known composition were prepared on a vacuum line. During a determination, one of these mixtures was admitted to the instrument through a given inlet, while a proton-donor reagent gas was flowed into the instrument through a different inlet. Both arsine and methane were used as proton-donor gases. Possible errors due to calibration of the pressure-measuring ionization gauge for the different gases were eliminated by the use of such mixtures made up on a vacuum line.

The observed equilibrium constant for reaction 8, corrected only for the ^{13}C contribution of the $(CH_3)_2C_6H_4^+$ and $(CD_3)_2C_6H_4^+$ ions, had a value of 1.00 ± 0.06, corresponding to a value of $\Delta G°_{300}$ of 0.00 ± 0.03 kcal/mol. This value was independent of the composition of the mixture used, independent of the pressure of the mixture or of the proton-donor gas, and independent of the energy of the ionizing electrons. A value for $\Delta G°_{300}$ of −0.185 ± 0.018 kcal/mol was reported for reaction 8 in the earlier investigation.[1]

One possible source of error in the measurements would be insufficient deuteration of the *p*-xylene-d_6. The isotopic purity of the *p*-xylene-d_6 used here[4] was listed as 99 at. %. If we assume that, indeed, the $C_8H_4D_6$ sample contained 6% $C_8H_5D_5$, and correct the composition of the mixtures accordingly, the observed equilibrium constant for reaction 8 is decreased to 0.94, which corresponds to a value of $\Delta G°_{300}$ of +0.04 kcal/mol. Another way of estimating the possible importance of insufficient deuteration is to observe the ratios of the two parent ions, $(CD_3)_2C_6H_4^+$ and $(CH_3)_2C_6H_4^+$, and assume that these will be approximately the same as the ratios of the corresponding molecules in the mixtures. This assumption leads to a value of K_{eq} of 0.85 ± 0.04, corresponding to a value of $\Delta G°_{300}$ of +0.099 ± 0.03 kcal/mol. Actually, it is certain that the latter assumption leads to a value of the equilibrium constant which is somewhat too low, and thus the value of 0.85 derived in this way may be considered as a lower limit. It is generally observed that deuterium-substituted compounds have ionization potentials higher than those of their nondeuterated analogues.[5] (For example, the ionization potential of cyclohexane-d_{12} is higher than that of cyclohexane by 0.46 kcal/mol;[3,5] the ionization potential of benzene-d_6 is higher than that of benzene by 0.03 kcal/mol.[6,7]) This expected difference will be reflected in the equilibrium constant of the charge transfer equilibrium

$$p\text{-}(CH_3)_2C_6H_4 + p\text{-}(CD_3)_2C_6H_4^+ \rightleftharpoons p\text{-}(CH_3)_2C_6H_4^+ + p\text{-}(CD_3)_2C_6H_4 \quad (9)$$

thus causing the ratio of deuterated to undeuterated parent ions to be slightly lower than the ratios of the corresponding neutral molecules in the mixture. (The results obtained here indicate that the equilibrium constant for reaction 9 is 1.11 ± 0.06, assuming 6% insufficient deuteration.)

In conclusion, the results obtained here show that the equilibrium constant for the proton transfer equilibrium in *p*-xylene and *p*-xylene-d_6 is in the range 0.85–1.00. Uncertainties in the equilibrium constant measurement result from uncertainties in the degree of insufficient deuteration; if the correction for insufficient deuteration is ignored, the importance of the proton transfer to the undeuterated species will be overestimated. The isotope effect on the proton transfer reaction, if it exists, is small (~0.05 kcal/mol).

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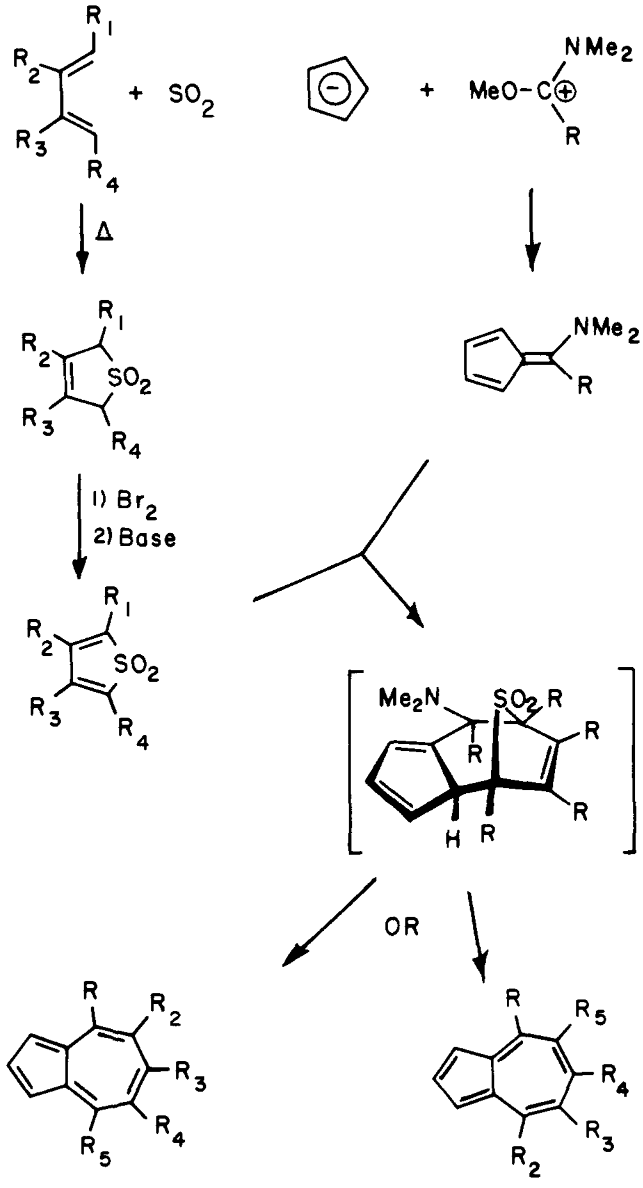
Synthesis of Azulenes by the [6 + 4] Cycloadditions of 6-Aminofulvenes to Thiophene *S,S*-Dioxides[†]

Sir:

Azulenes have been synthesized by a variety of methods,[1] of which the Ziegler-Hafner synthesis[2] has proven to be the most versatile. Recently, we reported an intermolecular version of this synthesis,[3] exploiting the propensity of very electron-rich dienes to add in a [6 + 4] fashion to fulvenes.[4] Reversing the

Scheme I



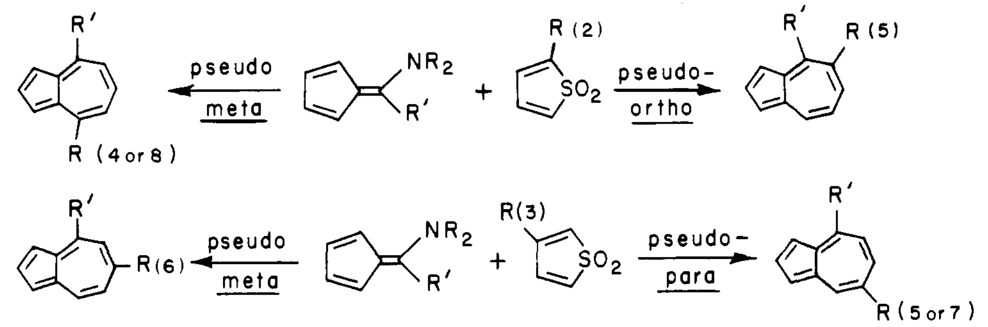
[†] This article and the "Woodward blue" 5,6-dichloroazulene are dedicated to Professor R. B. Woodward on the occasion of his sixtieth birthday.

Table I. Azulenes Obtained from Dimethylaminofulvenes and Thiophene Dioxides

Fulvene, 6 substituent	Thiophene dioxide			Azulene					Conditions[a]			Literature preparations	
	R_2	R_3	R_4	R_4	R_5	R_6	R_7	R_8	Time, h	T, °C	Yield, %	No. of steps	Yield, %[b]
H									12	25	10	5	46[c]
H		Me				Me			72	25	25	4 (2)	8–20[d] (6)[e]
H		Et				Et			48	25	12		
H		Ph			Ph	Ph			12	25	27	7	2[f]
											3		
H		Me	Me		Me	Me			48	50	8	2	12[e]
H		Cl	Cl		Cl	Cl			12	25	60		
H		Ph	Ph		Ph	Ph			24	25	13	1	30[g]
H	Me				Me				72	50	5	4	4[h]
H	Me		Me	Me		Me			48	50	10	2	41[e]
Me				Me					12	25	4	2 (2)	1[e] (67)[i]
Me		Me		Me		Me			72	25	10	2	41[e]
Me		Et		Me		Et			96	25	12		
Me		Ph		Me		Ph			48	25	5		
				Me			Ph				1		
Me		Me	Me	Me		Me	Me		72	50	7		
Me		Cl	Cl	Me		Cl	Cl		12	25	15		
Me	Me								360	50	0		
Me_2N				NMe_2					12	25	10	2	8[j]
Me_2N		Me		NMe_2		Me			24	25	5		
Me_2N		Et		NMe_2		Et			48	25	8		
Me_2N		Ph		NMe_2		Ph					6		
				NMe_2			Ph		12	25	1		
Me_2N		Ph	Ph	NMe_2		Ph	Ph		48	25	10		

[a] Reaction conditions were not optimized, but reactions were followed by TLC until the developing azulene spot appeared to reach a maximum value and remained constant. [b] Yields obtained by the previously preferred (highest yield and fewest steps) route. [c] Reference 2b. [d] L. T. Scott, *J. Chem. Soc., Chem. Commun.*, 882 (1973), from *p*-methyldihydrocinnamic acid. [e] R. W. Alder and G. Whittaker, *J. Chem. Soc., Perkin Trans. 2*, 714 (1975), via a modified Hafner procedure from the appropriate alkylated *N*-methylpyridinium iodide. [f] Yu N. Porshnev, E. M. Tereschenko, V. V. Titov, and V. B. Mochalin, *Zh. Org. Khim.*, **8**, 1492 (1972), from cinnamaldehyde and butyl vinyl ether using a modified Hafner procedure. [g] K. Hafner, J. Häring, and W. Jäkel, *Angew. Chem., Int. Ed. Engl.*, **9**, 159 (1970), along with 4,5,6-triphenylazulene from the cycloaddition of 6-phenyl-5-azaazulene to diphenylacetylene. [h] K. Hafner and K.-D. Asmus, *Justus Liebigs Ann. Chem.*, **671**, 31 (1964), from 3-picoline and cyclopentadiene. [i] K. Hafner, *ibid.*, **606**, 90 (1957), from azulene. [j] R. N. McDonald, H. E. Petty, N. L. Wolfe, and J. V. Paukstelis, *J. Org. Chem.*, **39**, 1877 (1974), from azulene.

Scheme II



polarity of the addends is also effective in promoting the [6 + 4] cycloadditions of fulvenes to dienes or other 4π electron systems. Thus, the [6 + 4] cycloadditions of 6-dimethylaminofulvene to nitrile oxides,[5] tetrazines,[6] and coumalic esters[7] have been reported. The last reaction gives azulenes in low yield. We wish to report a new general azulene synthesis which uses readily synthesized starting materials, has a simple workup procedure, and exhibits high regioselectivity.[8]

The reaction of 6-dimethylaminofulvene[9] with thiophene *S,S*-dioxide[10] proceeds at room temperature in chloroform to give azulene in low yield. Reactions with substituted compounds show that the reaction proceeds according to Scheme I, with the probable intervention of the [6 + 4] adduct shown in brackets. The reaction proceeds more rapidly and in much higher yield with the more stable 3,4-dichlorothiophene dioxide[11] than with the parent compound. Reaction of the dichloride with 6-dimethylaminofulvene occurs in several hours, to give 5,6-dichloroazulene in 60% yield.[12] The higher yield in this case is due at least in part to the lack of significant dimerization of the dichlorothiophene dioxide under these conditions.

Table I gives a summary of the reaction conditions and yields starting from the corresponding dibromotetrahydrothiophene dioxide. For comparison, some yields obtained in previous syntheses are given in the last column. The yields in this synthesis are often low owing to the tendency for many of the thiophene dioxides to dimerize[11,13] and to react with amines.[10,14] Nevertheless, the conditions are mild and the workup is simple (see the exemplary procedure below), since the by-products and reactants are all much more polar materials than the azulenes. Furthermore, the starting materials are readily prepared (Scheme I). The aminofulvenes are obtained by the condensation of cyclopentadienide with the appropriate alkylated amide[8,15] while the thiophene dioxides are most easily obtained by bromination–dehydrobromination of the [4 + 2] adducts of conjugated dienes with SO_2.[16] To date, the only aminofulvenes we have studied introduce a hydrogen, a methyl, or a dimethylamino substituent into the azulene 4 position. Other substituents should be readily introduced at C-4 by a similar sequence, and substituted cyclopentadienes can be used to introduce substituents on the five-membered ring. Thus, a variety of seven-membered ring substituted azulenes may be obtained from cyclopentadiene, an amide, and a butadiene in six steps with typical overall yields of 5–40%.

As with any cycloaddition, three possible mechanisms can be considered. Although the data are limited, the lack of pronounced rate or yield differences observed when these reactions are carried out in benzene, chloroform, and methanol suggest that no zwitterionic intermediates are formed. Nevertheless, the pronounced nucleophilicity of the 2 position of the aminofulvene should cause bond formation between this position and the thiophene dioxide 2 position to proceed faster than bond formation between the fulvene 6 and thiophene dioxide 2′ positions.

A qualitative pattern can be gleaned from the reaction times and yields reported in Table I. Alkyl substitution on the thiophene dioxide slows the reaction, while phenyl or chloro substitution accelerates the reaction. This is fully compatible with the idea that the electrophilicity of the thiophene dioxide determines its reactivity toward an aminofulvene. In terms of frontier orbital interactions, alkyl substitution lowers the thiophene dioxide electron affinity and lowers reactivity toward nucleophilic species, while chloro or phenyl substitution increases the electron affinity of the thiophene dioxide, and increases its reactivity toward nucleophilic species.[17]

Substitution of a 6-methyl or a 6-dimethylamino substituent on 6-dimethylaminofulvene should increase the nucleophilicity of the fulvene. Experimentally, a rate increase is not observed, probably because the addition of a 6 substituent sterically prevents the amino group lone pair from overlapping optimally with the fulvene π system. Thus, the ionization potentials of these 6,6-disubstituted fulvenes may be greater than that of 6-dimethylaminofulvene.[4]

For reactions of the unsymmetrical thiophene dioxides, two regioisomers can be formed, as shown in Scheme II. We suggest naming these in analogy to the regioisomers which can be formed in the Diels–Alder reaction. The dimethylamino substituent is considered the dominant substituent on the fulvene. The pseudo-meta-regioselectivity observed for the 3-alkyl- or arylthiophene dioxides (formation of 6-substituted azulene) is precisely that expected on the basis of frontier orbital predictions for reactions involving two addends, both of whose electronic asymmetry is caused by electron-releasing substituents.[17,18] Similarly, the 2,4-dimethylthiophene dioxide gives the predicted bis pseudo-meta regioisomer. However, the pseudo-para-regioselectivity observed for the reaction of 2-methylthiophene dioxide with 6-dimethylaminofulvene is opposite to the frontier orbital prediction, fitting better with a diradical-intermediate prediction. A satisfying explanation of the high regioselectivity observed must await further experimental and theoretical studies, but, in the examples now available, the attack of the nucleophilic fulvene occurs preferentially at the less substituted thiophene dioxide double bond, as is the case for Diels–Alder reactions of electron-rich dienes with benzoquinones.[19]

We are currently probing the general utility of this synthesis by studying the reactions of ring-substituted aminofulvenes and thiophene dioxides with other substituents and substitution patterns.

Preparation of 6-Methylazulene. 3-Methyl-3,4-dibromotetrahydrothiophene dioxide (3.0 g, 10 mmol) was dissolved in 75 mL of benzene. The solution was chilled to 0–5 °C, and triethylamine (3 mL, 20 mmol) was added. This solution was stirred for 2 h, the triethylammonium bromide was filtered off, and the resulting solution was added to dimethylaminofulvene (1.5 g, 12.5 mmol). This solution was stirred at room temperature under a gentle stream of nitrogen for 72 h. The reaction mixture was evaporated to dryness, and the crude product was dissolved in 20% chloroform–petroleum ether. Insoluble material was filtered off, and the solution was chromatographed on alumina with petroleum ether eluent. The first fraction consisted of 6-methylazulene (0.36 g, 25% yield, based on dibromotetrahydrothiophene dioxide).

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Hydrogenation of 1,3-Butadiene with 1,3-Cyclohexadiene and D_2 over ZrO_2 Catalysts

Sir:

Recent evidence indicates that the *molecular* identity of hydrogen is conserved during hydrogenation of unsaturated hydrocarbons over certain metal oxide catalysts.[1] We have extended these observations to a more complex system involving the competitive hydrogenation of 1,3-butadiene both directly with dihydrogen and indirectly via the hydrogen donor