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Novel fulvenes capto-datively substituted at C_6

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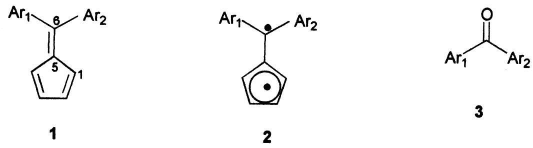
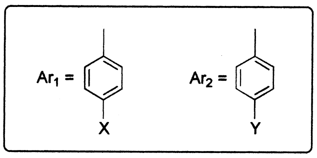
A set of four fulvenes bearing both electron-withdrawing and -donating aryl groups at C_6 was prepared and shown to be fairly stable, except for the dimerisation of the anisyl-nitrophenyl-fulvene **1a**, which also underwent a (4π + 2π) cycloaddition with *C,N*-diphenylnitrone.

Keywords: fulvenes, capto-dative substitution

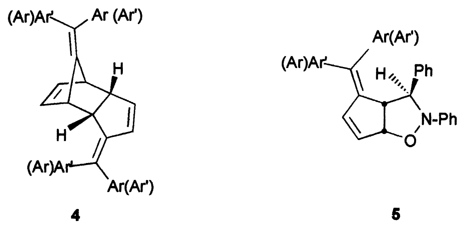
The fulvenes are an interesting class of cyclic cross-conjugated molecules, which display a wide range of reactions with nucleophiles, electrophiles and various cycloaddition partners.[1] Several possessing either electron-donating[1] or electron-withdrawing[4] groups at C_6 are known. It was of interest to prepare and study fulvenes possessing both such groups (simultaneously) at C_6 (**1**, Scheme I), which would thus be a centre of capto-dative substitution.[6] Notably, as the capto-dative effect is believed to stabilise a radical centre,[6] the diradical form **2** possessing a cyclopentadienyl radical moiety, was expected to be an important canonical contributor to the overall structure of **1**.



1 **2** **3**



1, 3	X	Y
a	NO_2	OMe
b	NO_2	Me
c	CN	OMe
d	CN	Me
e	CN	H
f	H	Me
g	NO_2	H
h	H	OMe



4 **5**

4, 5: Ar = 4-(MeO)C_6H_4-, Ar' = 4-(NO_2)C_6H_4-

Scheme 1

A set of eight such fulvenes **1a–1h** was prepared by condensing cyclopentadiene with the corresponding substituted benzophenones **3** under the usual basic conditions (NaOEt/EtOH), in yields of around 30%, and characterised spectroscopically. (Two of these, **1g** and **1h**, were known previously.[12,13] The benzophenones **3** had revealed the capto-dative effect by cyclic voltammetry and phosphoresecence spectra.[8]) The fulvenes **1a–1h** were red, crystalline solids, and relatively unreactive. Thus, they failed to undergo the usual cycloaddition reaction with *N*-phenylmaleimide that is shown by several other fulvenes.[1] However, the anisyl-nitrophenyl-fulvene **1a** furnished in dichloromethane solution at room temperature, a product (in 25% yield) to which the dimeric structure **4** has been assigned on the basis of NMR and mass spectrometry. Also, **1a** underwent a (4π + 2π) cycloaddition reaction in refluxing chloroform over three days, with C,N-diphenylnitrone, to furnish the (3+2) adduct **5** in 51% yield; the structure was assigned on the basis of NMR which was closely similar to that of the previously reported cycloadduct of 6,6-diphenylfulvene with *C,N*-diphenylnitrone, the structure of which had been confirmed by X-ray crystallography.[9] The NMR spectrum of **1a** in DMSO-d_6 remained unchanged up to 100°C, thus indicating a relatively high barrier to rotation around the C_5–C_6 bond, and ruling out a significant canonical contribution from the diradical form **2**. The UV spectra of **1** were also similar to those of other 6,6-diarylfulvenes.[1]

Thus the only evidence for any capto-dative effect in the fulvenes **1** is the dimerisation of the anisyl-nitrophenyl derivative **1a**, with little other evidence for any significant contribution from the diradical form **2** by the above criteria.

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