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THE SYNTHESIS AND CHARACTERIZATION OF SPIRO[3.4]OCTA-1,5,7-TRIENE

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We recently reported the synthesis of spiro[3.4]octa-5,7-diene 1.[1] The slight red shift in the UV maximum of 1 relative to model compounds 2 and 3 suggested the possibility of some through space σ-π interaction between the four membered ring and the diene system. Recent interest in the concept of spiroconjugation, both theoretical[2] and experimental,[3] led us to attempt the synthesis of the unsaturated analog spiro[3.4]octa-1,5,7-triene 4 in anticipation that the combination of spiroconjugative interaction in the π system and direct σ-π overlap between the four membered ring and the diene would produce interesting spectral and chemical properties. In addition, the hydrocarbon seemed a reasonable precursor to the corresponding cation 5, a material of theoretical interest,[2a,4] which has been predicted to be spiroaromatic. We report here the successful synthesis of the triene 4, the first member of its class, and its unusually facile thermal rearrangement.

1

2

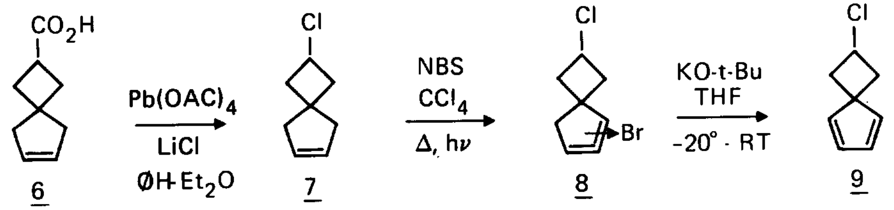
3

4

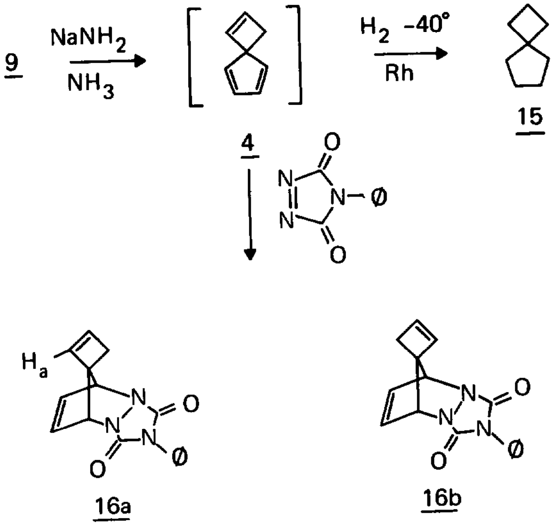
5

The starting point of the synthetic sequence was the acid 6 described by Grubbs and coworkers.[5] The chlorolefin 7 was obtained using a slight modification of the Kochi decarboxylation procedure.[6] The best yields (65%) resulted when a slight excess of acid (10%) was employed and the anhydrous lithium chloride was added portionwise. The allylic bromination of 7 was accomplished without skeletal rearrangement using 10% excess N-bromosuccinimide in CCl_4 initiated by a combination of heat (76°) and light.[7,8] The allylic bromide 8 was obtained in nearly quantitative yield as an unstable oil which was used without further purification. Attempts to generate the triene 4 directly from 8 by treatment with a variety of strong bases were unsuccessful due to extensive polymerization. Treatment of 8 with excess potassium t-butoxide in THF at -15° (the temperature was allowed to slowly rise to room temperature over 1.5 hr) resulted in dehydrobromination to yield the chlorodiene 9 in 85% yield: $^1H_{nmr}(CCl_4)$

τ 3.37(m,1H), 3.73(m,3H), 5.33 (quintet, J=8Hz,1H) and 7.05-7.41(m,4H); ir(neat) 3060, 3040, 2980, 2940, 2850, 1275, 895, 805, 770, 755, and 730cm^{-1}; UV(C_6H_{12}) λmax 261mn, ε=2900; mass spectroscopic molecular weight 140.



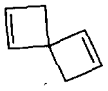
Treatment of the diene 9 with excess sodamide in liquid ammonia at -33° for 0.5 hr. and subsequent distillation of the ammonia through cold pentane (-50°) produced a colorless solution which turned red-orange upon warming to 0°. Hydrogenation of the colorless solution at -40°[9] produced spiro[3.4]octane 15 as the major volatile product (>90%). When the contents of the cold trap were treated at -30° with an acetone solution of N-phenyltriazoline-3,5-dione,[10] rapid decolorization occurred and a 1:1 adduct of the triene 4 was isolated as a *ca.* 50/50 mixture of isomers 16a and 16b: mp 151-157°, $^1H_{nmr}(CCl_4)$ τ 2.58-2.93(m,5H), 3.63-3.88(m,3.5H), 4.34(d,J=3Hz,0.5H), 5.4(m,2H), 7.40(s,1H) and 7.73(s,1H); ir(CCl_4) 3050(w), 2950(w), 2920(w), 1780, 1720, 1395, 1390, 1240, 1125 and 1015cm^{-1}. The upfield doublet at τ 4.34 was tentatively assigned to H_a in 16a which is shielded by the second double bond. In a similar fashion the upfield singlet at τ 7.73 was assigned to the allylic cyclobutene protons in the isomer 16b.



The spectral data for the triene 4 were obtained at -35°: $^1H_{nmr}$(toluene d_8) τ 3.85 (singlet superimposed on a broad base, 4H), 4.07 (d,J=2.0Hz,1H), 4.32 (d,J=2.0Hz,1H) and 7.38 (s, 1/2wd=1Hz, 2H). Again, the upfield doublet at τ 4.32 was assigned to the cyclobutene vinyl proton held over the plane of the diene system. The UV spectrum of 4 obtained in hexane at -35° showed a broad featureless maximum at λ 262nm which is almost identical in shape and position to that observed for the saturated derivatives 1 and 9. If there is a spiroconjugative interaction present in 4 it is not manifested by a significant change in the absorption spectrum.

The triene 4 is remarkably unstable ($t_{1/2(\text{toluene } d_8)}^{-4.5°}$ = 90 min.). At -10° the colorless pentane solution of 4 rapidly turns red-orange and the characteristic nmr signals and UV spectrum of 6-vinylfulvene 17 appear.[11] The disappearance of 4 is first order, and although 17 is the major product, catalytic hydrogenation (PtO_2) of the crude rearranged material consistently produced n-propylcyclopentane and cis-bicyclo[3.3.0]octane in a ratio of 2-2.5/1. Hydrogenation of 17 under identical conditions produced only n-propylcyclopentane (>95%). The nmr[12] and hydrogenation data supports the formation of a second product upon rearrangement of 4 and is strongly suggestive of a dihydropentalene derivative.

The ring opening of 4 to 17 is unusually facile for a 3,3-disubstituted cyclobutene derivative.[14] It seems unlikely that this instability can be solely attributed to excessive strain caused by the spiro junction, since the similarly strained spiro compounds 18[15], 19[16] and 20[16] do not show comparable thermal lability. Mechanistically a diradical intermediate in the ring opening of 4 cannot be ruled out solely by energetic criteria.[17] This possibility is particularly attractive due to the expected stabilization of the zwitterionic form of the singlet diradical by the generation of the aromatic cyclopentadienyl anion.



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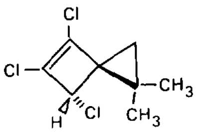

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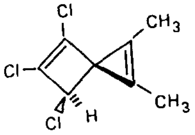

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Further mechanistic investigation of the rearrangement of 4 as well as attempts to produce the cation 5 at low temperatures are in progress.

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