

Thermodynamic Acidity of 6,6-Dimethylfulvene and 6-Phenyl-6-methylfulvene in Dimethyl Sulphoxide

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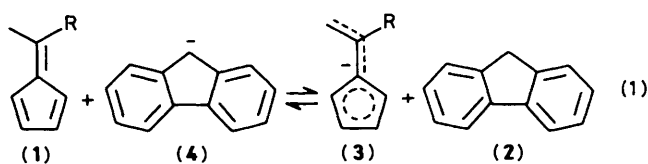
The thermodynamic acidity of 6,6-dimethylfulvene and 6-phenyl-6-methylfulvene in dimethyl sulphoxide have been determined to be 22.7 and 22.1, respectively.

We report the determination of the equilibrium acidity constants for 6,6-dimethylfulvene, (**1a**), and 6-phenyl-6-methylfulvene, (**1b**), in dimethyl sulphoxide (DMSO) solvent. Despite the growing importance of fulvenes in theoretical and synthetic studies, we are not aware of any previous study of the energetics of deprotonation in these systems.

Using the method of Bordwell,¹ the pK_a values of (**1a**) and (**1b**) in DMSO were determined to be 22.7 ± 0.1 and 22.1 ± 0.3 , respectively at room temperature. Fluorene, (**2**), ($pK_a = 22.6$)¹ was used as the indicator and the equilibrium in equation (1) was followed by u.v.-visible spectroscopy. Equilibrium absorbances appeared essentially on mixing and no further spectral changes were observed for periods ranging from 0.5 to 2 hours. By analogy with reports on other delocalized systems,¹ we assume that ion-pairing effects do not interfere with equilibrium (1).

Alkyl fulvenes are known to react with appreciably basic nucleophiles by at least two different mechanisms.^{2,3} As shown in Scheme 1, deprotonation by base gives rise to delocalized anions such as (**3**), while nucleophilic addition to the exocyclic double bond affords anions of type (**5**). In our study in DMSO we have found no evidence for the existence of (**5**). The u.v.-visible spectrum of the anion produced in DMSO by treatment of (**1**) with the fluorenyl anion (**4**) is clearly similar to the spectrum of the same anion that forms on treatment of (**1**) with potassium *t*-butoxide in *t*-butyl alcohol.^{3c} In the latter case, n.m.r. and mass spectral studies of H-D exchange in (**1a**) discount the intermediacy of (**5**).

The difference in acidity between fulvenes (**1a**) and (**1b**) is comparable with that of indene, (**6**), ($pK_a = 20.12$),⁴ and



a; R = Me

b; R = Ph

Table 1. pK_a values of methyl hydrogens in DMSO.^a

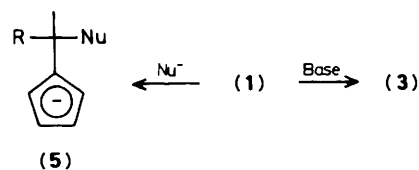
Acid	pK_a
MeCN	31.3
Me ₂ SO ₂	31.1
PhSO ₂ Me	29.0
Me ₂ CO	26.5
PhCOMe	24.7
(1a)	22.7 ^b
(1b)	22.1 ^b
MeNO ₂	17.2

^a Ref. 1. ^b This work.

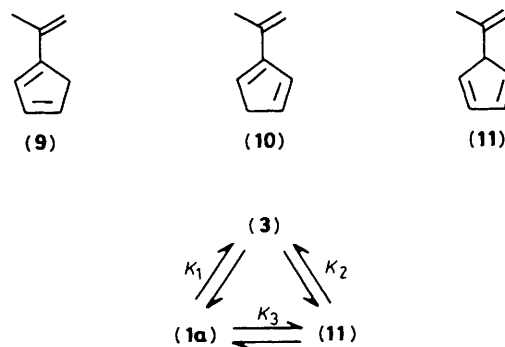
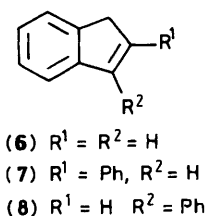
2-phenylindene, (**7**), ($pK_a = 19.37$).⁴ In the cases of both (**1b**) and (**7**), the dominant effect of the phenyl is that of induction and not direct conjugation. Such an effect on pK_a is smaller than that seen when direct conjugation is possible, as is the case in 3-phenylindene, (**8**), ($pK_a = 17.3$).⁴

As can be seen from Table 1, the methyl hydrogens of (**1a**) and (**1b**) are quite acidic. It appears that the acidifying power of the cross-conjugation in these fulvenes lies between that of a benzoyl group and a nitro group. Lo and Whitehead⁵ have calculated electron densities in the anion derived from 6-methylfulvene. Their calculations indicated that extensive delocalization of charge (about 85%) into the ring occurs. It is reasonable to expect that similar delocalization of charge into (**3**) also occurs. This extensive delocalization may account for substantial stabilization in (**3**), and thus the marked acidity of (**1a**) and (**1b**) is not surprising.

In our original report on the isomerization of dimethylfulvene,^{3a} we estimated that the equilibrium mixture was comprised of 98% (**1a**), 1.4% (**9**), 0.6% (**10**), and less than 0.001% (**11**). If we consider the equilibrium cycle shown in



Scheme 1



Scheme 2

Scheme 2, we can say that $K_1 = K_2K_3$. From our present work in DMSO, $K_1 = 1.99 \times 10^{-23}$. From our estimate of the relative stabilities of (1a) and (11), $K_3 = 1 \times 10^{-5}$. Thus K_2 is 1.99×10^{-18} , from which we can estimate the pK_a of (11) to be 17.7 or less. Bordwell has shown that in DMSO, the pK_a of cyclopentadiene is 18.0.⁶ Thus it appears that the effect of the isopropenyl substituent in (11) is to increase the acidity of cyclopentadiene by at least 0.3 pK_a units.

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