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6-DIMETHYLAMINO-6-LITHIOFULVENE, A NOVEL 6-FULVENYL ANION OF POTENTIAL SYNTHETIC UTILITY

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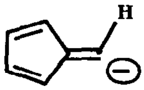
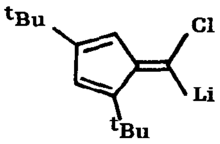
Summary: Treatment of 6,6-bis(dimethylamino)fulvene with 2.2 equiv. of lithium naphthalenide in THF generates, via two-electron reduction and deamination, 6-dimethylamino-6-lithiofulvene which is a new 6-fulvenyl anion of potential utility for the synthesis of a variety of 6-aminofulvenes and related compounds.

6-Fulvenyl anion **1** is expected to be a versatile synthon for cyclopentanoid compounds of theoretical and synthetic interest; however, only one such species **2** has so far been reported.[1] We here report simple generation and some reactions of 6-dimethylamino-6-lithiofulvene **3**, a new, synthetically versatile 6-fulvenyl anion.



1



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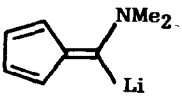
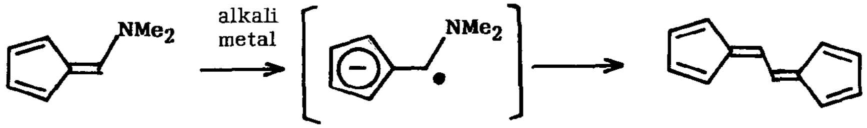


3

We have recently reported that alkali metal reduction of 6-dimethylaminofulvene **4** affords, in high yield, 6,6'-bifulvenyl **6** via coupling of the corresponding anion radical **5**, followed by deamination.[2]



4 **5** **6**

However, when 6,6-bis(dimethylamino)fulvene **7** was treated similarly with 1.0 equiv. of lithium naphthalenide (THF, -78°C), there were obtained no coupling products but the reduction product **4** (yield 33%) and unreacted **7** (55%) after usual work-up (water quenching and alumina chromatography). Use of 2.2 equiv. of the reagent led to complete disapperance of **7** and afforded **4** in good yields. Intermediacy of the 6-fulvenyllithium **3** in this reaction was verified by incorporation of deuterium at C-6 position of **4** when the reaction mixture was quenched with D_2O. Table 1 gives a rough view on the stability of **3** in THF. Generation of **3** is rapid at -78°C, and good chemical yield and high degree of deuterium incorporation into **4** was attained upon quenching after rather short reaction time (5-15 min). Longer reaction time or higher reaction temperature gave the poorer results due to decomposition of **3**. While the chloro anion **2** has been described to rearrange to a benzyne via a vinylidene carbene at around -10°C,[1] the amino anion **3** showed no sign of benzyne formation. This is probably due to poorer leaving ability of dimethylamino group compared to chlorine atom.

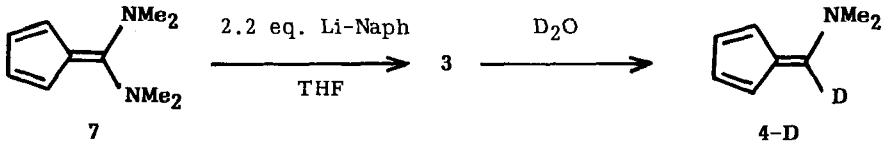


Table 1. Li-naphthalenide reduction and D_2O quenching of **7**[a]

Run	Temp/°C	Reaction time/min	Yield (D-content[b])/%
1	-78	10	78 (97)
2	-78	30	46 (84)
3	0	30	23 (48)

[a] Carried out in THF at 1 mmol scale using 2.2 equiv. of Li-naphthalenide.

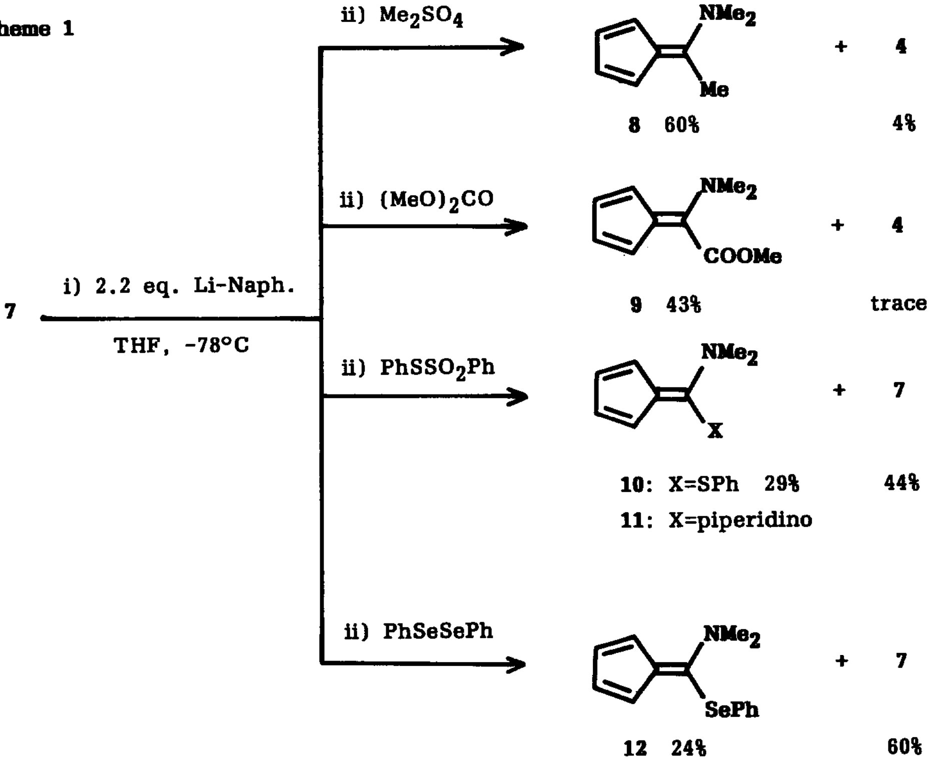
[b] Calculated from ^1H NMR and mass spectra.

Scheme 1 shows some reactions of **3** with electrophiles other than proton. Quenching with dimethyl sulfate gave the methylated fulvene **8**[3] in a good yield. Reaction with diethyl carbonate led to the captodative[4] fulvene **9**[5] as a fairly stable compound, where the stabilizing electronic effect of dimethylamino group seems to exceed the destabilizing effect of electron-withdrawing carboethoxy group. In the case of phenylsulfenylation with phenyl benzenethiosulfonate,[6] a considerable amount of the starting material **7** was recovered besides the desired fulvene **10**. Since treatment of **10** with lithium piperidide under similar conditions gave rise to the substitution product **11**, the recovered **7** has perhaps arisen from nucleophilic substitution reaction of **10** with lithium dimethylamide liberated in situ during the generation of **3** from **7**. Reaction of **3** with diphenyldiselenide yielded similarly the selenofulvene **12**.

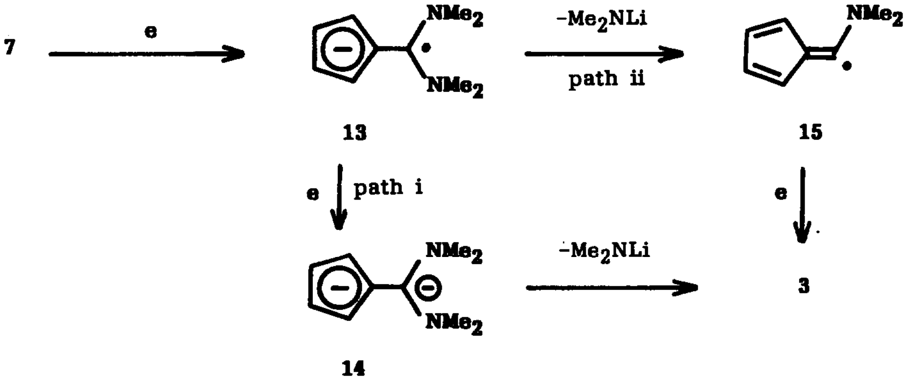
Although several 6-alkyl-6-aminofulvenes and 6-alkylthio-6-aminofulvenes have been prepared by reaction of cyclopentadienyl anion with appropriate heteroatom substituted methyl cations,[7] the present transformations involving **3** would provide a new method of wider applicability for synthesizing novel 6-aminofulvenes because a good variety of electrophiles can be applied to **3**. In addition, ready reductive coupling of 6-dimethylaminofulvenes[2] would add a promising prospect for the utility of the present method.

Probable pathways for the formation of **3** from **7** are shown in Scheme 2. One electron reduction of **7** generates the anion radical **13** which would be more stable than **5** owing to both electronic and steric effects of the second dimethylamino group. Further reduction of **13** produces the dianion **14** (path i). Electronic repulsion in **14** facilitates elimination of lithium dimethylamide to give 3. Another possibility is elimination of lithium dimethylamide from 13 giving the radical 15 followed by further reduction (path ii). Path i seems more plausible, since no dimers from 15 have been found in the reaction products. A similar dianion has been postulated in the reduction of 6,6-diphenylfulvene with sodium naphthalenide.[8]

Scheme 1



Scheme 2



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References and Notes

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4. H. G. Viehe, Z. Janousek, R. Merenyi, and L. Stella, Accounts Chem. Res., **1985**, 18, 148; and references therein.
5. **9**: deep yellow needles, mp 53-54°C; IR (KBr) ν 1745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.43 (3H, t, J=7.1 Hz), 3.24 (6H, s), 4.43 (2H, q, J=7.1 Hz), 6.25 (1H, m), 6.33 (1H, m), 6.51 (1H, m), 6.61 (1H, m); ^{13}C NMR ($CDCl_3$) δ 14.14, 43.09, 62.20, 115.94, 117.10, 122.21, 122.32, 126.24, 149.56, 165.45.
   10: yellow needles, mp 106.5-107°C; ^1H NMR ($CDCl_3$, 100 MHz) δ 3.25 (6H, s), 6.27 (1H, m), 6.47 (1H, m), 6.60-6.80 (2H, m), 7.05-7.30 (5H, m).
   12: yellow needles, mp 104.5-105.5°C; ^1H NMR ($CDCl_3$, 100 MHz) δ 3.27 (6H, s), 6.34 (1H, m), 6.46 (1H, m), 6.60 (1H, m), 6.80 (1H, m), 7.10-7.44 (5H, m).
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