

- chlorate is explosive.
- (5) The crystal is monoclinic, $a = 15.210(5) \text{ \AA}$, $b = 11.637(5) \text{ \AA}$, $c = 19.069(5) \text{ \AA}$, $\beta = 109.30(5)^\circ$, space group $C_{2/c}$, $Z = 4$. Independent reflections (1500) with $F_o > 3\sigma(F_o)$ were used in the structure solution and refinement. The structure was solved by the heavy atom method. Least-squares refinement converged to a discrepancy of 0.09 .
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The [6 + 4] Cycloadditions of Diethylaminobutadiene to Fulvenes. A New Synthesis of Azulenes

Sir:

Fulvenes can undergo concerted cycloadditions to dienes as 6π or as 2π addends.¹⁻³ We have previously rationalized variations in periselectivity of cycloadditions to fulvenes by an application of frontier molecular orbital theory.⁴ The argument follows from considerations of the coefficients of the HOMO and LUMO of fulvene, represented in Figure 1. The reactions of relatively electron-deficient 4π electron systems occur across the C-1, C-2 alkene moiety because of the high frontier density in these positions and the node through the exocyclic position. Only strongly electron-donating substituents at C-6 raise the second highest occupied MO sufficiently to afford reactions of fulvenes as trienes with electron-deficient 4π systems.^{4,5} Thus, alkyl or aryl fulvenes react as 2π dienophiles or dipolarophiles with most dienes and 1,3-dipoles, respectively.⁴ The LUMO of fulvene is more heavily centered at C-6 and C-1, so that sufficiently electron-rich 4π species were predicted to react across the 1 and 6 positions of fulvene, with the more nucleophilic atom of the diene or 1,3-dipole becoming attached to C-6 of fulvene.⁴ Diazoalkanes³ and azomethine ylides⁶ are the only 1,3-dipoles which have been investigated that are sufficiently electron-rich to add in a [6 + 4] fashion to fulvenes. Troponone, the first molecule observed to cycloadd across the fulvene 6π system, apparently does so because of ideal secondary orbital interactions.^{1,6} On the basis of these considerations, we predicted that electron-rich dienes would add in a [6 + 4] fashion to fulvenes.⁴ We wish to report a confirmation of this prediction, and a new synthetic route to azulenes.

A 1:3 mixture of 1-diethylaminobutadiene and dimethylfulvene became dark red after 2 days at room temperature. Evaporation of excess dimethylfulvene, treatment with MeI to remove amines, and chromatography on silica gel (cyclohexane) gave a 65% yield of deep orange **1a** (Scheme I) resulting from loss of diethylamine from a 1:1 adduct. This adduct could be purified by short path distillation ($36-37^\circ\text{C}/0.05 \text{ mm}$). The NMR spectrum of **1a** (CDCl_3) has a sharp singlet at $\delta 1.10$ due to the protons of methyl groups attached to a saturated carbon, a doublet at $\delta 2.25$ ($J = 5.0 \text{ Hz}$) due to two allylic protons,⁷ and a complex multiplet at $\delta 5.8$ to 6.5 due to six olefinic protons. The ultraviolet spectrum of **1a** ($\lambda_{\text{max}}^{\text{cyclohexane}} 317 \text{ nm}$, $\log \epsilon 4.10$) is very similar to that of alkyl substituted vinylfulvenes (e.g., 6-propenylfulvene, $\lambda_{\text{max}}^{\text{cyclohexane}} 317 \text{ nm}$, $\log \epsilon 4.31$).⁸

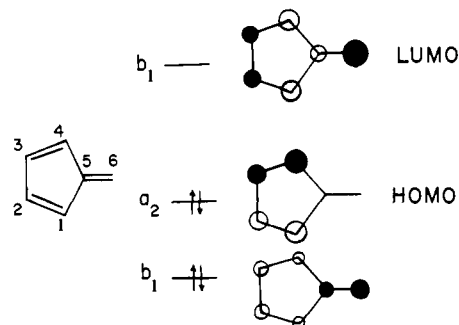
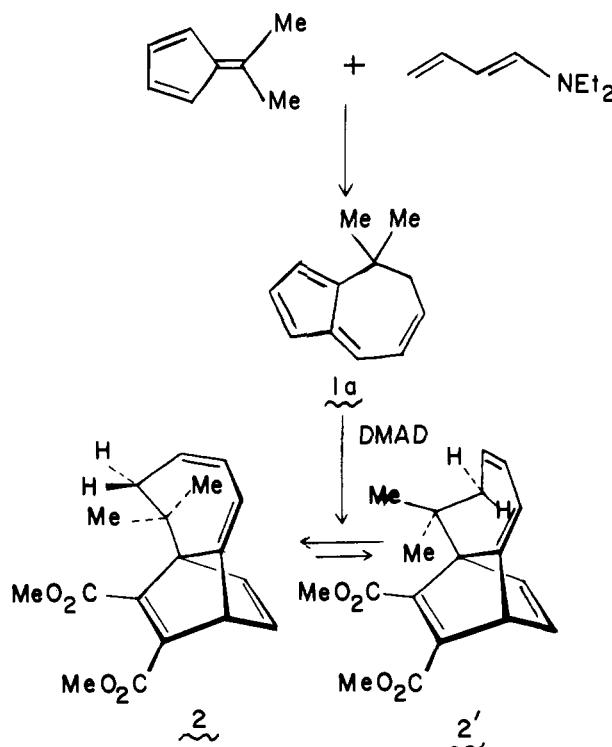


Figure 1. The frontier molecular orbitals of fulvene.

The reaction of **1a** with dimethyl acetylenedicarboxylate (DMAD) provided further evidence for the identity of the carbon skeleton in **1a**. Heating **1a** and DMAD in CCl_4 at 80°C for 24 h gave, after chromatographic purification, a 79% yield of a white crystalline solid, mp $62-63^\circ\text{C}$. The Diels-Alder adduct proved to be an inseparable mixture of conformational isomers, **2** and **2'**. The NMR spectra of this adduct (Figure 2) indicated the presence of two isomers in a ratio of about 2:1. Thus, in CDCl_3 , methyl singlets at $\delta 1.00$ and 1.17 were twice as intense as those at $\delta 1.09$ and 1.35 . A complex pattern at $\delta 1.6-2.05$ and at $2.4-3.0$ can be attributed to overlapping multiplets due to the methylene protons in each isomer. Two methoxyl singlets overlapped at $\delta 3.72$, and methoxyl resonances at $\delta 3.81$ and 3.82 were also observed. The bridgehead protons in both adducts accidentally have the same chemical shift and appear as a doublet of doublets at $\delta 4.11$ ($J = 3.2$ and 1.1 Hz), coupled to the olefinic protons on the norbornadiene moiety. In the major isomer, these appeared as a pair of doublets of doublets at $\delta 6.82$ ($J = 5.5, 1.1 \text{ Hz}$) and 7.06 ($J = 5.5, 3.2 \text{ Hz}$). These couplings were confirmed by double resonance experiments. The three cycloheptadiene vinyl protons appeared as partially resolved multiplets centered at $\delta 4.85$ (one proton from each isomer) and 5.6 (two protons from each isomer). In C_6D_6 , the four high-field methyl singlets changed position, those due to the major isomer now appearing at $\delta 0.98$

Scheme I



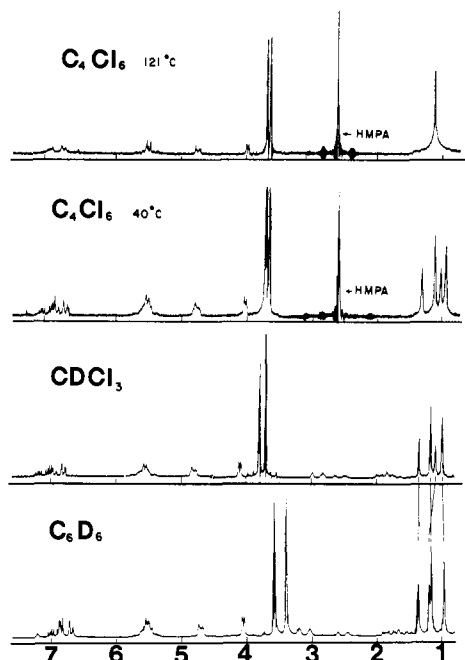
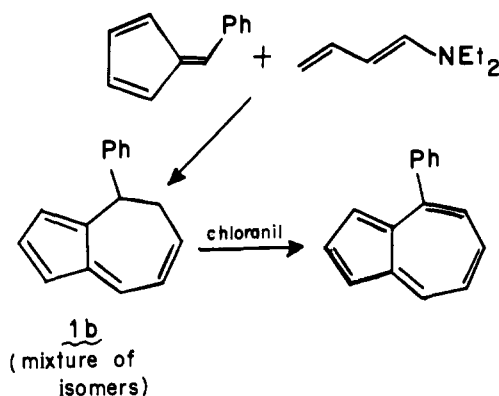


Figure 2. NMR spectra of the mixture of conformational isomers, **2** and **2'**.

Scheme II



and 1.17, while those in the minor isomer appeared at δ 1.23 and 1.38. That these isomers were conformational and not structural is demonstrated by both the similarity of the spectra of the isomers, and by the temperature dependent NMR spectrum of this mixture. At 120 °C (in hexachlorobutadiene), the four methyl singlets apparent at room temperature collapse to a single sharp resonance. The methoxy resonances collapse into two sharp singlets at 60 °C, while the remaining resonances simplify as expected. Cooling the sample results in restoration of the original spectrum. Steric considerations and the chemical shifts of the methyl groups in the two isomers in CDCl_3 and C_6D_6 lead to the tentative conclusion that **2** is the more stable conformer.

This relatively high barrier to conformational inversion (ΔG^\ddagger estimated as 18–20 kcal/mol from coalescence temperatures) is probably the consequence of the quaternary center attached to the bridgehead. Dibenzobarrelenes with quaternary carbons attached to bridgeheads show even larger barriers.⁹

The potential of this reaction in the synthesis of azulenes is demonstrated by the sequence of reactions beginning from 6-phenylfulvene (Scheme II). Reaction of 6-phenylfulvene with 1-diethylaminobutadiene (1:1) in CCl_4 for 1 day, followed by MeI workup and column chromatography, gave, in 62% yield, a mixture of dihydroazulenes, as indicated by the com-

plexity of the NMR spectrum. Reaction of 1 g of this mixture with chloranil in refluxing xylene for 15 min gave royal blue 4-phenylazulene (110 mg) after silica gel chromatography. The spectroscopic properties of this compound (uv, ir)^{10,11} are identical with those of the authentic material.

The general availability of fulvenes from cyclopentadienes and ketones, and of dienamines from α,β -unsaturated carbonyl compounds, along with the simple workup procedures required for these reactions, indicate that this procedure may provide a useful alternative to the related Hafner azulene synthesis,¹² which utilizes an electrocyclization analogous to the cycloaddition reported here.

Returning to the theoretical impetus for this work, our preliminary results with the less electron-rich 1-methoxybutadiene system indicate that only powerfully nucleophilic and nonelectrophilic 4π systems such as 1-diethylaminobutadiene (ionization potential (IP) = 6.96 eV; electron affinity (E.A.) ~ -2 eV) and diazomethane (I.P. = 9.03 eV, E.A. ~ -1.5 eV) will react with alkyl or aryl fulvenes in a [6 + 4] sense. However, fulvenes substituted at the 6-position by electron-withdrawing groups are expected to show this behavior more generally. These reactions, and the generality of the azulene synthesis, are subjects of continuing investigations.

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Bond Fixation in Annulenes. 4. The Ability of 1,2,3-Trimethylcyclooctatetraene to Support Optical Activity¹

Sir:

Incremental introduction of double bonds into medium-sized rings so alters the interplay of nonbonded interactions that widely divergent ground state conformational preferences frequently result. Cyclooctane and its derivatives, for example, appear to exist predominantly in boat-chair or crown conformations² while cyclooctatetraenes (COT's) are decidedly tub-shaped.³ Understandably, the dynamics of conformational mobility must differ significantly in the two families. As con-