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SYNTHESIS AND A $[_{\pi}2_{s}+{}_{\pi}2_{s}+{}_{\pi}2_{s}]$ CYCLOADDITION REACTION OF 5,8-DIMETHYLENE-1,3,6-CYCLOOCTATRIENE

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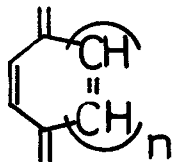
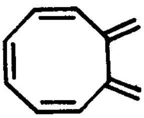
Dimethylenecyclopolyenes of type 1 are an interesting class of compounds. The n=1 member of this class is 3,6-dimethylene-1,4-cyclohexadiene 2 which is an important intermediate for [2.2]paracyclophane.[1] Of two possible dimethylenecyclooctatrienes, 7,8-dimethylene-1,3,5-cyclooctatriene 3 was synthesized as a substantially reactive substance.[2] As to 5,8-dimethylene-1,3,6-cyclooctatriene 4, we have reported the synthesis of the tetraphenyl derivative 5 by thermal ring opening of its valence isomer.[3] We wish here to report the synthesis of the parent compound 4 by a similar strategy and its cycloaddition reaction with N-phenyltriazolinedione.



1

2



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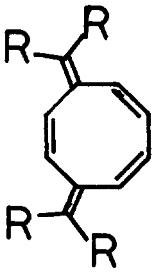


4 R=H
5 R=Ph

Reaction of bicyclo[4.2.0]octa-3,7-diene-2,5-dione 6[4] with anthracene in the presence of a small amount of borontrifluoride etherate in refluxing benzene gave the Diels-Alder adduct 7 in 94% yield [m.p. 225-226°C decomp.; ν_{max}(KBr) 1708, 1700 cm^{-1}; δ_{ppm} ($CDCl_3$) 3.47 (2H, s), 3.50 (2H, t, J=1 Hz), 4.88 (2H, t, J=1 Hz, 6.40 (2H, s), 7.0-7.5 (8H, m)]. The stereochemistry of 7 was tentatively assigned to be *exo* from steric point of view. The Wittig reaction of 7 with methylenetriphenylphosphorane (five molar folds) in dimethyl sulfoxide at room temperature gave the monomethylene compound 8 and the dimethylene compound 9 in 43% and 3% yield, respectively [8: m.p. 195-196°C; ν_{max}(KBr) 1700, 1640, 910cm^{-1}; δ_{ppm}($CDCl_3$) 3.3 (3H, m), 3.56 (1H, br. d, J=4.5 Hz), 4.64 (1H, br. d, J=2 Hz), 4.75 (1H, br. d, J=2 Hz), 4.98 (1H, br. s), 5.18 (1H, br. s), 6.11 (1H, dd, J=2.8, 1 Hz), 6.48 (1H, dd, J=2.8, 1 Hz), 7.0-7.5 (8H, m); 9: m.p. 178-180°C; ν (KBr) 1640, 1470, 1284, 884, 765, 745 cm^{-1}; δ ($CDCl_3$) 2.97 (2H, br.s), 3.21

(2H, s), 4.43 (2H, br. s), 4.81 (2H, br. s), 5.03 (2H, br. s), 6.10 (2H, s), 6.9-7.4 (8H, m)]. Further treatment of 8 with the reagent at a similar condition provided 9 in 58% yield. The requirement of rather large excess of the reagent for the reaction may be due to steric crowdedness around the carbonyl groups.

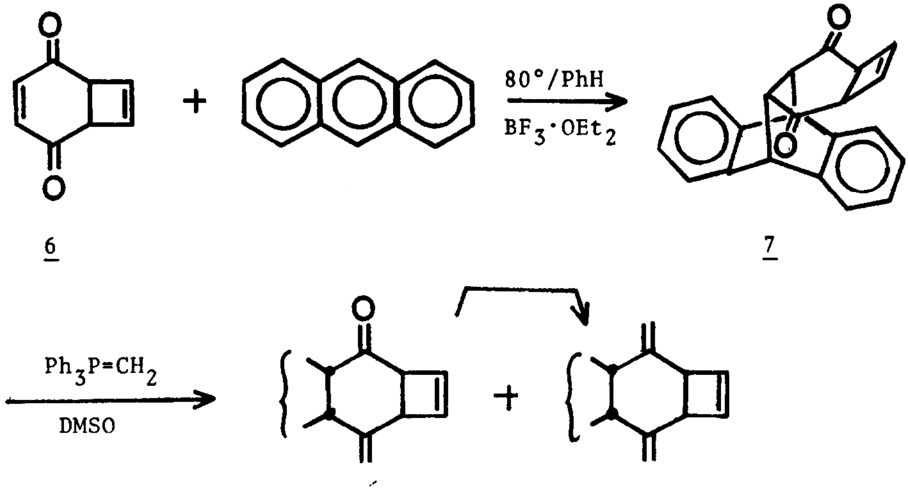
When 9 was pyrolyzed at 310°C at 0.2 mm/Hg by a flash method[5] and the volatile product was trapped at -60°C, 2,5-dimethylenebicyclo[4.2.0]octa-3,7-diene 10 was obtained in 19% yield, besides anthracene (38%) and unreacted 9 (50%)[6] [10: colorless liquid; ν_{max}(liquid) 1600 m, 1555 w, 870 s, 787 s cm^{-1}; λ_{max}(n-hexane) 248 sh (ϵ 14500), 257 (24500), 267 (32500), 278 nm (25500); δ_{ppm}($CDCl_3$) 3.84 (2H, s, bridgehead), 5.00 (4H, s, methylene), 6.04 (2H, s, cyclohexene), 6.12 (2H, s, cyclobutene)]. Although fairly stable in neutral solutions, 10 was liable to polymerize in neat state in air at room temperature.

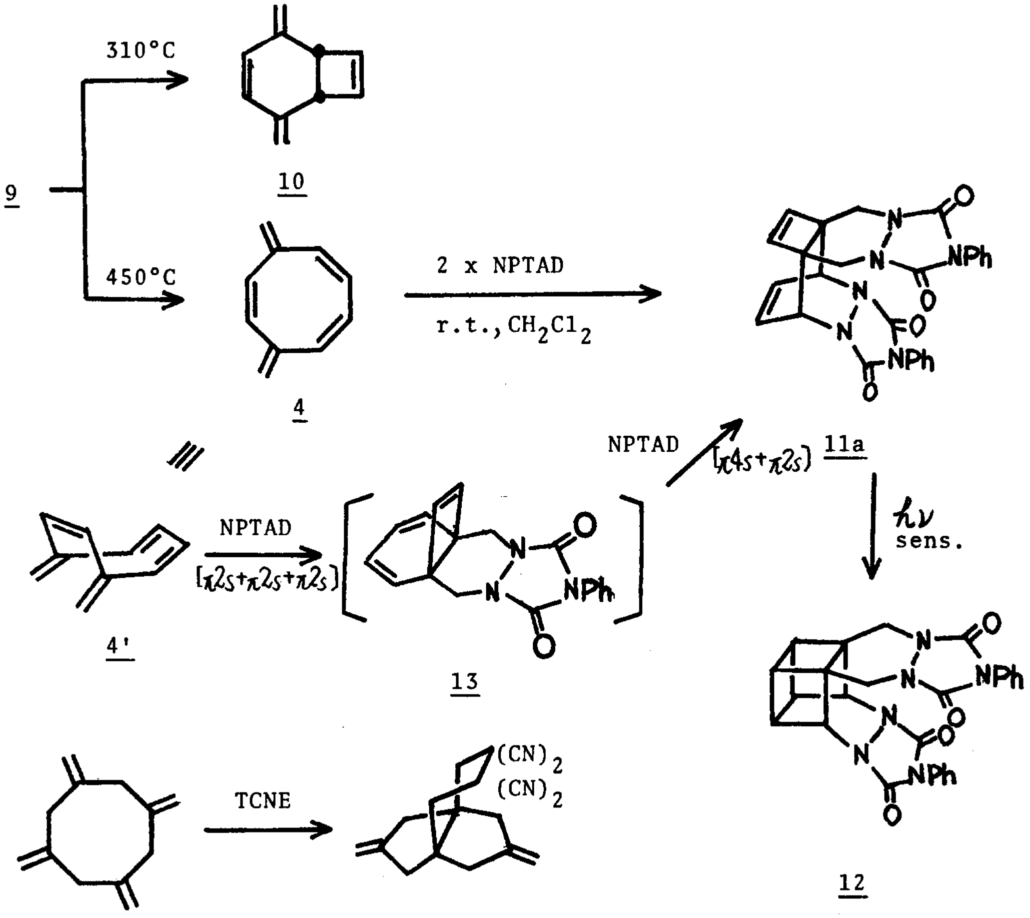
However, when the pyrolysis was performed at 450°C, was obtained in 77% yield a reddish-yellow mixture of hydrocarbons which contained 70-80% of 4 (PMR analysis). The material of about 90% purity (PMR) was able to be obtained, with some loss of the compound, by passing the mixture through a short silica gel column using n-pentane as an eluent [(pale yellow ?) liquid; ν_{max}(liquid) 1600 m, 880 s, 787 s, 692 s cm^{-1}; λ_{max}(n-hexane) 256 nm (ϵ $\approx$19000); δ_{ppm} (C_6D_6) 5.05 (4H, m, methylene), 5.85 (4H, m, H-1$\sim$H-4), 6.04 (2H, s, H-6,7)].

Compound 4 was less stable than 10. The PMR sample mostly decomposed in two days at room temperature. In chlorinated solvents such as chloroform and carbon tetrachloride, the decomposition was faster probably due to a trace of acid present in the solvents. The PMR signals of 4 in ca 1:1 mixture with 10[7] in carbon tetrachloride disappeared in few hours separating out amorphous solids, while the signals of 10 remained a few days.

On an attempt to obtain a stable cycloadduct with N-phenyltriazolinedione (NPTAD), it was found that 4 undergoes a double cycloaddtion with the dienophile. The reaction of 4 with NPTAD smoothly took place in methylene chloride at room temperature, giving the 1:2 adduct 11 in about 80% yield (53% from 9) [colorless needles from EtOH-CH_2Cl_2; m.p. 280-282°C decomp.; ν_{max}(KBr) 1750 sh, 1700, 1560 cm^{-1}; δ_{ppm}($CDCl_3$) AB quartet at 4.11 and 4.66 (4H, J=15 Hz), 4.94 (2H, t, J=3.6 Hz), 6.07 (2H, s), 6.30 (2H, t, J=3.6 Hz), 7.45 (10H, br. s)]. The PMR spectrum indicates the symmetric nature of the molecule and the presence of four olefinic protons and six aliphatic protons adjacent to nitrogen, four of them being of isolated two methylenes. These data best fit the structure 11a and its *anti* isomer. The structure 11a was proved to be the correct one because acetone sensitized photoreaction of 11 gave the cage molecule 12 in 68% yield [m.p. 260-262°C decomp.; δ_{ppm}($CDCl_3$) 3.24 (2H, t, J=3.6 Hz), 3.70 (2H, m), AB quartet at 3.85 and 4.40 (4H, J=15 Hz), 4.96 (2H, t, 3.5 Hz), 7.50 (10H, br. s)].

The formation of 11 may be rationalyzed by the intermediacy of the propellatriene 13 which subsequently underwent Diels-Alder reaction with the second


80°/PhH
BF₃·OEt₂
6
7
Ph₃P=CH₂
DMSO
8
9


310°C
450°C
9
10
4
2 x NPTAD
r.t., CH₂Cl₂
NPh
11a
NPTAD
[π4s+π2s]
hν
sens.
4'
NPTAD
[π2s+π2s+π2s]
13
12
14
TCNE
(CN)₂
(CN)₂

mole of NPTAD. Another process that is initial Diels-Alder reaction at C-1~C-4 diene part followed by $[_{\pi}2_s + _{\pi}2_s + _{\pi}2_s]$ cycloaddition is also probable; however, by this process, we can not justify the stereospecificity of the reaction. For the first-stage cycloaddition, following three processes can be considered: (i) $[_{\pi}2_s + _{\pi}2_s + _{\pi}2_s]$ cycloaddition; (ii) $[_{\pi}8_s + _{\pi}2_s]$ cycloaddition leading to a 1,6-bridged cyclooctatetraene followed by 6-electron electrocyclic ring closure; (iii) formal [6+2] cycloaddition leading to a 1,4-bridged cyclooctatetraene followed by double bond shift and then ring closure. While the processes (i) and (ii) are thermally allowed and therefore likely occur, the reality of (iii) may not be likely because $[_{\pi}6_s + _{\pi}2_s]$ cycloaddition is thermally forbidden and, in addition, resulting 1,4-bridged cyclooctatetraene would be considerably strained.[8] The ready cycloaddition, coupled with the shorter wave-length UV absorption and the smaller extinction coefficient compared with 10, suggests non-planarity of 4. In a sort of tub-form such as 4', the spacial distance between the methylene carbons would become considerably short in favor of the cycloaddition. Such a geometry seems to favor the process (i) rather than (ii), since the best geometry for (ii) may be coplanarity of the 8π moiety, which contradicts the deduced geometry. A $[_{\pi}2_s + _{\pi}2_s + _{\pi}2_s]$ cycloaddition has been found in the thermal reaction of 1,3,5,7-tetramethylenecyclooctane 14 and tetracyanoethylene (TCNE).[9]

Reagarding the second cycloaddition, such propellatrienes as 13 are known to be attacked by NPTAD exclusively from the endo face in accordance with the present result.[10]

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5) The pyrolyses were performed by passing the vapor of 9, generated by heating a sample probe at ca 300°C, through a preheated column packed with pyrex glass chips in vacuum.

6) The liberated anthracene and unreacted sample condensed just out of oven and did not come into the trap at all.

7) This ca 1:1 mixture was obtained when the pyrolysis was done at 350°C.

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