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Ene Reaction of Azulenes with Some Dienophiles

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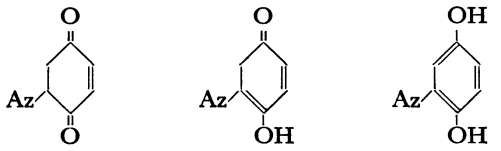
The thermal reaction of azulenes with maleic anhydride and *p*-benzoquinone was reported by Treibs.[1)]

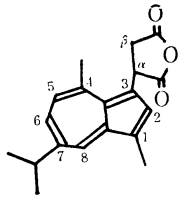


Ia Ib Ic

Az = 1-azulyl or 4-guaiazulyl

However, the structures of the products, especially Ia—Ic, said to be isolated after the reaction of azulenes and benzoquinone, seemed somewhat unconvincing. A reexamination conducted as a part of cycloaddition reactions of non-benzenoid aromatic compounds revealed that the reaction conditions are not appropriate, each reaction yielding a single product, and that the structures of the products must be revised. Our results are described herewith.

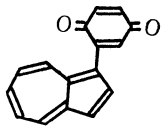
Guaiazulene (II) and maleic anhydride (III) react in chloroform or benzene even at room temperature to give 1-azulyl succinic anhydride (IV) as the single product. The structure of IV was confirmed from its mass spectrum (m.w. 294), IR spectrum ($\nu_{c=o}$ 1862, 1785 cm^{-1}) and NMR spectrum [δ 1.32 (6H, d, J= 6 Hz, isopropyl group), 2.63 (3H, s, methyl group at C_1), 2.97 (3H, s, methyl group at C_4), 2.98 (3H, m, C_β–H and methine proton of isopropyl group), 5.40 (1H, t, J=9 Hz, C_α–H), 6.90 (1H, d,d, J=11, 2 Hz, C_6–H), 7.50 (1H, d, J=11 Hz, C_5–H), 7.51 (1H, s, C_2–H), and 8.15 (1H, d, J=2 Hz, C_8–H)].



IV

The alternative structure in which succinic anhydride moiety is attached to 2-position of guaiazulene, was excluded when guaiazulene-3-d_1 yielded deuterium free IV (NMR and MS). Attempts to hydrolyze IV resulted only in the formation of a complex acidic mixture. Azulene (V) failed to react (complete recovery) with III even at elevated temperatures. The reaction in the presence of a catalytic amount of aluminum chloride resulted only in reddish brown resinous material.

Although guaiazulene reacted with *p*-benzoquinone (VI) rapidly to give only a mixture of green resinous



VII

products, azulene and VI at room temperature afforded the single product, 1-azulyl-*p*-benzoquinone (VII), as dark violet crystals. Structure elucidation was made on MS (1:1 adduct), IR ($\nu_{c=o}$ 1650 cm^{-1}) and NMR spectra [δ 6.87 (3H, overlapping, quinone hydrogens), 7.00—7.80 (4H, m, C_3, C_5, C_6, C_7–H), 8.11 (1H, d, J=4 Hz, C_2–H)], 8.48 (1H, d, J=11 Hz, C_4–H), 8.60 (1H, d, J=11 Hz, C_8–H)]. The ene-dione, the initial ene-reaction product, should have been dehydrogenated to VII by excess VI present. The difference in the reactivity of azulenes II and V can be explained by the inductive effect or hyperconjugation of alkyl groups which increase the electron density at C_1 position in II.

Experimental

Reaction of Guaiazulene (II) and Maleic Anhydride (III). II(540 mg) and III(530 mg) were dissolved in anhydrous benzene and kept at room temperature under stirring for 12 hours. After removal of benzene, the mixture was washed with petroleum ether to remove unreacted II(130 mg) and sublimed (steam bath) at reduced pressure (25 mmHg). The residue was recrystallized from petroleum ether to yield blue scaly crystals (IV), mp 127—128°C (450 mg, 56% yield).

Found: C, 77.41; H, 6.94%. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80%. λ_{max}^{MeOH} (ε) 248 nm (6600), 291 nm (8200), 306 nm (5200).

Reaction of Guaiazulene-3-d_1 (II-d_1) and Maleic Anhydride (III). II-d_1 (120 mg) and III (450 mg) were allowed to react under the conditions described above. The isolated adduct (35 mg) was identical with (IV) (mixed mp, MS, NMR).

Attempted Hydrolysis of IV. IV (35 mg) was kept at room temperature in aqueous methanol (30%). Silica gel thin layer chromatogram showed the development of complex green or dark brown spots with no definite shape. Attempts to isolate hydrolysate from the mixture failed.

Attempted Reaction of Azulene (V) and Maleic Anhydride (III). *i*) V (128 mg) and III (196 mg) were autoclaved at 250°C in anhydrous benzene for an hour. Silica gel thin layer chromatogram indicated the absence of spots other than starting material. *ii*) A catalytic amount of aluminum chloride was added to V (55 mg) and III (100 mg) in anhydrous benzene. The solution soon became red and resinous matter was separated out. No crystalline product was obtained.

Attempted Reaction of Guaiazulene (II) and p-Benzoquinone (VI). Benzene solution of II (198 mg) and VI (216 mg) was kept at room temperature for 24 hr in the dark. Silica

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1) W. Treibs, *Naturwissenschaften*, **43**, 156 (1960); **48**, 452 (1965).

gel column chromatography of the mixture first eluted a small amount of recovered II. No indication of the formation of adducts was obtained from silica gel thin layer chromatogram of the subsequent elutes.

The Reaction of Azulene (V) and p-*Benzoquinone (VI).* V (128 mg) and VI (216 mg) were kept in benzene at room temperature for 12 hours in the dark. The reaction mixture was chromatographed on a silica gel column to give 80 mg of recovered V and subsequently the adduct VII, blue black crystals, mp 111.5—112.5°C, 56 mg (24%).

Found: C, 82.07; H, 4.24%. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. $\lambda_{max}^{MeOH}(\varepsilon)$ 237 nm (4300), 292 nm (4100), 522 nm (broad).