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CYCLOADDITION OF 6-AMINOFULVENES WITH COUMALIC ESTERS.
A NOVEL AZULENE FORMATION

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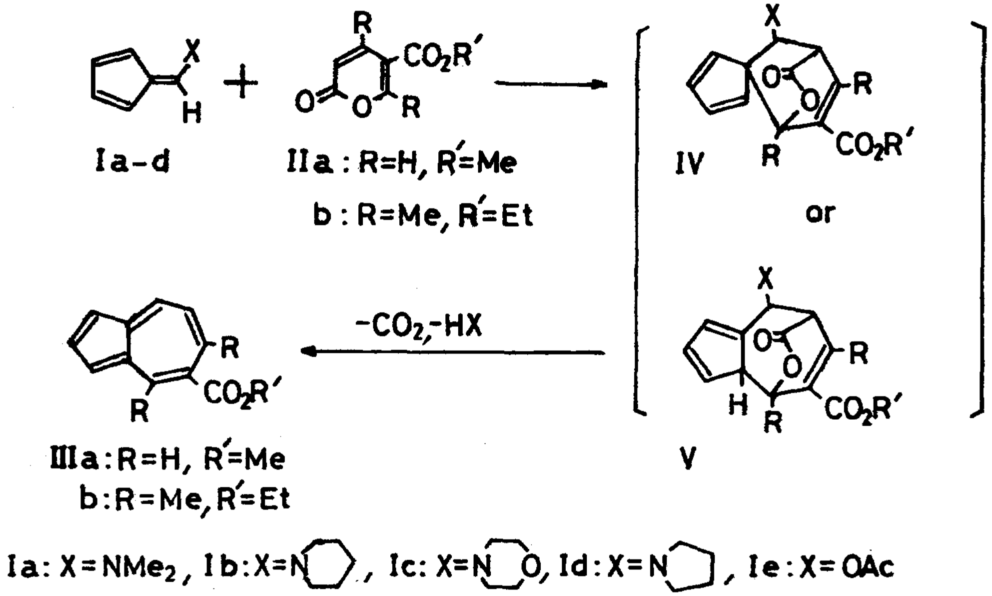
Azulenes have recently been prepared from oxazulanone and enamines via 8+2 cycloaddition.[1] We here report that the reaction of 6-aminofulvenes (higher analogs of enamine) with α-pyrones (lower analogs of oxazulanone) proceeds successfully to give azulenes by one-step.

6-Dimethylaminofulvene (Ia) and methyl coumalate (IIa) were dissolved in benzene and stirred for five days in dark at room temperature. After chromatographic separation on silica gel and subsequent sublimation, methyl azulene-5-carboxylate (IIIa)[2] was obtained as a deep blue-violet oil in 9% yield, the structure of which was identified by the agreement of the u.v. and i.r. spectra with those of the literature,[2] and further by conversion to an authentic complex with trinitrobenzene.[2] An alternative isomer, methyl azulene-6-carboxylate, was not detected in the reaction mixture by n.m.r. spectrum. The reaction of 6-piperidinofulvene (Ib)[3] and 6-morphorinofulvene (Ic) (mp 75-77°)[4] with IIa gave IIIa in 12 and 17% yields, respectively. 6-Pyrrolidinofulvene (Id) (mp 104-105°)[4] with IIa, however, gave a tiny yield of the azulenic product. The reaction of I with IIa in a polar solvent such as chloroform or ethanol, instead of benzene, resulted in a marked decrease of azulenic product. The intriguing reaction of substituted fulvenes to give azulenes is likely limited to the amino-substituted, because 6-acetoxyfulvene (Ie) gave no azulenic product. The reaction of ethyl 4,6-dimethyl-5-coumalate (IIb) with Ia in benzene solution gave a violet oil of ethyl 4,6-dimethylazulene-5-carboxylate (IIIb) in low yield; i.r.(neat),ν_{CO} 1725 cm^{-1}; u.v.(n-hexane),λ_{max}565 nm(ε 334); n.m.r.($CDCl_3$),δ 8.14(1H,d,J=10Hz,H-8), 7.15(1H,t,J=4Hz,H-2), 7.5(1H,broad d,J=4Hz) and 7.3(1H,broad d,J=4Hz)(H-1 and H-3), 7.04(1H,d,J=10Hz,H-7), 4.43(2H,q,J=7Hz,$OC\underline{H}_2$), 2.83(3H,s) and 2.58(3H,s)(4- and 6-CH_3), and 1.41(3H,t,J=7Hz,$OCH_2C\underline{H}_3$).[4]

It is known that, in cycloaddition, fulvenes act as 2π-[5] or 6π-addends[5] and coumalic esters do as 4π-addends.[6] The present reaction, therefore, would be represented by the following mechanism via 4+2 cycloadduct (IV) or 6+4 cycloadduct (V).



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4) Satisfactory elemental analyses were obtained for new compounds (Ic), (Id) and (IIIb).

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