Reaction of Tetracyclopropylethylene with Tetracyanoethylene

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Summary Tetracyclopropylethylene reacts with tetracyanoethylene to give a cyclopropane-cleaved tricyclopropylvinylcyclopentane derivative; this is in striking contrast to the 2 + 2 cycloadditions of di- and tricyclopropylethylene with tetracyanoethylene in which cyclobutane derivatives are formed.

IN a previous communication,[1] we described the ready 2+2 cycloaddition reactions of various di- and tri-cyclopropylethylene with tetracyanoethylene. We now report on the reaction of tetracyclopropylethylene (**1**)[2] with tetracyanoethylene (**2**).

When (**1**) and (**2**) were mixed in acetonitrile in the absence of air, a red-brown solution was obtained. The colour slowly faded with time at room temperature and a light green solution was obtained after three days. Evaporation of the solvent gave a colourless crystalline adduct (m.p. 100—101°, 81%). On the bases of analytical and spectral data, this material is assigned to be 1-tricyclopropylvinyl-2,2,3,3-tetracyanocyclopentane (**3**). This is confirmed by the fact that ozonolysis of (**3**) gave 2,2,3,3-tetracyanocyclopentyl cyclopropyl ketone (**4**) (m.p. 155·0—156·5°, 91%) and dicyclopropyl ketone. A similar cycloaddition involving cleavage of the cyclopropane ring was also observed in the corresponding reaction of 1,1-dicyclopropyl-2,2-diphenylethylene (**5**) with (**2**) in acetonitrile (70%). These cyclopropane cleaved cycloadditions are designated as *type a* cycloadditions in the following discussion.

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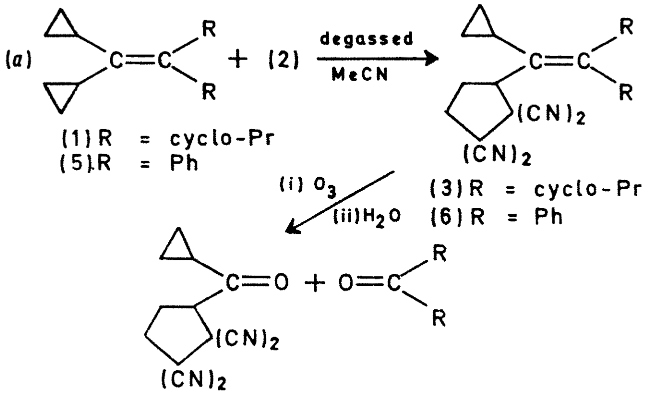

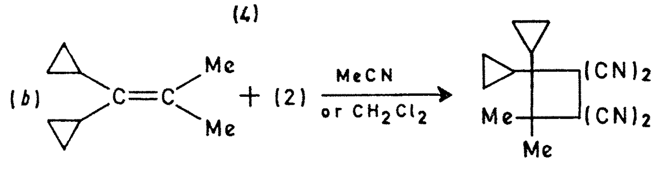

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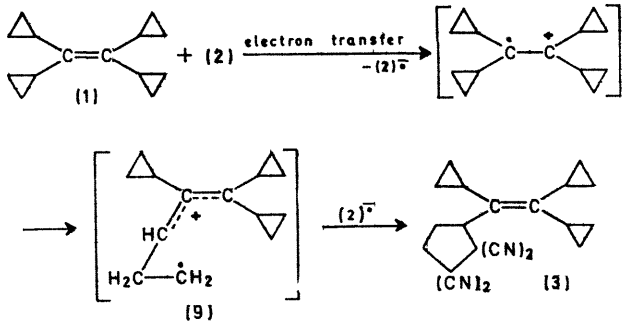
1,1-Dicyclopropyl-2,2-dimethylethylene (**7**), however, produced a blue solution with (**2**) either in acetonitrile or in methylene dichloride and a 2+2 cycloadduct (**8**) (m.p. 148—149°, 70% in both solvents) was isolated from the solution after 40 h at room temperature. The course of this reaction is the same as that observed in the reactions of di- and tri-cyclopropylethylene with tetracyanoethylene.[1] These reactions are termed *type b* cycloadditions.

There are notable differences between cycloadditions *a* and *b*: (i) a charge transfer colour develops in *b* but not in *a*; (ii) the absence of oxygen is required for *a* but not for *b*; and (iii) a cyclopropane cleaved adduct is formed in *a*, but a 2+2 cycloadduct is produced in *b*. These observations suggest that the radical species of considerable life-time may exist in the cycloaddition *a*. In fact, e.s.r. and visible spectral investigations of the freshly prepared solution of (**1**) with (**2**) in degassed acetonitrile exhibited signals (the intensities slowly decreased with time) which agreed with those of (**2**)$^{\overline{\cdot}}$.[3,4]



The formation of (**3**) may be explained as follows. An electron transfer from (**1**) to (**2**) will produce (**2**)$^{\overline{\cdot}}$ and (**1**)$^{\overset{+}{\cdot}}$ and the latter will rearrange to an allylic cation radical (**9**). The cycloaddition of (**9**) with (**2**)$^{\overline{\cdot}}$ may lead to the five-membered cycloadduct. The formation of (**6**) from (**5**) and (**2**) will also follow a similar route. Recently, Martini and Kampmeier[5] have reported that 1,1-diphenylcyclopropane can also react with tetracyanoethylene at 125° to afford a cyclopropane cleaved cycloadduct.

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