Reaction of Thiobenzophenones with the Dicarbonylcyclopentadienyliron Anion: a Novel Fulvene Synthesis *via* Desulphurization

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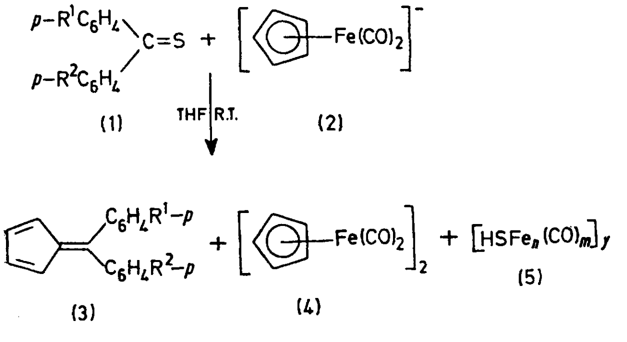
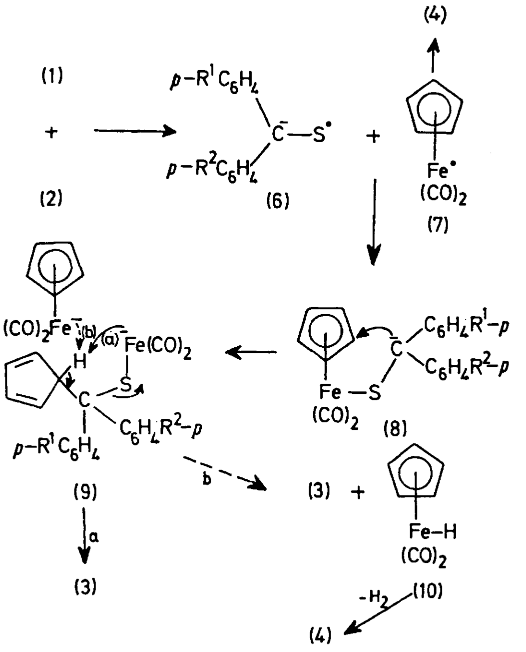
Summary Thiobenzophenones react with the dicarbonylcyclopentadienyliron anion with coupling to afford fulvenes, *via* a novel desulphurization and metal–ring cleavage reaction.

Recently, we began an investigation of the reactions of thioketones with metal carbonyl anions. One goal of this study was to determine the effect of metal carbonyl anion nucleophilicity on the reaction pathway. Thiophilic addition[1] of pentacarbonylmanganese anion to a thiobenzophenone, and subsequent work-up, affords complexes of the type $[Ar_2CHSMn(CO)_4]_2$.[2] The dicarbonylcyclopentadienyliron anion is considerably more nucleophilic than $[Mn(CO)_5^-]$[3] This communication describes the unusual reaction of thiobenzophenones (**1**) with the carbonyliron anion (**2**).



Treatment of (**1**; $R^1 = R^2 =$ H, Me, or OMe; $R^1 =$ H, $R^2 =$ OMe) with (**2**) [generated from the dimer (**4**) and NaK in tetrahydrofuran (THF)][4] in anhydrous THF for 18 h at room temperature gave the fulvenes [**3**; $R^1 = R^2 =$ H (7·5%), Me (58%), OMe (82%); $R^1 =$ H, $R^2 =$ OMe (62%)], the dimer (**4**), and an unidentified complex (**5**).

The highly coloured fulvenes (**3**) were identified by comparison of their melting points and u.v. spectral data with those reported in the literature.[5,6] N.m.r. and mass spectra are in accord with the fulvene structure.



Scheme

This reaction constitutes a novel synthesis of fulvenes by the rather unusual cleavage of the cyclopentadienyl ligand from (**2**) and desulphurization of (**1**). A possible mechanism for the formation of (**3**) is outlined in the Scheme. Initial electron transfer from the iron atom of (**2**) to (**1**) would give the radical anion (**6**) and the dicarbonylcyclopentadienyliron radical (**7**). Coupling of (**6**) and (**7**) would afford (**8**), the product of formal thiophilic addition of (**2**) to (**1**). Intramolecular attack of the carbanion at a carbon atom of the cyclopentadienyl ring of (**8**) and cleavage of the iron-ring bond would give (**9**) which must be generated easily since no alkylation occurs when (**2**) is treated with (**1**) in the presence of methyl iodide. Conversion of (**9**) into the fulvene may then take place either by intramolecular (path a) or intermolecular (path b) abstraction of hydrogen. The dimer (**4**) may arise either by dimerization of (**7**) or by dimerization and elimination of hydrogen from (**10**).

The following general procedure was used (solvents, reagents, and glassware were rigorously dried). A mixture of (**4**) (0·65 g, 1·84 mmol) and NaK (78% by wt. of K) in THF (50 ml) was stirred at room temperature for 1 h. The bright red solution was filtered into a flask containing tetrabutylammonium perchlorate (1·30 g, 3·82 mmol) and the mixture was stirred for 20 min and then filtered (to remove $KClO_4$). Compound (**1**) (3·3 mmol) was added to the filtrate containing $[Bu_4N]^+[C_5H_5Fe(CO)_2]^-$ (isolated[4] first if desired) and the solution was stirred overnight at room temperature. The solution was concentrated *in vacuo*, dissolved in the minimum amount of benzene, and then chromatographed on silica gel with light petroleum (b.p. 60—80 °C) to give the fulvene (**3**).

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