Zwitterion Mediated Cocyclo-oligomerization of Small Ring Ethers. Cycloadditions to a Spiroanellated Bicyclopropyl Unit

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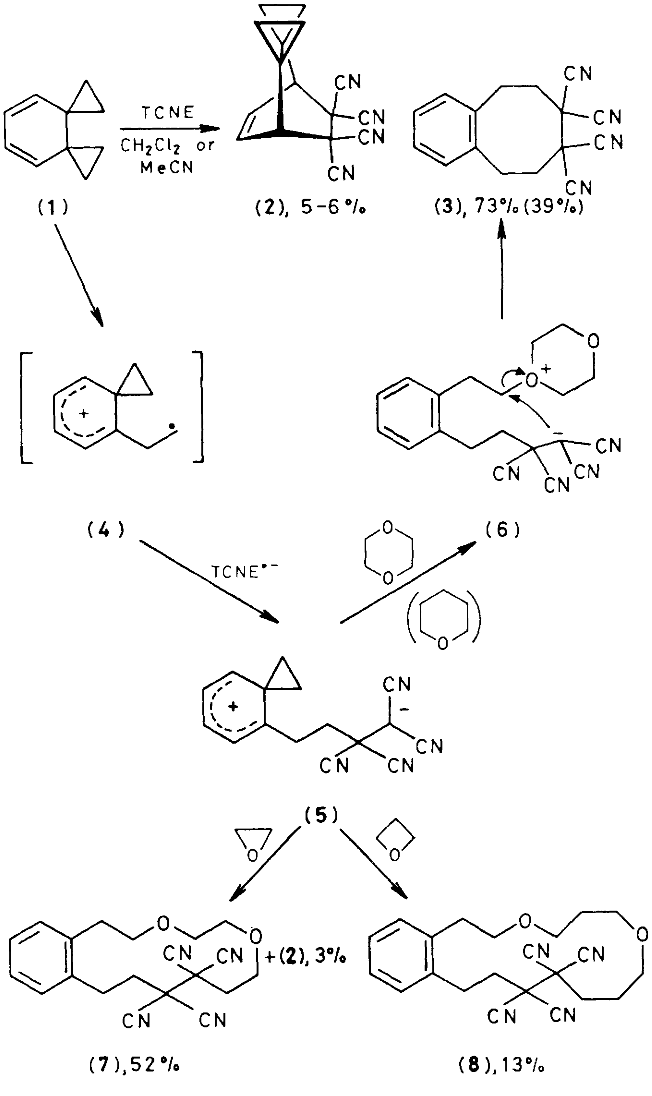
The diene (**1**) reacts with tetracyanoethylene in the presence of oxirane or oxetane to yield the macrocyclic 1:1:2 cocycloadducts (**7**) and (**8**) respectively; only small amounts of the normal [4 +2] cycloadduct (**2**) are formed in any solvent, whereas the abnormal benzocyclo-octene derivative (**3**) is obtained in 1,4-dioxane almost exclusively.

Dispiro[2.0.2.4]deca-7,9-diene (**1**) which features a unique cyclic array of a 1,3-diene and a bicyclopropyl ('bishomodiene') unit, can undergo two different types of cycloadditions. Various dienophiles[1,2] add to its 1,3-diene moiety in a normal Diels–Alder reaction, whereas tetracyanoethylene (TCNE) in tetrahydrofuran (THF) attacks its bicyclopropyl unit and yields, after incorporation of two molecules of solvent, an 18-membered macrocycle.[3] To test for the possible generalization of this type of cocycloaddition we treated (**1**) with TCNE in a variety of cyclic ethers.

Equimolar amounts of (**1**) and TCNE were added separately to an excess of the dry ether (neat or in CH_2Cl_2) at room temperature (−20 °C with ethylene oxide solution) under an atmosphere of dry nitrogen. The products were purified by column chromatography on silica gel and characterized by their ^1H n.m.r. and mass spectra.† With oxirane and oxetane respectively the 1 : 1 : 2 cocycloadducts (**7**) and (**8**) were formed in addition to homopolymers of the ethers. The 14-membered ring compound (**7**) was isolated in 52% yield‡ when the reaction was carried out in CH_2Cl_2 with 33 mol. equiv. of ethylene oxide. Surprisingly, (**7**) was not formed in 1,4-dioxane; in this solvent the vastly predominating product (73%)‡ was the new 1 : 1 cycloadduct, the benzo-cyclo-octene-tetracarbonitrile (**3**). The same compound (**3**) was obtained in tetrahydropyran albeit in lower yield. This constitutes the first formal cycloaddition of a dienophile to a bicyclopropyl unit.[4]

Since the diene (**1**) has a high lying HOMO,[1] its sequential reactions with TCNE most probably start with an electron transfer. It is likely that the initial diene radical cation instantaneously ring-opens at one of its cyclopropyl spiro carbon atoms[5] to give (**4**) which is too short-lived to be detected by e.s.r. spectroscopy.[6] Formation of the $TCNE^{\cdot -}$ radical anion, though, was observed by e.s.r.[7] spectroscopy upon addition of (**1**) to TCNE in both THF[7] and methylene dichloride solutions. Apparently, the intimate radical ion pair (**4**)–$TCNE^{\cdot -}$ rapidly collapses to the 1,9-zwitterion (**5**). In contrast to the 1,4-zwitterionic intermediates from enol ethers and TCNE,[8] the longer-lived (**5**) can be attacked by the nucleophilic cyclic ether to give new zwitterions, which prefer to cyclize after another attack by a second molecule of the ether. An attempt to trap (**5**) with ethanol[9] was unsuccessful.



Because of their smaller tendency for ring opening the unstrained 6-membered cyclic ethers as in (**6**) are not incorporated in the adduct.[10] The normal Diels–Alder cycloadduct (**2**) is formed as a by-product (3%) in dioxane; in CH_2Cl_2 and acetonitrile (**2**) is obtained in small yields as the only low molecular weight product.

The cocyclo-oligomerizations of THF, oxetane, and oxirane reported here are interesting in that they complement the known zwitterion initiated homopolymerizations of such ethers observed by J. K. Stille *et al.*[11]

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† Characteristic data [n.m.r. chemical shifts from δ(Me_4Si), cm = centre of multiplet] for (**2**), m.p. 231 °C, ^1H n.m.r.(100 MHz, C_5D_5N–CH_2Cl_2), δ 6.44 (dd, 2H), 2.88 (dd, 2H), 0.88 (cm, 4H), and 0.10 (cm, 4H); (**3**), m.p. 210 °C, ^1H n.m.r. (60 MHz, $CDCl_3$), δ 7.34 (cm, 4H) and 3.00 (centre of complex m, 8H); (**7**), ^1H n.m.r. (60 MHz, C_5D_5N), δ 7.10 (br. s, 4H), 4.16—3.76 (m, 2H), 3.76—3.24 (complex m, 9H), and 3.24—2.34 (complex m, 5H); *m/z* 348 (M^-); (**8**), m.p. 175—176 °C, ^1H n.m.r. (60 MHz, C_5D_5N), δ 7.23 (br. s, 4H), 3.85 (cm, 2H), 3.42 (cm, 9H), 3.16—2.54 (complex m, 5H), and 2.20—1.34 (complex m, 4H); *m/z* 376 (M^+).

‡ Yields correspond to isolated products. All new compounds gave satisfactory elemental analysis data.

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