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8 + 2 CYCLOADDITION REACTIONS OF 1,6-DIMETHYLENE CYCLOHEPTA-2,4-DIENE

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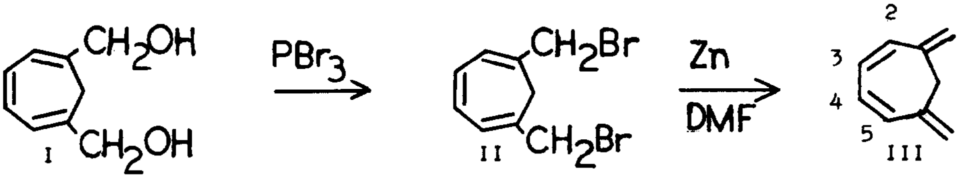
In the course of finding new ways to form bridged annulenes[2] we have synthesized the tetraene 1,6-dimethylene cyclohepta-2,4-diene III as a potentially useful intermediate. It was reasoned that III would undergo 8 + 2 cycloadditions with some dieneophiles to form both carbocyclic and hetrocyclic ring systems, depending upon the dienophile employed. Although 8 + 2 cycloaddition reactions are symmetry allowed, according to the Woodward-Hoffmann Theory,[3] they have only been rarely observed. In the instances in which 8 + 2 cycloaddition reactions have occurred the initial products have either undergone susequent reactions or have not been fully characterized spectroscopically. We wish to report that III forms 1 : 1 adducts with both tetracyanoethylene and dimethyl azodicarboxylate and the products of these two reactions have been produced by a 8 + 2 cycloaddition process.

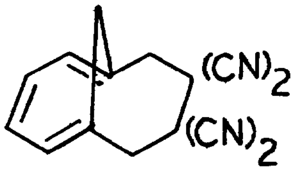
Synthesis of the tetraene III was accomplished in two steps starting from the known diol I[5] which was prepared by the method outlined by Vogel, Feldmann, and Düwel.[6] Treatment of I with PBr_3 in ether at 0° produced the dibromide II (m.p.=42-43) in 60% yield. III could be obtained in 79% yield by reaction of II with zinc dust in DMF at 20° for five hours. Since III is air sensitive, all reactions were carried out under an argon atmosphere. III was isolated by extraction into oxygen free pentane, washing with air-free water, drying over magnesium sulfate, removal of solvent at 12 torr, and evaporation into a cold trap (-78°) at 20° at 0.6 torr. An analytically pure sample of III could be prepared by elution over silica gel with pentane, removal of the solvent, and distillation into a cold trap ($b.p._{12}=60^{\circ}$; $n_D^{20} = 1.5900$).

The structure of III was confirmed by its spectroscopic properties and elemental analysis. ^1H NMR-spectrum (CCl_4) $\tau = 3.8, 4.4$ (AA'BB'-system, 4

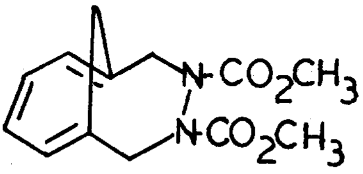


vinyl protons; $J_{2,3} = J_{4,5} = 12.1$ Hz, $J_{3,4} = 7.9$ Hz, $J_{2,4} = J_{4,5} = 0.9$ Hz, $J_{2,5} = 1.0$ Hz), $\tau = 5.0$ (multiplet, 4 exo-vinyl protons, $\tau = 6.7$ (singlet allyl protons). Mass spectrum: $m^+ = 118$ (100%), $m^+-1 = 117$ (80%), $m^+-15 = 103$ (13%). UV-spectrum: (cyclohexane) λmax:= 222 mu ($\epsilon = 22800$), 322 mu ($\epsilon = 9440$), 308 ($\epsilon = 7740$, shoulder, 335 ($\epsilon = 6710$, shoulder). IR-spectrum: (neat), 3025 cm^{-1} C = C stretch. (Anal calcd for C_9H_{10}: C, 91.47; H, 8.57; Found: C, 91.62; H, 8.39.

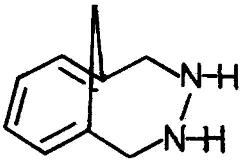
Reaction of III with tetracyanoethylene in THF or with dimethyl azodicarboxylate in methylene chloride at 20° produced the monoadducts IV (m.p. 168.8 - 170.0° decomp.) and V in yields of 74% and 40% respectively. The products were isolated by elution chromatography over silica gel. The structure of the monoadducts are confirmed by their ^1H NMR- and UV-spectra shown in Table I.



IV



V



VI

TABLE I

^1H NMR absorption spectra in units with TMP as internal standard

IV	V	VI	System	Proton Type
3.1, 3.7	3.3, 3.8-4.3	3.4, 4.1	AA'XX'	4 vinyl
6.28, 6.76 ($J_{AB} = 14.6$ Hz)	1.8-7.1 (complex)	6.34, 6.82 ($J_{AB} = 12.5$ Hz)	AB	4 allyl
6.88, 8.92 ($J_{AB} = 12$ Hz)	6.98, 8.93 ($J_{AB} = 10$ Hz)	9.38, 6.46 ($J_{AB} = 9$ Hz)	AB	2 Bridge
	6.25, 6.50		singlets	Methyl
		7.5	singlet	N-H

TABLE II - UV DATA

	IV	V	VI
UV λmax (ε)	211 (16250 257 (3540)	208 (23300) 257 (3900)	213 (19450) 260 (3930)

The large chemical shift differences and the large coupling constant of the bridge protons indicate that the monoadducts have the cycloheptatriene rather than the valence isomeric norcaradiene structure.[7]

The methyl as well as the allyl protons of V are magnetically non-equivalent at 35° and remain so even at 200°. Although the two non-symmetrical methyl absorption peaks have become equal in height and considerably broadened at this high temperature, the two peaks have not yet coalesced. The situation of the allyl proton absorption is even more complex, for a series of absorptions sharpen up but still overlap in part with the methyl absorption at higher temperatures. From the temperature dependence of the spectrum it is clear that the barrier to inversion at nitrogen and/or hindered rotation of the carbomethoxy groups must be greater than 24 kcal.[7] How much of this barrier is due to inversion at nitrogen and how much is due to hindered rotation about the nitrogen atom by the carbomethoxy groups has not yet been determined.

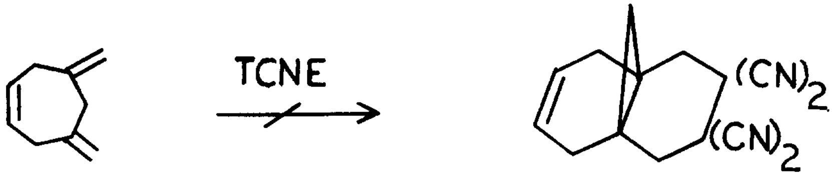
In order to obtain a more simplified spectrum the carbomethoxy groups were removed by refluxing V in 25% methonolic KOH: yield 38%, $b.p._{.06} = 63^{\circ}$. The ^{1}H NMR spectrum of VI (Table I) is first order and except for the N-H protons resembles that of IV.

The UV-spectra of compounds IV-VI are practically superimposable (Table I), indicating similar structural features.

Reaction of III with the dienophiles maleic anhydride, N-phenyl-1,2,4-triazo-3,5-dione, and benzyne produced diadducts as the major product even in the presence of three mole equivalents of III. All of the compounds herein described had elemental analyses well within the acceptable limits.

Reaction of the triene VII[8] with tetracyanoethylene or diethyl azodicarboxylate under the same conditions used for the formation of IV and V or at elevated temperatures and longer reaction times failed to produce any "homo"

Diels-Alder product. Thus, it is clear, that the inner double bonds of III must participate in the formation of IV and V or, in other words, IV and V are formed via 8 + 2 cycloaddition reactions.



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7. If the compounds IV-VI had the valence isomeric norcaradiene structure it would be expected that the bridge methylene protons would both absorb at high field strength characteristic of cyclopropyl protons (τ = 8.5-11) and the coupling constant would be much smaller (J_{AB} = 0.3-5 Hz) rather than the J_{AB} = 9-12 Hz actually observed for these protons.
8. The magnetic non-equivalence of a number of alkyl azodicarboylate derivatives have been studied in detail. See the following papers: B. Price, J.O. Sutherland, and F.G. Williamson. Tetrahedron 22, 3477 (1966); J. Wagner, W. Wojarowski, J.E. Anderson, and J.M. Lehn, ibid. 25, 677 (1969); J.M. Lehn and J. Wagner, ibid. 25, 677 (1969).