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COMPETITIVE DIPOLAR CYCLOADDITIONS OF TETRACYANOETHYLENE TO BICYCLO[3.2.1]OCTA-2,6-DIENE

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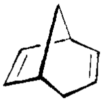
Summary: Reaction of tetracyanoethylene with bicyclo[3.2.1]octa-2,6-diene (1) produces three cycloadducts. Isolation and characterization of the products is described and possible mechanisms are discussed.

Bicyclo[3.2.1]octa-2,6-diene (1) contains both the strained norbornene and the less strained cyclohexene sections and lends itself ideally to explore site selectivities in electrophilic addition reactions. For instance, the acid catalyzed addition of acetic acid[1] to 1 affords 2, acetoxymercuration[2] and acetoxypalladation[2] give rise to 3 and 4, respectively.

The facility of electrophilic additions to 1 and our interest in cycloaddition reactions in general[3,4,5,6] encouraged an investigation of addition of electron-deficient cycloaddends to this olefin. A recent report by Adam et al.,[7,8] stating that 1 gives with tetracyanoethylene an intractable product mixture prompted us to describe our own results from this reaction.



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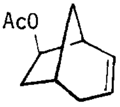

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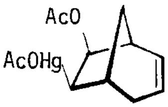

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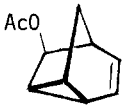

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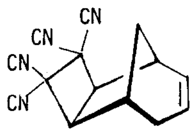
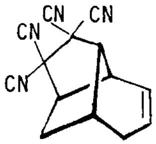
When a carefully degassed solution of equimolar amounts of TCNE and 1 in benzene was heated in a sealed tube at 100°C for 3 hours, a dark solution resulted. An ^{1}H NMR spectrum of the crude mixture indicated that it consisted of more than one cycloadduct. A separation of the products by column chromatography on Silica gel could not be achieved, however, repeated fractional crystallizations ($CHCl_3$) permitted the isolation of two major products. The less soluble component was identified as the 2+2 adduct 5. The component which was isolated from the mother liquor proved to be a mixture of 6 and the homocycloadduct 7. An unequivocal structural assignment of the adducts 6 and 7 was possible by means of their distinctly separated signals in the 400 MHz ^1H NMR spectrum. Also, satisfactory elemental analysis and IR spectral data support the proposed structures of the three adducts[9,10] (total yield 67%).



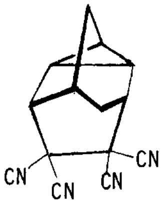
5

31%



6

53%

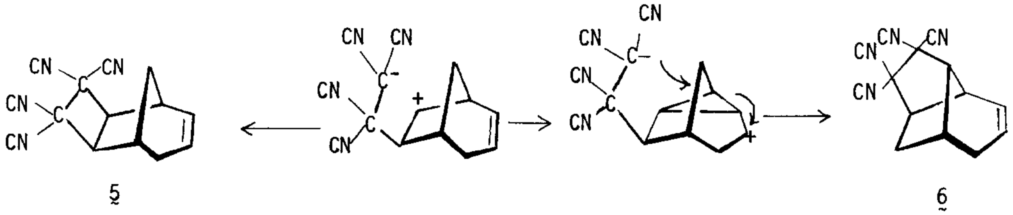


7

16%

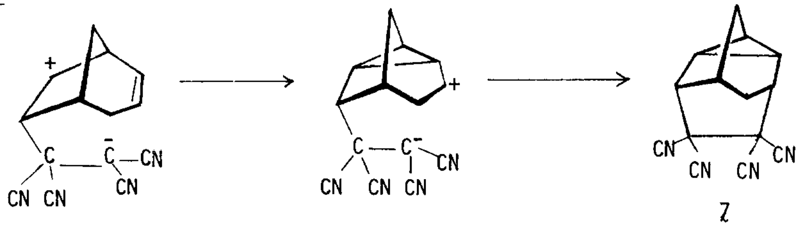
The formation of 5 and 6 is most reasonably explained by the mechanism depicted in Scheme I. Thus, initial exo-attack of TCNE at C-6 should generate a dipolar species which cyclizes in a stepwise fashion to the 2+2 adduct. Alternatively, involvement of the remote double bond would result in a cyclopropylcarbinyl cation which then rearranges to 6.

Scheme I



The Homo-Diels-Alder type cycloadduct could arise from a symmetry-allowed concerted [2+2+2]cycloaddition mode. Alternatively, an initial endo-attack at C-6 with transient intervention of the cyclopropylcarbinyl cation could preceed ring closure to 7 (Scheme II).

Scheme II



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The Homo-cycloadduct comprises less than 20% of the total; the dominant mode of the cycloaddition involves a dipolar exo-attack of TCNE at the more strained double bond in **1**[11]. The predominance of the dipolar cycloadducts is yet another example of the strong dipolar character of TCNE cycloadditions. It is also interesting to note that not even traces of products that might have arisen from an attack of TCNE at the less strained cyclohexene moiety of **1** were detected. Thus, **1** appears to be a sensitive probe of cyclic and noncyclic addition processes.

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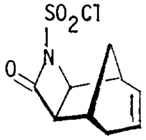
9) TCNE-Adduct (5), mp. 167-170°C (dec., needles from $CHCl_3$/n-hexane); ^1H NMR (d_6-acetone, TMS) ∂ (ppm): 2.08 (d, 1H, A part of an AB-system, $J_{10,10'}$ = 13.0 Hz); 2.17 (dm, 1H, A part of an AB-system, $J_{9,9'}$ = 18.4 Hz); 2.40 (dm, 1H, B part of an AB-system, $J_{10,10'}$ = 13.0 Hz); 2.55 (dm, 1H, B part of an AB-system, $J_{9,9'}$ = 18.4 Hz); 2.75 (dd, 1H); 2.88 (dd, 1H); 3.74 (d, 1H, A part of an AB-system, $J_{2,5}$ = 7.2 Hz); 3.79 (d, 1H, B part); 5.53 (m, 1H); 5.96 (m, 1H). IR (KBr) ν (cm^{-1}): 3000, 2940, 2850, 2225, 1620, 1470, 1430, 1300, 1100, 730.

10) TCNE-Adduct (6), mp. 156-157°C (dec., mixture of 6 and 7, needles from $CHCl_3$/n-hexane), ^1H NMR (d_6-acetone, TMS) ∂ (ppm): 1.87 (ddd, 1H, A part of an AB-system, $J_{6,6'}$ = 15.0 Hz, $J_{6',7}$ = 5.2 Hz, $J_{5,6'}$ = 2.4 Hz); 1.97 (dd, 1H, B part of an AB-system, $J_{6,6'}$ = 15.0 Hz, $J_{5,6}$ = 7.6 Hz); 2.17 (dm, 1H, A part of an AB-system, $J_{4,4'}$ = 18.4 Hz); 2.57 (d, 1H, B part); 2.65 (m, 1H); 2.99 (d, 1H, J = 6.0 Hz); 3.17 (s, 1H), 3.55 (d, 1H, J = 5.2 Hz); 5.81 (m, 1H); 5.86 (m, 1H). Adduct (7), ^1H NMR (d_6-acetone, TMS) ∂ (ppm): 1.72-2.0 (m, 3H); 1.78 (m, 2H); 1.63 (dd, 1H, J = 6.0 Hz, J = 15.0 Hz); 1.48 (dt, 1H, J = 6.0 Hz, J = 7.4 (Hz); 2.38 (q, 1H, J = 6.0 Hz); 3.42 (m, 1H); 3.50 (m, 1H).
IR (KBr, 6+7) ν (cm^{-1}): 3010, 2925, 2830, 2250, 1630, 1460, 1300, 1230, 1195, 710.

11) In contrast, chlorosulfonyl isocyanate gave with 1 (in CH_2Cl_2 at room temperature) exclusively the 2+2 adduct 8. ^1H NMR (60 MHz, $CDCl_3$, TMS) ∂ (ppm): 1.70 (m, 1H); 2.05 (m, 2H); 2.30 (m, 1H); 2.70 (m, 1H); 3.05 (m, 1H); 3.50 (d, 1H, A part of an AB-system); 4.50 (d, 1H, B part); 5.35-6.05 (m, 2H). IR (film) (cm^{-1}): 3025, 2950, 2900, 2820, 1820, 1425, 1190, 1110, 1030, 760.



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