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SYNTHESIS OF AZULENE FROM 6-ACYLOXYFULVENES

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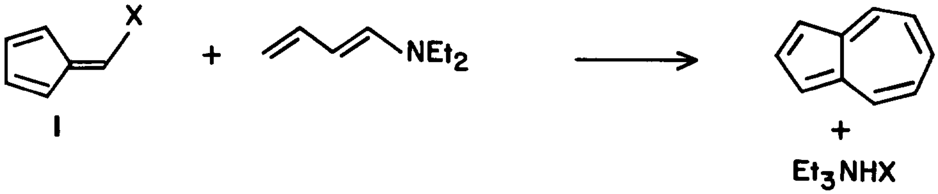
Summary: The 6-acetoxy, tosyloxy, and p-nitrobenzoyloxy derivatives of fulvene undergo [6+4] cycloadditions with 1-diethylaminobutadiene to give azulene in 12, 14, and 68% yield, respectively. The p-nitrobenzoyloxyfulvene is a crystalline, stable substance which is highly reactive towards nucleophilic dienes.

Dienamines undergo [6+4] cycloadditions with alkyl or aryl fulvenes to give dihydroazulenes, which can be dehydrogenated subsequently to form azulenes in moderate yields.[2] The dehydrogenation step can be avoided by the [6+4] cycloaddition of 6-aminofulvenes to thiophene dioxides, since both the amine and SO_2 are lost spontaneously to form azulene.[3] However, these cycloadditions generally proceed in poor yields. In order to develop a high-yield, dehydrogenation-free, synthesis of azulenes, we have investigated the cycloadditions of dienamines to fulvenes which have a potential leaving group at the 6-position. The 6-acetoxy[4] and 6-tosyloxy[5] derivatives of fulvene have been reported by Hafner and coworkers. These fulvenes are prepared by the reaction of acetyl chloride or tosyl chloride with the sodium salt of formylcylopentadiene, which is made, in turn, from sodium cyclopentadienide and ethyl formate.[4,5] The acetoxy derivative, 1a is a moderately stable oil,[4] while the tosyloxy derivative, 1b, is a low-melting, air sensitive solid.[5] Both of these fulvenes react readily with nucleophiles at the 6-position to give substitution products.[4,5] Since the acetoxy group is a very mild electron acceptor,[6] it may be expected to enhance slightly the reactivity of a fulvene towards nucleophilic dienes. On the other hand, the tosyloxy and p-nitrobenzoyloxy groups are more potent electron-acceptors, and should more strongly enhance reactions of the [6+4] variety.[7]

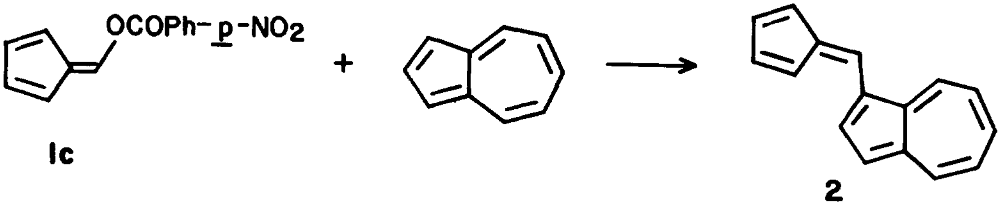
We have found that all three of these fulvenes can be used for the synthesis of azulene, but the stable, crystalline 6-p-nitrobenzoyloxyfulvene, **1c**, is a highly preferred precursor, both because of the ease of handling of **1c** and because of the good yields obtained with this compound. As shown below, **1a** and **1b** react readily with 1-diethylaminobutadiene, but give poor yields of azulene.

However, the reaction of **1c** with 1-diethylaminobutadiene proceeds at room temperature to give azulene in a respectable yield, even when compared to the classic Ziegler-Hafner synthesis.[8]

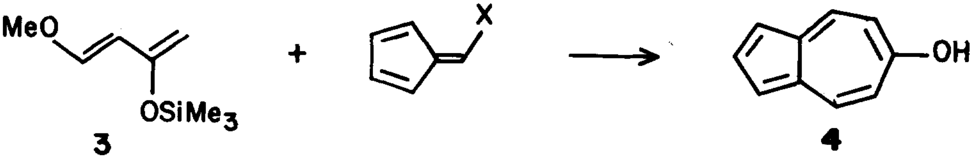


X	Conditions	Yield
a: $OCOCH_3$	25°, $CHCl_3$	12%
b: OSO_2Ph-*p*-Me	25°, CCl_4	14%
c: OCOPh-*p*-NO_2	25°, PhH	68%

In some experiments, the reaction of **1c** with diethylaminobutadiene gave a second product which was found to arise from the reaction of azulene with **1c**. The violet 6-(1-azulenyl)fulvene, **2**, obtained in this way, was reported previously by Hafner.[9] However, formation of this by-product occurs only when **1c** is used in excess. To eliminate formation of the 2:1 adduct, an excess of the dienamine was employed.



These acyloxyfulvenes also react with Danishefsky's diene, **3**,[10] to form 6-hydroxyazulene[11] in low yield. Details of this reaction, as well as other uses of **1c** will be reported at a later date.



Synthesis of p-Nitrobenzoyloxyfulvene (**1c**)

A solution of p-nitrobenzoyl chloride (7.5 g, 0.04 mol) in anhydrous ether (150 ml) was added dropwise to a suspension of the sodium salt of formylcyclopentadiene (5.8 g, 0.05 mol) in 100 ml of ether at 0°C under nitrogen. After the resulting suspension was stirred for five hours, 250 ml of chloroform was added, and the insoluble salts were removed by filtration. After washing the filtrate with water and drying over $MgSO_4$, the solution was concentrated on a rotary evaporator and chromatographed on silica gel with 25% ethyl acetate in petroleum ether. After complete elution of the yellow band from the column, this fraction was concentrated to give a yellow solid. Recrystallization of this solid from petroleum ether/chloroform gave 4.96 g (51% yield) of yellow crystals of **1c**, mp 128-132° (dec.). The nmr spectrum of **1c** in $CDCl_3$ exhibited resonances at 6.3-6.6 ppm (multiplet, 4H, fulvene ring protons), 7.9 ppm (singlet, C-6 proton) and 8.4 ppm (singlet, 4H, aromatic protons). Analysis. Calcd. for C: 64.19%; H: 3.70%; N: 5.76; Found: C: 63.95%; H: 3.81%; N: 5.59%.

Synthesis of Azulene from 1c.

To a solution of 1c (1.21 g, 5 mmol) in benzene, 1-diethylaminobutadiene (1.25 g, 10 mmol) was added. The solution was stirred under nitrogen at room temperature and was constantly monitored by TLC. The spot due to 1c disappeared after 7 hours. After evaporation of the excess of benzene, the mixture was chromatographed over a silica gel column (300 g of silica). The dark blue band was eluted from the column with 5% ethyl acetate in cyclohexane. Concentration give 435 mg (68% yield) of fine blue crystals of azulene, mp. 98-99°C, whose nmr spectrum is identical to that of authentic azulene.

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References and Notes

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