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SYNTHESES AND PROPERTIES OF 2,5-ETHENO[4.2.2]PROPELLA-3,7,9-TRIENE AND ITS DERIVATIVES

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Summary: Syntheses of 2,5-etheno[4.2.2]propella-3,7,9-triene and the methoxycarbonyl derivatives are described; their electronic spectra suggest the presence of orbital interactions among the four π-bonds.

Polycyclic unsaturated compounds having an unique carbon framework have intrigued organic chemists on account of peculiar properties and chemical reactivities often exhibited by them. In this respect, 2,5-etheno[4.2.2]-propella-3,7,9-triene, 6a, is of considerable interest.[1] The π-bonds in 6 are so aligned that longicyclic interaction through space[2] in addition to the interaction through the σ-bonds[3] may be expected for them. Orbital interactions through space and bond are of considerable current interest.[2,3] The reactivities of 6a and its derivatives are particularly interesting since they may be regarded as potential precursors of highly elusive butalene.[4] In this report we describe the preparation and the spectroscopic properties of 6a and its derivatives, 6b and 6c.

In the course of the preparation of [4.2.2]propella-2,4,7,9-tetraene-7-carboxylate which was previously reported,[5] we obtained a stereoisomeric mixture (~85:15) of the carboxylic acids, 1a. They were converted to the isocyanates, 1b, with $(PhO)_2P(O)N_3/Et_3N$[6] and subsequently treated with $EtOH/Et_3N$ to give ethyl carbamates, 1c. The LAH reduction of the carbamates in ether or THF, however, did not produce the expected methylamines,[7] but a complex mixture of products from which two major components were isolated and

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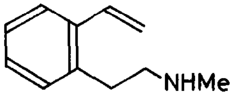

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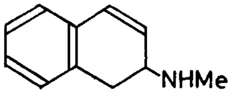
a, X = CO_2H
b, X = NCO
c, X = $NHCO_2Et$
d, X = $NHCO_2CH_2CH_2SMe$
e, X = $NHCO_2CH_2CH_2\overset{+}{S}Me_2\cdot MeSO_4^-$
f, X = NH_2
g, X = $\overset{+}{N}Me_3\cdot I^-$



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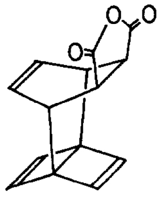
characterized as 3 and 4. These observations indicate that high steric strain in 1c induced the extensive rearrangement during the reduction. Therefore, the isocyanates were treated with 2-methylthioethanol and then with dimethyl sulfate to give the sulfonium salts, 1e, which were hydrolyzed in an alkaline solution.[8] The resulting amines, 1f, were led to the ammonium salts, 1g, and subjected to elimination by t-BuOK in DMF, which gave [4.2.2]propella-2,4,7,9-tetraene, 2, as colorless plates, mp 32.0-32.5°. An overall yield of 2 from 1a was 35%. 2[9]: ^{1}H-NMR, δ 5.85-5.95(AA'BB' m, 4H), 6.43(s, 4H); ^{13}C-NMR, δ_C 56.1, 120.8, 124.2, 142.8; IR(CCl_4), 3090, 3040, 1375, 1273, 1192, 725 cm^{-1}; Mass, m/e 129(11), 128(M^+, 100), 127(25), 102(43), 76(12), 63(10), 51 (15); UV(EtOH), λmax(logε) 204(3.69), 271(3.29), 279 nm (3.29).

The reaction of 2 with maleic anhydride proceeded smoothly giving a Diels-Alder adduct, 5,[10] in a quantitative yield. The treatment of the adduct with $Ni(CO)_2(PPh_3)_2$[11] in refluxing diglyme under argon afforded 2,5-etheno-[4.2.2]propella-3,7,9-triene, 6a, in ca. 30% yield accompanied by a few minor products including biphenyl. 6a: mp 129-130° (in sealed tube); ^{1}H-NMR δ 3.60-3.83(m, 2H), 6.05-6.30(m, 4H), 6.32(s, 4H); ^{13}C-NMR, δ_C 42.7, 57.4, 132.8, 141.3; IR(KBr), 1580, 1525, 1265, 785, 767 cm^{-1}; Mass, m/e 154(M^+, 39), 153 (100), 152(71), 128(16), 76(26), 50(26). Upon heating the tetraene, 2, with excess methyl propiolate for 40 h at 120°, a mixture of 1:1 and 1:2 adducts was formed. The former product was a normal Diels-Alder adduct, 6b.[12] For the latter product, the structure represented by 7 was assigned on the basis of the examination of spectroscopic properties including the NOE study.[13] The observation of two AB quartets in the range δ 6.3-6.7 in the NMR spectrum of 7 unambiguously indicated that the Dewar benzene moiety remained intact.[14] The formation of 7 may be rationalized by a homo-Diels-Alder addition of another molecule of methyl propiolate to 6b.[15] In fact, the prolonged reaction time resulted in a increase in the amount of 7 at the sacrifice of 6b. The reaction of 2 with dimethyl acetylenedicarboxylate was complete after 20 h at 80° affording a 1:1 adduct, 6c, in a quantitative yield.[16] The formation of a 1:2 adduct was not observed under these reaction conditions.



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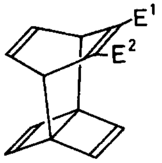

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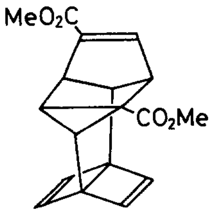
a, $E^1 = E^2 = H$
b, $E^1 = H$;
$E^2 = CO_2Me$
c, $E^1 = E^2 = CO_2Me$



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The electronic spectra of 3,5-etheno[4.2.2]propella-3,7,9-triene, 6a, and its derivatives, 6b and 6c, are shown in Figure 1. Despite the absence of formal conjugation among the four carbon-carbon double bonds, 6b and 6c exhibit absorption maxima at 274 (logε = 3.12) and 277.5 nm (2.93),

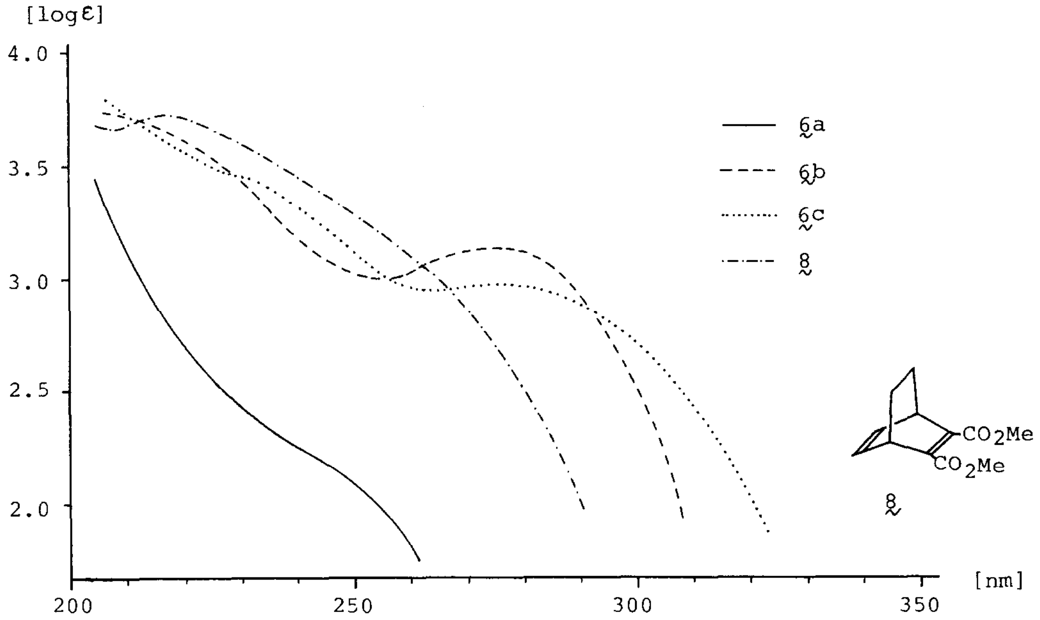

Figure 1. Absorption spectra of 6_{a-c} and 8 in EtOH.

respectively. The parent compound, 6a, in contrast, shows only an end absorption extending to 270 nm. The absorptions in the region of 270-280 nm observed in 6b and 6c are not attributable to the 1,4-cyclohexadiene chromophore, since bicyclo[2.2.2]octa-2,5-dienedicarboxylate, 8,[17] does not display an absorption maximum in such long wavelength region (Figure 1).[18] Thus, it appears that the absorptions exhibited by 6b and 6c in the long wavelength region arise from the interaction, presumably of charge-transfer type, between the Dewar benzene and the electron-deficient 1,4-cyclohexadiene moieties.[19] For the electronic interaction between those two chromophores, the operation of two modes of interactions may be expected; *i.e.*, the longicyclic interaction through space[2] and the through-bond interaction *via* the σ-bonds connecting the two chromophores, which are in a highly favorable stereochemical arrangement for such interaction.[3] It has recently been demonstrated that not only through-space, but also through-bond interactions between an electron-donor and an electron-acceptor chromophores lead to the occurrence of charge-transfer absorption.[20] At present, however, it is not clear which mode of the interactions is predominant in 6b and 6c.

The chemical behavior of 6 is of considerable interest since they may be regarded as potential precursors of highly labile butalene.[4] Upon heating a solution of 6a in degassed benzene for 70 h at 200°, however, the complete recovery of the starting material resulted. Apparently, 6a is thermally quite stable in spite of its high strain. We are now examining the thermal and the photochemical behaviors of 6, which will be reported in due course.

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Scientific Research, No. 57470015) is gratefully acknowledged.

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(9) Satisfactory elemental analysis was obtained for each new compound. NMR spectra were taken in $CDCl_3$. Mass spectra were recorded at an ionizing voltage of 70 eV and relative intensities are given in parenthesis.

(10) 5: mp 181-182°. ^{1}H-NMR, δ 3.35(t, J=1.5 Hz, 2H), 3.63(br s, 2H), 6.02-6.15(m, 2H), 6.22(s, 2H), 6.74(s, 2H); IR(KBr), 1860, 1790 cm^{-1}.

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(12) 6b: bp ~105°/1 mmHg. ^{1}H-NMR, δ 3.72(s, 3H), 3.83(t of d, J=6.4 and 1.5 Hz, 1H), 4.28(d of t, J=5.9 and 1.5 Hz, 1H), 6.10-6.40(m, 6H), 7.22(d of d, J=6.4 and 1.5 Hz, 1H); IR(neat), 1710, 1625, 1590 cm^{-1}; Mass, m/e 212(M$^+$, 51), 153(69), 152(100), 105(47), 76(50).

(13) 7: mp 124-125°. ^{1}H-NMR, δ 1.98(d, J=7.3 Hz, 1H), 2.26(s, 1H), 2.89(d, J =7.3 Hz, 1H), 3.21(s, 1H), 3.25(m, 1H), 3.63(s, 3H), 3.73(s, 3H), 6.40 (d, J=2.0 Hz, 1H), 6.44(d, J=2.0 Hz, 1H), 6.60(d, J=2.0 Hz, 1H), 6.64(d, J=2.0 Hz, 1H), 7.40(d, J=3.0 Hz, 1H); IR(KBr), 1705, 1595 cm^{-1}; Mass, m/e 296(M$^+$, 1.4), 237(32), 205(49), 178(100), 177(68).

(14) For the cycloaddition to Dewar benzene derivatives in a homo-Diels-Alder fashion, see: H. Iwamura, Y. Tanabe, H. Kobayashi, Tetrahedron Lett., 1987 (1976) and references cited therein.

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(16) 6c: bp ~80°/5x10^{-3} mmHg. ^{1}H-NMR, δ 3.76(s, 6H), 4.10(d of d, J=4.4 and 1.5 Hz, 2H), 6.25(d of d, J=4.4 and 1.5 Hz, 2H), 6.31(s, 2H), 6.42(s, 2H); IR(KBr), 1725, 1710, 1640, 1600 cm^{-1}; Mass, m/e 270(M$^+$, 97), 211(35), 163(100), 152(77), 76(53).

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(19) In hexane, 6c displays an absorption maximum at 273 nm (logε=3.00) and 8 at 217 nm (logε=3.73).

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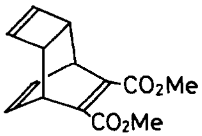

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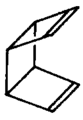

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