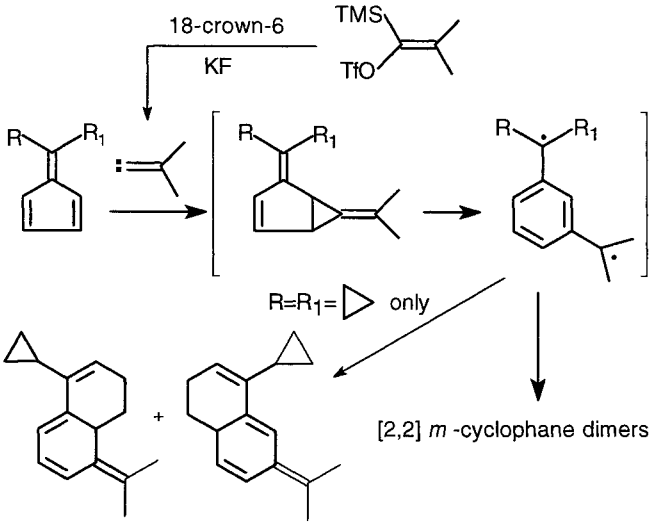
Unexpected Coupling Reaction of 9-Lithiobromomethylene-9*H*-fluorene with 6,6-Dicyclopropylfulvene

Gitendra C. Paul, Joseph J. Gajewski*
Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA
Fax +1(812)8558300; E-mail: GAJEWSKI@INDIANA.EDU
Received 1 August 1996; revised 29 October 1996

Metallation of 9-bis(bromomethylene)-9*H*-fluorene with one equivalent of BuLi at −78 °C followed by quenching with 6,6-dicyclopropylfulvene and subsequent warming (room temperatue, 18 h) gave an adduct identified as compound **5** (~70% yield). Under identical conditions dimethylfulvene and cyclopropylmethylfulvene failed to give a similar adduct. Simple and efficient syntheses of 9-bromomethylene- and 9-bis(bromomethylene)-9*H*-fluorene are also described.

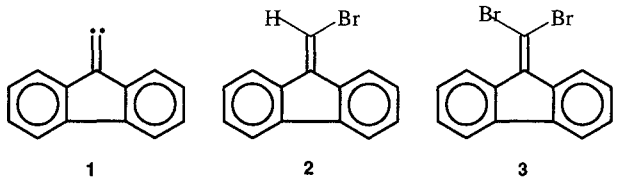
High spin organic molecules are of considerable interest because of their importance in making ferromagnets and magnetic materials.[1] One of the important ferromagnetic coupling units is *m*-xylylene. We have generated alkyl substituted *m*-xylylenes by reaction of isobutylidene with various fulvenes.[2] Observed *m*-cyclophane dimers and/or monomeric cyclopropane ring-opened compounds could account for the intermediacy of *m*-xylylenes (Scheme 1). However, under our experimental conditions, we were unable to characterize them spectroscopically.



Scheme 1

In order to retard dimerization of the *m*-xylylene species, 6-*tert*-butyl-6-methylfulvene was reacted with isobutylidene, but this reaction resulted in coupling at the dimethyl site and disproportionation at the methyl-*tert*-butyl site.[2] To retard dimer formation of the subsequent carbene addition adduct with fulvene, we chose to explore generation and reaction of the carbene 9-methylenefluorenylidene (**1**). As carbene precursors some standard choices are 9-bromomethylene- and 9-bis(bromomethylene)-9*H*-fluorene (**2** and **3**, respectively).

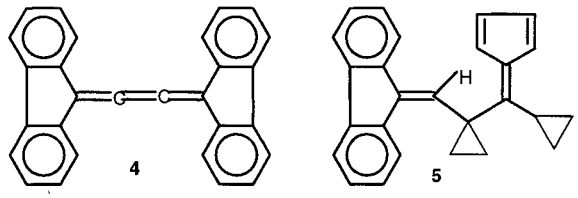
Preparation of **2** involves a modification of the method described by Kuhn et al.[3] Our procedure involves a high yield one-pot synthesis using readily available starting materials. Thus reaction of the ylide derived from (bromomethyl)triphenylphosphonium bromide and sodium bis(trimethylsilyl)amide with fluorenone gives after chromatography >80% yield of the desired product. Use of piperidine-lithium base at 0–25 °C, as described by Kuhn et al.,[3] gave little if any of the desired product. The method described by DeTar et al.[4] was also found to be unsatisfactory in our hands.



1 **2** **3**

Reimlinger's synthesis of **3** involves preparation of 9-diazofluorene and then reaction with dibromocarbene.[5] Our procedure involves an efficient synthesis in which **3** was obtained in one pot by reacting fluorenone with (dibromomethylene)triphenylphosphorane which was generated in situ from carbon tetrabromide and triphenylphosphine. The reaction was run in heptane under reflux for 48 hours with stirring (mechanical stirrer).

To generate and to trap carbene **1**, a diethyl ether solution of **2** was reacted with phenyllithium in the presence of cyclohexene and dimethylfulvene, respectively, at −35 °C. This however, did not result in any carbene addition adduct; rather after aqueous workup **2** was recovered along with a small amount of difluorene-9-ylideneethene (**4**), the dimer of **1**. Under similar conditions in the absence of trapping agent, **2** is reported to give a 50–54% yield of **4**.[6]



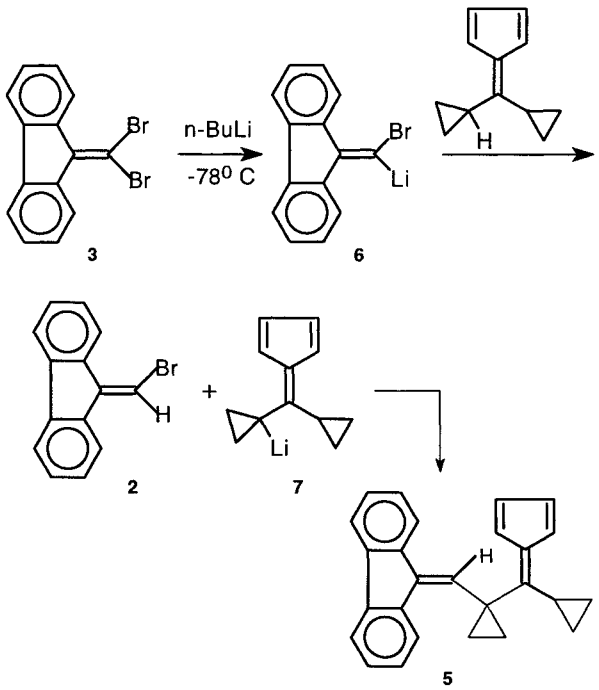
4 **5**

Reaction of 9-bis(bromomethylene)-9*H*-fluorene (**3**) with BuLi in hexane at −78 °C (or at −100 °C) followed by addition of large excess of cyclohexene resulted in no cyclohexene adduct; instead **2** was obtained after aqueous workup. Similar results were obtained with methyllithium except that some coupling product was also observed. However metallation of **3** with one equivalent of BuLi at −78 °C followed by addition of one equivalent of 6,6-dicyclopropylfulvene (−78 °C, 1.5 h) and then warming to room temperature (16–18 h) resulted in the formation of an adduct which was characterized as compound **5** (see below) in 70% yield as judged by ^{1}H NMR

integration along with 20% of **2** (yields were not optimized). Neither dimethylfulvene nor 6-cyclopropyl-6-methylfulvene under the same experimental conditions gave any adduct with **3**. Metallation of dicyclopropylfulvene with one equivalent of BuLi followed by quenching with **2** was also found to give the same product **5** in good yield.

Identification of **5** rests on proton, carbon-13, PMR simulation and exact mass determination. Aromatic and olefinic proton signals are straightforward to identify. But the splitting patterns of the cyclopropyl protons, that of two apparent quartets, could be simulated as an AA'XX' system with appropriate coupling constants (see experimental).

It is apparent from the above results that a free carbene **1** is not involved in these reactions, and it is a remote possibility that carbene **1** is unreactive toward cyclohexene and fulvenes. Formation of **5** can easily be explained by the sequence of reactions shown below. As has been demonstrated, independent generation of **7** and its reactions with **2** to give **5** lend support to this reaction scheme (Scheme 2).



Scheme 2

Failure to observe similar reactions with either dimethylfulvene or cyclopropylmethylfulvene could be associated with the stability of the anion formed and its relative reactivity toward proton abstraction versus adduct formation. Undoubtedly, in both cases a proton from the methyl group[7] is being abstracted by the 9-lithiobromomethylene-9*H*-fluorene **(6)** giving an anion delocalized into the cyclopentadienyl unit and is therefore stabilized. In the dicyclopropyl case such delocalized anion formation creates at the same time a strained methylenecyclopropane ring so that it then appears to make the anion in the cyclopropane ring more reactive toward **2**.

^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-400 MHz. All chemical shifts are reported in ppm downfield from TMS and were taken in $CDCl_3$ solution. HRMS were recorded on a KRATOS MS-80/RFAQ spectrometer. All chemicals used are available commercially.

9-Bromomethylene-9*H*-fluorene (2):
To a stirred suspension of (bromomethyl)triphenylphosphonium bromide (9.60 g, 22.0 mmol) in THF (60 mL) at −60 °C was added sodium bis(hexamethylsilyl)amide (22.0 mL, 1.0 M in THF). After 40 min of stirring a THF (10 mL) solution of fluorenone (3.60 g, 20.0 mmol) was added to the blood red solution. It was then allowed to warm slowly to r.t. (1.5 h) and stirred overnight. An aqueous workup, Et_2O extraction, drying ($MgSO_4$), filtration followed by solvent removal (rotary evaporation) gave an orange solid (5.1 g). It was purified by silica gel flash chromatography (hexane) to obtain light yellow crystals; yield: 4.2 g (16.3 mmol, 82%); mp 72–73 °C (Lit.[4] mp 72–73 °C).

^{1}H NMR: δ = 8.58 (d, J = 7.8 Hz, 1 H), 7.72 (d, J = 7.8 Hz, 1 H), 7.68 (d, J = 7.8 Hz, 1 H), 7.57 (d, J = 7.8 Hz, 1 H), 7.45 (dt, J = 7.8, 1.4 Hz, 1 H), 7.40 (s, 1 H), 7.39–7.34 (dt, 10 lines, J = 7.8, 1.2 Hz, 2 H), 7.28 (dt, J = 7.8, 0.8 Hz, 1 H).

9-Bis(bromomethylene)-9*H*-fluorene (3):
A mixture of fluorenone (1.80 g, 10.0 mmol), CBr_4 (6.63 g, 20.0 mmol) and PPh_3 (10.49 g, 40.0 mmol) in anhyd heptane (80 mL) was refluxed under N_2 (mechanical stirrer was used) for 48 h. After cooling, the solution was filtered through a glass frit containing Celite. The residue was washed several times with hexane and was filtered. Removal of solvent gave a yellow solid. Crystallization from hexane produced light yellow needle-like crystals of **3**; yield: 2.84 g (8.46 mmol, 84%); mp 132–133 °C (Lit.[5] mp 131–132 °C).

^{1}H NMR: δ = 8.62 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.42 (t, J = 7.8 Hz, 2 H), 7.32 (t, J = 7.8 Hz, 2 H).

6-Cyclopropyl-6-[1-(fluorene-9-yl)cycloprop-1-yl]fulvene (5):
To a THF (6 mL) solution of **3** (120 mg, 0.36 mmol) at −78 °C was added BuLi (0.38 mmol). After stirring for 0.5 h dicyclopropylfulvene (0.4 mmol) was added and stirred for 1.5 h at −78 °C. Then the cooling bath was removed and the mixture was stirred overnight (18 h). Aqueous workup, Et_2O extraction and solvent removal as above left a residue which from ^{1}H NMR integration was found to contain **2** (20%), unreacted fulvene and compound **5** (~70%). A sample of **5** (>98% pure) as a sticky solid (brownish yellow) was obtained after silica gel flash chromatography (5% Et_2O in hexanes) (R_f 0.445 for **5** and R_f 0.545 for fulvene). Both fulvene and **5** partially decomposed in the column.

^{1}H NMR: δ = 8.35 (d, J = 7.2 Hz, 1 H), 7.74 (dd, J = 1.2, 8.0 Hz, 1 H), 7.68 (d, J = 7.2 Hz, 1 H), 7.64 (d, J = 8.0 Hz, 1 H), 7.38 (dt, J = 1.2, 7.8 Hz, 1 H), 7.32 (dt, J = 1.2, 7.8 Hz, 2 H), 7.26 (dt, J = 1.2, 7.8 Hz, 1 H), 6.99 (s, 1 H), 6.93 (app. td, J = 1.6, 5.2 Hz, 1 H), 6.70 (ddd, J = 1.6, 2.4, 5.6 Hz, 1 H), 6.51 (app. td, 5.2, 1.6 Hz, 1 H), 6.43 (app. td, J = 1.6, 5.6 Hz, 1 H), 1.97 (m, 1 H, cyclopr. H), 1.57 and 1.35 (each having app. q, simulates with $J_{AA'}$, $J_{XX'}$ = 7 Hz, $J_{AX(gem)}$ = −3 Hz and $J_{AX'}$ = 2 Hz, 4 H), 0.96–0.90 (m, 4 H).

^{13}C NMR: δ = 156.40, 145.26, 141.29, 139.95, 138.75, 135.76, 135.52, 132.91, 130.99, 130.58, 128.25, 127.92, 126.90, 126.73, 126.46, 122.12, 120.0, 119.64, 119.45, 27.70, 18.48, 17.67, 8.38.

HRMS (CI): $C_{26}H_{23}$(M+H); m/z found 335.17854, calcd 335.18009.

Reaction of Lithiodicyclopropylfulvene (7) with 9-Bromomethylene-9*H*-fluorene (2):
In a flask containing THF (3 mL) solution of dicyclopropylfulvene (80 mg, 0.50 mmol) at −78 °C was added BuLi (0.40 mmol) with stirring. The temperature was gradually raised to −5 to 0 °C and

was kept there for 40 min. The solution was then cooled to −78 °C and **2** (80 mg, 0.31 mmol) was added. After 2 h the cooling bath was removed. The color of the solution remained green after 20 h of stirring at r.t. After 2 d the solution turned red. Following workup as above, ^{1}H NMR of the residue showed fulvene and **5** in a ratio of 2:3 along with a trace amount of **2**. Thus from PMR integration conversion of **2** to **5** appears quantitative.

We thank the Department of Energy for support of this work.

(1) Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 5550.
Rajca, A. *Chem. Rev.* **1994**, *94*, 871.
Borden, W.T.; Iwamura, H.; Berson, J.A. *Acc. Chem. Res.* **1994**, *27*, 109.
Miller, J.S.; Epstein, A.J. *Angew. Chem.* **1994**, *106*, 399; *Angew. Chem. Int. Ed. Eng.* **1994**, *33*, 385.
Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346.
Dougherty, D.A. *Acc. Chem. Res.* **1991**, 24, 88.
(2) Paul, G.C.; Gajewski, J. *J. Tetrahedron Lett.* **1995**, *36*, 8549.
Gajewski, J.J.; Paul, G.C.; Chang, M.J.; Gortva, A.M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.
Gajewski, J.J.; Chang, M.J.; Stang, P.J.; Fisk, T.E. *Ibid.* **1980**, *102*, 2096.
(3) Kuhn, R.; Fischer, H.; Rewicki, D.; Fischer, H. *Liebigs Ann. Chem.* **1965**, *689*, 1.
(4) DeTar, D.F.; Broderick, E.; Foster, G.; Hilton, B.D. *J. Am. Chem. Soc.* **1950**, *72*, 2183.
(5) Reimlinger, H. *Chem. Ber.* **1964**, *97*, 339.
(6) Curtin, D.Y.; Richardson, W.H. *J. Am. Chem. Soc.* **1959**, *81*, 4719.
(7) Brickhouse, M.D.; Squires, R.R. *J. Am. Chem. Soc.* **1988**, *110*, 2706, and references cited therein.