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REACTION OF CYCLOPROPANONE ACETALS WITH TETRACYANOETHYLENE

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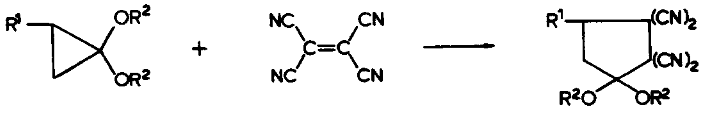
Only a few examples of thermal [2+2+2] cycloadditions are reported [2] where a C-C single bond participates as a two-electron component. To our knowledge no reaction is known in which an electron-rich C-C single bond is involved in a ($_{\sigma}2+_{\pi}2$) cycloaddition. Recently Bakker [3] described such a cycloaddition between 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and cyclopropanone methyl hemiacetal and cyclopropanone dimethyl acetal to thermally unstable products. In order to simplify the analysis of the reaction we studied the cycloadditions with tetracyanoethylene (TCNE).



1 a) $R^1 = C_6H_5$, $R^2 = CH_3$
b) $R^1 = H$, $R^2 = C_2H_5$

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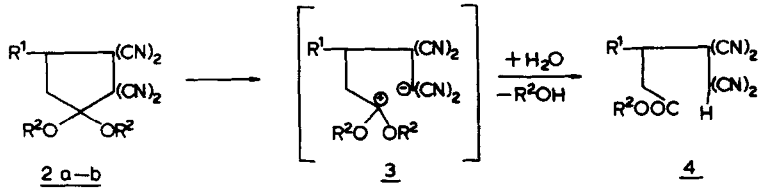
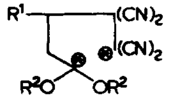
When a solution of 2-phenylcyclopropanone dimethyl acetal 1a in benzene was added to a yellow solution of TCNE in benzene at room temp., the solution turned immediately deep red and faded within a few seconds, indicating that the reaction was complete. Only the cycloadduct 2a was obtained in 93% yield [4]. NMR ($CDCl_3/CD_2Cl_2$): δ 2.65-2.9(m,CH_2),3.60(s,OCH_3),4.25(t,ØCH) and 7.50 ppm (s,C_6H_5). IR (KBr): 3000-2950(CH),2850(OCH_3),2260(CN) and 1100-1050 cm^{-1} (COC). Cyclopropanone diethyl acetal 1b and TCNE gave in refluxing methylene chloride for 17 hrs. the cycloadduct 2b in about 81% yield. NMR (CD_2Cl_2): δ 1.30(t,CH_3),2.2-3.0(m,CH_2) and 3.80 ppm (q,OCH_2). IR ($CHCl_3$): 3000-2900(CH), 2250(CN) and 1050-1150 cm^{-1} (COC).

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● = ⊕ resp ⊖

or ● = ⊙ resp ⊙

An attempt to recrystallise 2b from a (not dried) chloroform-pentane mixture afforded however ethanol and the ring-opened product 4b. NMR (CD_2Cl_2): δ 1.30 (t,CH_3),2.4-3.05(m,CH_2),4.22(q,OCH_2) and 4.83 ppm (br.s,$CH(CN)_2$). IR ($CHCl_3$): 3650($(CN)_2CH$),3000-2900(CH),2280(CN),1735(C=O) and 1220-1190 cm^{-1}(COC).

It appeared that a solution of 2b and 1 eq. of water in methylenechloride could smoothly be converted into ethanol and 4b at room temp. The single proton at δ 5.20 (in CD_3CN) disappeared after shaking with D_2O and its chemical shift is almost equal to that of the exchangeable tetracyanoethane [5] proton (δ 5.06 in CD_3CN). The phenyl-substituted cycloadduct 2a reacted with water more slowly in the more polar solvent acetonitrile (60°C,18 hrs.) to give the ester 4a and methanol (R^2=CH_3). NMR (CD_3CN): δ 3.2-3.3(m,CH_2),3.58(s,OCH_3), 4.05(t,OH),4.82(s,$CH(CN)_2$) and 7.50 ppm (s,C_6H_5). IR ($CHCl_3$):3650($(CN)_2CH$), 2950-2850(CH),2250(CN),1740(C=O) and 1220-1170 cm^{-1}(COC).

At this stage we cannot be certain whether the aforementioned reactions are true ($_\sigma 2+_\pi 2$) with more or less synchronous bond-making and -breaking or that the reaction takes place step-wise through a zwitterionic or a diradical intermediate 5. A study of solvent effects and pressure dependence will be undertaken in order to get more evidence about the mechanism.

References

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