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CYCLOADDITION REACTIONS OF SOME 7-ALKYLIDENECYCLOOCTA-1,3,5-TRIENES

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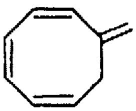
Abstract: Novel adducts are formed when 7-methylenecycloocta-1,3,5-triene is treated with reactive dienophiles and chlorosulphonyl isocyanate. Other 7-alkylidenecycloocta-1,3,5-trienes form analogous adducts with tetracyanoethylene.

We wish to report that some 7-alkylidenecycloocta-1,3,5-trienes undergo novel cycloaddition reactions. 7-Methylenecycloocta-1,3,5-triene (1)[1] reacts rapidly with tetracyanoethylene in ethyl acetate to give two adducts, (2) (43%), m.p. 141.5-143°, and (3) (11%)[3], m.p. 126-127.5°. On being warmed, (3) is converted quantitatively into (2). The structure (2) for the major product (designated as the "8 + 2" adduct[4]) is based on spectral data.[5] Likewise, the structure (3) for the minor adduct (designated as the "cyclopropyl" adduct) is also based on spectral data.[6]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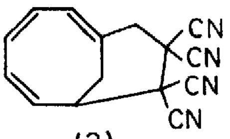

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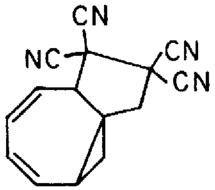

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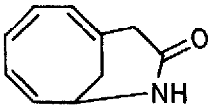
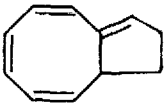


(4)

With 4-phenyl-1,2,4-triazoline-3,5-dione, a very reactive dienophile, the tetraene (1) gives quantitatively the "8 + 2" adduct, m.p. 213-214°, almost instantaneously. Diethyl azodicarboxylate reacts slowly with (1) to give the "8 + 2" adduct (22%), m.p. 116-118°, and two minor, unidentified products. No adducts could be isolated when (1) was treated with maleic anhydride and dimethyl acetylenedicarboxylate, two relatively unreactive dienophiles. Treatment of (1) with chlorosulphonyl isocyanate followed by alkaline sodium sulphite[7] gives the "8 + 2" adduct (4) (29%), m.p. 141-142.5°.

Bicyclo[6,3,0]undeca-2,4,6,1(11)-tetraene (5)[8] reacts readily with tetracyanoethylene in ethyl acetate to give the "8 + 2" adduct (*c.* 79%), m.p. 203-203.5°, as the only product. On the other hand, bicyclo[6,4,0]dodeca-2,4,6,1(12)-tetraene (6)[8] reacts rapidly with tetracyanoethylene in ethyl acetate to give the "cyclopropyl" adduct (*c.* 35%), m.p. 174-175°, and an inseparable mixture of the "8 + 2" adduct and an unidentified compound.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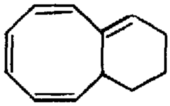
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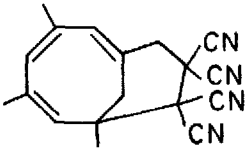

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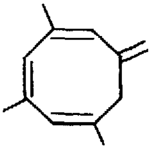
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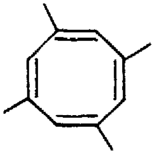
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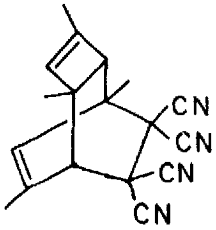
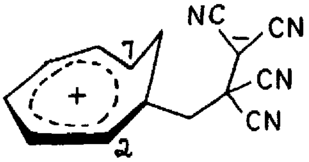


(10)

Recently, Simons and Lagowski[4] reported the isolation of the "8 + 2" adduct (7) from the treatment of a mixture of propyne oligomers with tetracyanoethylene in ether/dioxane. It was proposed that (7) arose from 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (8) which was itself derived from 1,3,5,7-tetramethylcyclooctatetraene (9) through isomerization induced by tetracyanoethylene radical anion. In our hands, treatment of 1,3,5,7-tetramethylcyclooctatetraene[10] with tetracyanoethylene under three sets of conditions gives the following results: (1) in ether/dioxane at room temperature for 20 days - no adducts are formed; (2) in ethyl acetate at room temperature for 2 days - the "8 + 2" adduct (7) (5%) is produced; and (3) in boiling ethyl acetate for 4 hours - the "8 + 2" adduct (10%) and the 2 + 4 adduct (10) (90%), m.p. 173.5-174.5°, are formed. The action of potassium t-butoxide in dimethyl sulphoxide on 1,3,5,7-tetramethylcyclooctatetraene gives a mixture of unchanged compound (42%) and 7-methylene-1,3,5-trimethylcycloocta-1,3,5-triene (58%,by ^{1}H n.m.r. spectroscopy). When this mixture is treated with tetracyanoethylene in ethyl acetate at room temperature for 15 min, a quantitative yield (based on the methylene derivative) of the "8 + 2" adduct (7) and the unchanged 1,3,5,7-tetramethylcyclooctatetraene (95%) are obtained.



(11)

It is suggested that homotropylium zwitterions are involved in the reactions mentioned above. Taking the reaction of 7-methylenecycloocta-1,3,5-triene (1) with tetracyanoethylene as an example, it is believed that the zwitterion (11) is initially formed. Charge annihilation at C$_2$ and C$_7$ would yield the "cyclopropyl" and "8 + 2" adducts, respectively.

Acknowledgement: We are grateful to the Australian Research Grants Committee for support of this work.

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3. Satisfactory microanalytical and spectral data have been obtained for each of the new adducts mentioned.
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5. ^{1}H n.m.r. (CDCl$_3$) δ 6.40-5.90 (5H, complex), 3.73 (1H, singlet), 3.15 (2H, singlet), 3.12 and 2.20 (2H, AB quartet, J_{AB} 14Hz with further splitting into doublets J 2 and 3Hz, respectively; double irradiation at *c.* δ 3.1 caused the doublet of doublets at δ 2.20 to collapse to a broad "singlet"); ^{13}C n.m.r. δ 27.8 (triplet, J 137Hz), 42.9 (triplet, J 131Hz), 47.8 (doublet, J 137Hz), 125.5 (doublet, J 163Hz), 128.2 (doublet, J 169Hz), 128.8 (doublet, J 169Hz), 131.1 (doublet, J 156Hz), 131.6 (doublet, J 156Hz), 132.5 (singlet); λ_{max}^{EtOH} 218 nm (ε 3.1 x 10^3), shoulder at 257 nm.

6. ^{1}H n.m.r. (CDCl$_3$) δ 6.50-5.50 (4H, complex), 3.78 (1H, doublet, J 3Hz), 2.95 and 2.62 (2H, AB quartet, J_{AB} 14Hz), 1.90-0.77 (3H, complex); ^{13}C n.m.r. δ 21.01 (triplet, J 163Hz), 23.56 (doublet, J 169Hz), 35.35 (singlet), 45.91 (triplet, J 138Hz), 55.75 (doublet, J 138Hz), 123.04 (doublet, J 163Hz), 124.38 (doublet, J 163Hz), 132.03 (doublet, J 155Hz), 135.78 (doublet, J 163Hz); λ_{max}^{EtOH} 203 nm (ε 3.9 x 10^3) and 258 (ε 2.9 x 10^3).

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8. Compounds (5) and (6), both very unstable, were obtained from the solvolysis of 3-cyclooctatetraenylpropyl and 4-cyclooctatetraenylbutyl *p*-nitrobenzenesulphonates in trifluoroethanol and hexafluoropropan-2-ol.[9] The reactions of (5) and (6) with tetracyanoethylene prompted the more detailed study of the addition reactions of the tetraene (1) that is reported here.

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