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SYNTHESIS AND DIELS-ALDER REACTIONS OF SPIRO(2.6)NONA-4,6,8-TRIENE (1)

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Cycloheptatriene (CHT) reacts with common dienophiles, e.g. maleic anhydride, (2) dimethyl acetylenedicarboxylate, (2,3) dicyanoacetylene, (4) and tetracyanoethylene (TCNE), (5) to give adducts having a tricyclo(3.2.2.$0^{2,4}$) nonane skeleton. The explanation for the formation of these products is that the dienophile reacts preferentially with a small equilibrium concentration of 2,4-norcaradiene. At this time, we wish to report the synthesis of the parent spirononatriene † (1a) and our observation that this tropylidene reacts with maleic anhydride and dicyanoacetylene to give, as the only isolable products, adducts which arise from addition to the triene and have bicyclo(3.2.2)nonadiene and nonatriene structures, respectively.

The parent spirononatriene (1a) was synthesized as outlined in the scheme.

Isomers 2 and 3 were separated (vpc, 20M carbowax) for characterization but it was found that for the synthesis of 1a it was simpler to brominate (CCl_4, 0^o followed by reflux with excess Br_2) the mixture, partially separate the dibromides by selectively crystallizing out some of the insertion product and finally separating phenylcyclopropane from 1a (21%) by vpc on an SE-30 column to yield reasonably pure 1a as a liquid of characteristic odor: (nmr (CCl_4) τ3.50-4.29 (broad m, 5,6,7, and 8 protons, 3.8H), 4.77 and 4.88 (two peaks, 4 and 9 protons,

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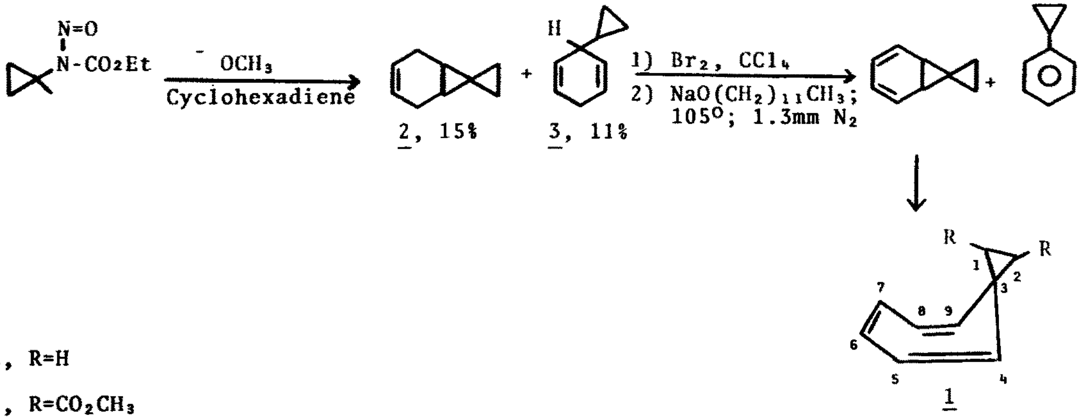
† This ring structure (substituted with ester and nitrile groups) has previously been reported (6) to arise from the addition of cycloheptatrienylidene to electron deficient olefins. The two stereoisomeric 1,2-dimethyl spirononatrienes (1, R=CH_3) have recently been synthesized by M. Jones, Jr. and his group at Princeton University (accompanying communication).

2.0H), 9.42 (s, cyclopropyl protons, 4.0H); ir ν_{max}^{film} 3007, 1019, 747, 701, 614 cm^{-1}; mass spectrum at 70 eV, m/e (relative intensity) 119 (3.72), 118 (M$^+$, 37.8), 117 (100), 115 (23.2), 91 (27.8), 90 (22.6), 89 (21.7), 78 (13.7), 39 (20.0); uv λ_{max}^{EtOH} 262 mμ (ε=2,700). Since 1a could not be obtained analytically pure due to oxidation, the elemental composition C_9H_{10} was established by the $(M+1)^+/M^+$ peaks of its mass spectrum. The region of the nmr spectrum 3.5-4.9τ, corresponding to the cycloheptatrienyl protons, is virtually superimposable with the corresponding region of the nmr spectrum of the dicarbomethoxy derivative (1b, R=CO_2CH_3). (6) The cyclopropyl protons appear as a sharp singlet presumably because of rapid ring inversion. 1a is stable to vpc conditions at 150° in contrast to the diester (1b, R=CO_2CH_3) which is isomerized to the corresponding indane derivative at 130°. (6)



a, R=H

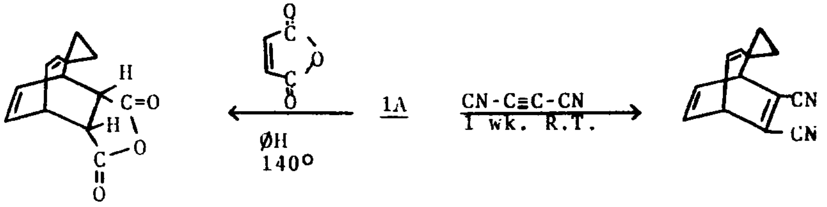
b, R=CO_2CH_3

Spirononatriene (1a) was treated with maleic anhydride at 140° for four days to give, after elution from silica gel with benzene and recrystallization from methylene chloride/petroleum ether, a 15% yield of adduct (4),[†] mp 159-161°. *Anal*. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.33; H, 5.29.

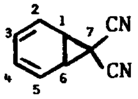
The spectral data were: nmr ($CDCl_3$) τ3.35-4.35 (10 peaks, 3H, =CH), 5.3 (doublet, 1H, =CH, J=11 cps), 6.25 (doublet, 2H, O=C-C-CH, J=1 cps), 6.8 (triplet, 1H, Bridgehead, J=7 cps), 7.95 (doublet, 1H, Bridgehead, J=7 cps), 9.2 and 9.4 (2 doublets, 4H, cyclopropane, J=2 cps); ir ν_{max}^{KBr} 1840, 1775, 1635, 1235 cm^{-1}

[†] From the nmr of the crude product (after solvent removal), 4 is by far the predominant and probably the only adduct.

The dicyanoacetylene adduct (5) was obtained by mixing crude 1a with excess dicyanoacetylene, degassing and evacuating the solution, and allowing the ampoule to stand for one week at room temperature. Chromatography of the black reaction mixture and recrystallization of the resulting oil from ether/petroleum ether at -15° gave approximately 10% of 5, mp 130-133° (Anal. smpl, mp 133-134°) (nmr ($CDCl_3$) τ3.70-3.92 (m, vinyl protons, 4.0H), 7.01-7.32 (m, allyl protons, 2.0H), 9.06-9.76 (m, cyclopropyl hydrogens, 4.0H); ir ν_{max}^{nujol} 2240, 1030, 933, 777 cm^{-1}. Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19. Found: C, 80.05; H, 5.19. It is clear from the nmr spectra that adducts 4 and 5 do not have a tricyclo(3.2.2.$0^{2,4}$)nonadiene structure. In fact, the nmr of 4 is a "textbook" spectrum for the assigned structure. The spectrum for 5 is not as well resolved but it also leaves little question of its structure for the following reasons. Aside from the number of vinyl protons, the position of the allyl protons in (5) is much closer to the value reported for the corresponding protons of bicyclo(3.2.2) nonatriene (7) (6.9τ), than to the value for the norcaradiene adducts of CHT with TCNE (5.77τ) (5) or dicyanoacetylene (5.19τ). (4) Also, the nmr spectrum of (5) lacks any absorption which might be attributed to tertiary cyclopropyl protons. †



4 5



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The addition of a reagent to the triene form of a cycloheptatriene system is not unprecedented. While the norcaradiene adduct predominates by a 3:1 ratio in the reaction of CHT with acrolein, (8) nitrosobenzene and hexachlorocyclopentadiene (9) give only the adducts derived from the triene form of CHT. The nitrosobenzene adduct, mp 106-107°, has been described as a 1,4 adduct (10) or a 1,6 adduct. (11)

The fact that 4 and 5 are formed by 1,4 addition to the triene (1a) can be taken as evidence that if the spirononatriene is in equilibrium with its valence

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† The protons in the 2 and 4 position of the TCNE-CHT adduct appear at 8.33 (ref. 4).

tautomer - the corresponding norcaradiene - the equilibrium lies far to the triene side. E. Ciganek has clarified the relationship between cycloheptatrienes and norcaradienes by the isolation of the first simple norcaradiene (6) (12) and the observation of the rapidly equilibrating system of 7-cyano-7-trifluoromethylcycloheptatriene and 7-cyano-7-trifluoromethylnorcaradiene. (13) A possible explanation advanced for the stability of the norcaradiene (6) was the decreased C-1-C-7-C-6 bond angle favored by the dipole-dipole interactions between the two cyano groups. (12) The results with spirononatriene would tend to support this line of reasoning since 1a would represent the extreme case in which the large C-4 to C-9 distance caused by compression of the C-1-C-3-C-2 bond angle prevents tautomerization to the norcaradiene form. The effect of substituents on the relative stability of the norcaradiene and triene forms is still not completely established. (14)

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