6-Substituted Fulvenes from Trifluoromethylcyclopentadiene

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Trifluoromethylcyclopentadiene has been prepared from trifluoroiodomethane, nickelocene, and triphenylphosphine in ether. On treatment with nucleophiles such as piperidine or alkoxides, trifluoromethylcyclopentadiene gives 6-fluorofulvenes and 6,6-dipiperidinofulvene or 6,6-dialkoxyfulvenes. Diols, trifluoromethylcyclopentadiene, and base give cyclic ketals of fulveneketene.

It is well-known that coordination of organic groups with transition metals can alter the reactivity of the ligands dramatically. Lithium or sodium cyclopentadienides are often useful sources of reactive cyclopentadienyl groups, whereas in most cyclopentadienyl-transition metal compounds the cyclopentadienyl group is strongly bonded and not easily substituted. However, nickelocene and cyclopentadienyl-copper tributylphosphine are less stable and more reactive than, e.g., ferrocene. Although electronically different, they often react similarly with organic halides to form new carbon-carbon bonds under mild and neutral conditions.[1-4] They may thus be alternative reagents to the alkali metal cyclopentadienides in preparations of base-sensitive products.

Moberg and Nilsson have reported the preparation of trichloromethylcyclopentadiene and 6,6-dichlorofulvene from nickelocene and carbon tetrachloride.[5] The present paper deals with the synthesis of trifluoromethylcyclopentadiene from nickelocene and trifluoroiodomethane and its reactions with nucleophiles such as piperidine and some alkoxides.

RESULTS AND DISCUSSION

Nickelocene and trifluoroiodomethane react in the presence of triphenylphosphine in ether

to give trifluoromethylcyclopentadiene and (η^5-cyclopentadienyl)bis(triphenylphosphine)-nickel(II) iodide (Scheme 1). Trifluoromethylcyclopentadiene is most easily handled as an ether solution and purified as such by trap to trap distillation on a vacuum line. The concentration is determined by UV spectroscopy.
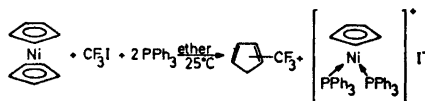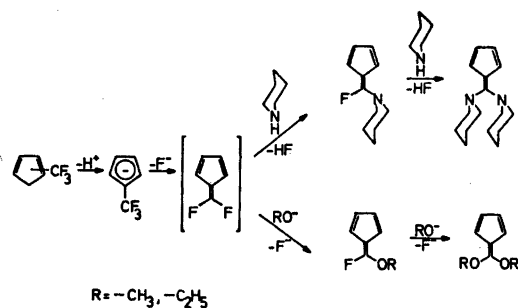

Scheme 1.

Trifluoromethylcyclopentadiene was obtained as a mixture (70/30) of 1- and 2-trifluoromethylcyclopentadiene (NMR evidence). In contrast, trichloromethylcyclopentadiene was isolated as the 5-isomer from an analogous reaction,[6] although the reaction and separation conditions were similar. Breslow et al. have studied the rearrangement of halocyclopentadienes and found that the order of increasing rate of thermal rearrangement is 5-iodo- < 5-bromo- < 5-chlorocyclopentadiene < cyclopentadiene.[7] We have found that trifluoromethyl- and methylcyclopentadiene rearrange faster than trichloromethylcyclopentadiene. Methylcyclopentadiene is known to rearrange by a 1,5-sigmatropic shift of hydrogen in non-polar solvents.[8] 5-Trifluoromethylcyclopentadiene should be more acidic and be able to rearrange to the more stable isomers via the anion. However, the isolated mixture of 1- and 2-trifluoromethylcyclopentadiene does not incorporate deuterium on treatment with deuterium oxide.

In contrast to cyclopentadiencarboxylic acid and its derivatives, trifluoromethylcyclopenta-

diene dimerises only slowly on standing (half life 30 days in CDCl$_3$, initial concentration *ca.* 10 %, room temperature) to a mixture of dimers. GLC-MS showed four different dimers with very similar mass spectra (*m/e* 268 parent peak and 134 base peak).

On treatment with piperidine, trifluoromethylcyclopentadiene gives 6-fluoro-6-piperidinofulvene. The reaction should proceed *via* elimination of hydrogen fluoride from trifluoromethylcyclopentadiene to give 6,6-difluorofulvene, which should be extremely reactive to nucleophiles and which so far has escaped detection. At higher concentrations of piperidine trifluoromethylcyclopentadiene gives 6,6-dipiperidinofulvene in a few minutes (Scheme 2).


R = −CH$_3$, −C$_2$H$_5$

Scheme 2.

When a solution of potassium hydroxide in an alcohol is added to an ether solution of trifluoromethylcyclopentadiene, a fast reaction gives a 6-fluoro-6-alkoxyfulvene as the first observable product. Further reaction with the alkoxide ion gives the 6,6-dialkoxyfulvene (Scheme 2). The reactions are run at room temperature for 15 min and give almost complete conversion of trifluoromethylcyclopentadiene into fulvenes. When the reaction was run in perdeuteriomethanol, deuterium was only incorporated into the methoxy groups and not into the ring.

The unstable 6-fluoro-6-methoxyfulvene and 6-fluoro-6-ethoxyfulvene have been prepared with this method. The amount of base and nucleophile must be carefully controlled since substitution of the second fluorine atom is fast. It is probable that even the reaction of weak nucleophiles with difluorofulvene is generally much faster than the loss of a fluoride ion from the trifluoromethylcyclopentadienyl anion (Scheme 2).

The reaction between trifluoromethylcyclopentadiene and some terminal diols has also been investigated. Thus, 1,2-dihydroxyethane, trifluoromethylcyclopentadiene and base give a good yield of the cyclic ketal of fulveneketene (Scheme 3). The product is a rather stable crystalline compound, but it polymerises irreversibly in the presence of traces of acid.
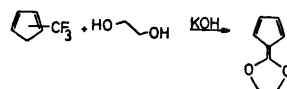
Scheme 3.

Similarly, 1,3-, 1,4-, and 1,5-dihydroxyalkanes and trifluoromethylcyclopentadiene give cyclic ketals of fulveneketene in the presence of base. There is a small change in the position of the maxima in the UV spectra of the ketals. The size of the saturated ring influences the overlap of the lone pair of electrons on the oxygen atoms with the π-cloud of the fulvene. The ketal with a five-membered saturated ring shows the maximum absorption at 292 nm, a six-membered ring at 302 nm, a seven-membered ring at 296 nm, and an eight-membered ring at 300 nm in ethanol.

Dibromodifluoromethane is an alternative reagent for trifluoroiodomethane in the preparation of 6-substituted fulvenes. Dibromodifluoromethane is commercially available and easy to handle. It reacts smoothly with nickelocene in the presence of triphenylphosphine to give bromodifluoromethylcyclopentadiene. The product is more reactive and also less stable than trifluoromethylcyclopentadiene but can be used for the same general purpose.

The present method, which seems quite general for the preparation of 6-substituted fulvenes, has also been successfully used for the preparation of 6,6-diallyloxyfulvenes and related compounds as well as for the preparation of unsymmetrical and cyclic diamino- and oxyaminofulvenes, which will be reported elsewhere.

EXPERIMENTAL

UV spectra were recorded on a Beckman DK 2A, NMR spectra on a Bruker WH 270, IR spectra on a Beckman IR 9, and mass spectra on an AEI MS 902 instrument.

Trifluoromethylcyclopentadiene. Nickelocene (40 mmol) and triphenylphosphine (80 mmol) were dissolved in dry diethyl ether (100 ml) in a pressuresafe bottle and cooled in acetone/dry ice under nitrogen atmosphere. Trifluoroiodomethane (*ca.* 70 mmol), prepared from potassium trifluoroacetate and iodine,[9] was added to the cooled bottle, which was then sealed. After 20 h at room temperature the bottle was opened and the green precipitate of (η^5-cyclopentadienyl)bis(triphenylphosphine)nickel(II) iodide filtered off, m.p. 90 °C, decompl. NMR (CDCl$_3$): δ 7.5 (30 H, m) and 5.25 (5 H, s). Trifluoromethylcyclopentadiene, being a low-boiling liquid, was conveniently transferred as an ether solution on a vacuum-line for further reactions. The yield of trifluoromethylcyclopentadiene was estimated to be 55 – 60 %, on the assumption of a quantitative reaction with piperidine (see below). For characterisation, a small sample of trifluoromethylcyclopentadiene was separated from the solvent by preparative GLC. NMR (CDCl$_3$): 1-Trifluoromethylcyclopentadiene δ 6.97 (1H, m), 6.62 (1H, m), 6.52 (1H, m) olefinic protons, 3.21 (2H, m) methylene protons; 2-trifluoromethylcyclopentadiene 6.85 (1H, m), 6.61 – 6.54 (2 H, m) olefinic protons, 3.16 (2H, m) methylene protons. UV (hexane): λ_{max} 242 nm, log ε 3.67 (calc. *via* conversion into dipiperidinofulvene). MS (70 eV): *m/e* 134 (100 %, M$^+$), 115 (56, M$^+$ – F), 84 (54, M$^+$ – CF$_2$), 69 (72, M$^+$ – C$_5$H$_5$), 65 (47, M$^+$ – CF$_3$), and 45 (91, C$_2$H$_2$F$^+$). Abs. mass: 134.032; calc. for C$_6$H$_5$F$_3$: 134.034.

6-Fluoro-6-piperidinofulvene. A 2 M solution (1 ml) of piperidine in diethyl ether was added to 10 ml of a 0.1 M solution of trifluoromethylcyclopentadiene in ether. After 20 min at room temperature, the piperidinium fluoride formed was precipitated by an addition of 20 ml of pentane to the reaction mixture. The salt was filtered off, and the solvents were evaporated to give 168 mg (94 %) of 6-fluoro-6-piperidinofulvene, m.p. 39 – 40 °C, after recrystallisation from pentane. NMR (CDCl$_3$): δ 1.71 (6 H; broad s), 3.68 (4 H, broad s), 6.24 (1 H, m), 6.39 (1 H, m), 6.54 (1 H, m), 6.69 (1 H, m). UV (hexane): λ_{max} 318 nm, log ε 4.48. MS (40 eV): *m/e* 179 (100 %, M$^+$), 178 (35), 152 (37), 136 (26), 96 (36). Abs. mass: 179.112; calc. for C$_{11}$H$_{14}$NF: 179.111.

6,6-Dipiperidinofulvene. Piperidine (1 ml) was dissolved in 5 ml of ether and added to 10 ml of a 0.1 M solution of trifluoromethylcyclopentadiene in ether. After 30 min the fulvene was obtained as above. The product was purified from the excess of piperidine by recrystallisation from cyclohexane to give 230 mg (94 %) of 6,6-dipiperidinofulvene. Melting

point (140 – 144 °C) and spectroscopic data agree with those previously reported.[5]

6-Fluoro-6-ethoxyfulvene and 6,6-diethoxyfulvene. A solution of potassium hydroxide in ethanol (2 ml, 0.30 M) was slowly added to an ether solution of trifluoromethylcyclopentadiene (2 ml, 0.15 M). After a few minutes the ether and most of the ethanol were distilled off. The residue was purified by filtration through a short silica gel column with chloroform as solvent. The yield of 6-fluoro-6-ethoxyfulvene, estimated by UV spectroscopy and by further reaction with ethoxide to give the known 6,6-diethoxyfulvene,[10] was almost quantitative. GLC-MS showed the parent peak at *m/e* 140 (100 %) and important fragments at 112 (94, M$^+$ – C$_2$H$_4$), 92 (91, M$^+$ – C$_2$H$_5$F), and 84 (95, M$^+$ – C$_2$H$_4$ – CO). The main fragmentation is of a McLafferty-type. NMR (C$_6$D$_6$): δ 0.73 (3 H, doublet of triplets, $J = 7.0$ and 0.6 Hz), 3.52 (2 H, q, $J = 7.0$ Hz), 6.5 (2 H, m), 6.75 (1 H, m) and 6.83 (1 H, m). UV (hexane): λ_{max} 276 nm, log ε 4.23.

6-Fluoro-6-methoxyfulvene. The compound was prepared as described for 6-fluoro-6-ethoxyfulvene above. GLC-MS showed the parent peak at *m/e* 126 (100 %) and the main fragment at 92 (45, M$^+$ – CH$_3$F). UV (hexane): λ_{max} 279 nm, log ε 4.23. NMR (C$_6$D$_6$): δ 2.97 (3 H, d, $J = 0.6$ Hz), 6.5 (2 H, m) 6.75 (1 H, m) and 6.81 (1 H, m).

2-Cyclopentadienyliden-1,3-dioxacyclopentane. A solution of trifluoromethylcyclopentadiene in ether (0.1 M, 10 ml) was added to 5 ml of a 1 M solution of potassium hydroxide in 1,2-dihydroxyethane, and the two-phase system was stirred vigorously for 1 h. The ether solution was washed with water several times to remove potassium fluoride and excess diol. After evaporation of the ether, the fulvene was recrystallised from carbon tetrachloride to give 106 mg (77 %) of 2-cyclopentadienyliden-1,3-dioxacyclopentane, m.p. 153 – 155 °C. NMR (C$_6$D$_6$): δ 4.56 (4 H, s), 6.31 and 6.63 (2 + 2 H, AA'XX'-system). UV (ethanol): λ 292 nm, log ε 4.42 and λ 301 nm, log ε 4.40. MS (40 eV): *m/e* 136 (58, M$^+$), 92 (100, M$^+$-CH$_2$CHO). Abs. mass: 136.053; calc. for C$_8$H$_8$O$_2$: 136.052.

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