.5—127 °C (52—70%), and (**8**), m.p. 217.5—218 °C (25—26%). Compound (**8**) was identical in all respects with an authentic specimen prepared from furan-2,5-dicarbaldehyde and malonitrile. If argon was bubbled through the starting mixture for a long period, the proportion of (**8**) was reduced.

In contrast to (**3a**), the bismethoxycarbonyl-substituted (**3b**) failed to react with TCNE under similar conditions.

The formation of (**7**) and (**8**) may be rationalized as follows. The first step will be the homolytic cleavage of the cyclobutane ring bond activated by the four cyano groups.[5] The resultant diradical (**9**) would produce the dihydrofuran (**10**), which would rearrange to (**7**) to produce the aromatic furan ring. In the reaction system, one of these species might be oxidized by oxygen to give (**8**). In support of this mechanism, heating of the hydrocarbon analogue (**11**) at 150 °C yielded (**12**), m.p. 125—127 °C (84%). Hydrogen migration did not take place in this case because aromatic stabilization is not possible after the migration.



(7) (8)



(10) Y = O
(12) Y = CH_2

In conclusion, the reaction of (**3a**) with TCNE proceeds in a [$_\pi2 + {}_\sigma2 + {}_\sigma2$] manner, the cycloaddition most probably being the concerted reaction predicted on the basis of MO analysis.[4] This conclusion is supported by the fact that the present reaction did not require an elevated temperature, which has been shown to be necessary to generate the intermediate 'diradical',[2,4] and that the methoxycarbonyl-substituted (**3b**) did not react with TCNE in a similar manner.

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† All new compounds described herein exhibited satisfactory elemental analysis and spectral data, which were available to the referees.