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Communications

Carbanion: The First Example To Generate Thermodynamically Unfavorable 9-(Dicyanomethyl)fluorenide Anion

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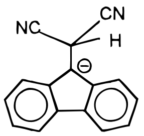
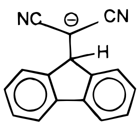
Carbanions as a class of very important intermediates in many organic and bioorganic reactions have been extensively studied and continue to be of interest. Generally, two methods are used in the preparation of carbanions, i.e., (1) addition of a nucleophile with a negative charge to unsaturated neutral species (precursors) and (2) removal of a group with a positive charge (e.g., proton) from neutral saturated substrates (the other precursors).[1] For 9-(dicyanomethyl)fluorenide carbanion (**1**) as a thermodynamically unfavorable anion, 9-fluorenylidenemalononitrile (**3**) and 9-fluorenylmalononitrile (**4**) would be its two typical precursors. In fact, the former only gave 9-fluorenylmalononitrile carbanion (**2**) rather than anion **1** by addition of a hydride (from $LiAlH_4$ as an example),[2] and the latter by removal of a proton also gave sole anion **2**,[2] which were rationalized by the much larger thermodynamic stability of **2** than that of **1** (pK_a = 22 for fluorene and pK_a = 11 for dicyanomethane in DMSO).[3,4] In this paper, we wish to report the first example of the generation of carbanion **1** by a hydride transfer from 1-benzyl-1,4-dihydronicotinamide (BNAH) to compound **3** in dry CH_3CN.



1



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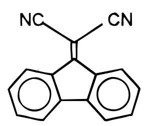

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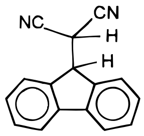

4

3 (214 mg, 1 mmol) and BNAH (228 mg, 1 mmol) were dissolved in dry acetonitrile to make a suitable oversaturated solution. The solution (yellow) was rigorously deaerated and stirred under argon in a closed system at room temperature, and a deep red color gradually appeared. Sixteen hours later, UV−vis spectroscopy showed the appearance of a new absorption at $\lambda_{max} = 540$ nm (Figure 1), which is close to that of a reported fluorenide carbanion ($\lambda_{max} = 521$ nm).[5] Mass spectrometry of the reaction mixture exhibited a strong peak at $m/z = 164$ (100) and a weak peak at $m/z = 165$ (16) owing to the fragments of fluorenylidene and fluorenyl, respectively. In the ^1H NMR spectrum of the reaction mixture, no characteristic peaks of compound **4** were observed, but the peaks at δ (CD_3CN) 9.24 (1H, s), 8.92 (1H, d), 8.75 (1H, d), 8.03 (1H, t), 7.36 (5H, s), 5.75 (2H, s) were originated from the BNA^+ cation.[6] When the red solution was treated with acetic acid, the red color disappeared immediately and the solution subjected to chromatography to give product **4** of yield 86% based on **3**. Treatment of the red solution with CH_3CO_2D gave 9-D-fluorenylmalononitrile (yield 71% based on **3**).[7,8] These obtained results clearly indicate the formation of carbanion **1** in the reaction of **2** with BNAH (see eq 1).[9,10]

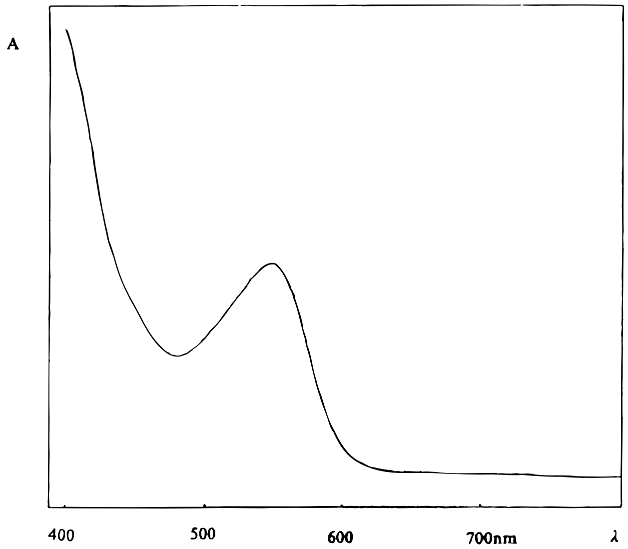

Figure 1. UV−vis spectrum of the reaction mixture.

Table 1. Products and Yields[a] (%) at Different Time Intervals for the Thermolysis of Salt 5

time (h)	**6**	**7**
0	trace	0
5	8	trace
10	16	7
20	24	11
40	36	15
60	41	17

[a] The yields are based on the amount of compound **3** used.

To further confirm the carbanion **1** mentioned above, the thermolytic reaction of salt (**5**) was studied. When the red

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(1) McManus, S. P. *Organic Reaction Intermediates*; Academic Press: New York and London, 1973; pp 337−422.

(2) Zhu, X. Q. Ph.D. Thesis, Lanzhou University, 1996.

(3) Bordwell, F. G. *Acc. Chem. Res.* **1988**, 21, 456−463.

(4) The hyperconjugative cyano group stabilization of ion **1** could be quite substantial, making the stability difference much smaller than that predicted by the difference between fluorene and dicyanomethane, but the stability of ion **2** is still quite larger than that of ion **1**, which can be confirmed by the fact that treatment of compound **4** with NaH in dry CH_3CN and followed by addition of CH_3OD gave solely α-D-fluorenylmalononitrile.

(5) Chan, L. L.; Smid, J. *J. Am. Chem. Soc.* **1968**, *90*, 4654.

(6) Caughey, W. S.; Schellenberg, K. A. *J. Org. Chem.* **1966**, *31*, 1978.

(7) Zhu, X.-Q.; Yang, L.; Guo, Q.-X.; Wu, L.-M.; Liu, Y.-C. *Chin. J. Magn. Reson.* **1996**, *13*(3), 248.

(8) In addition, there was a small amount of compound **4** obtained from the products, which is attributed to hydrogen−deuterium exchange between the deuterated product and the media during the workup (cf. Cram, D. J.; Gosser, L. *J. Am. Chem. Soc.* **1964**, *86*, 5445).

(9) Although the thermodynamic stability of ion **2** is quite larger than that of ion **1**, the rearrangement of ion **1** into ion **2** by proton [1,2] transfer was forbidden in the reaction based on the orbital correlation rule.

(10) The transfer of amide protons in BNAH and BNA^+ to ion **1** was not observed from the ^1H NMR spectrum of the reaction mixture. The reason could be the weaker acidity of the amide protons compared to the 9-proton in compound **4** (pKI_a = 22 for nicotinamide in DMSO, cf. ref 3). In fact, ion **1** was not free in the reaction system, which must combined with BNA^+ to be more stable.

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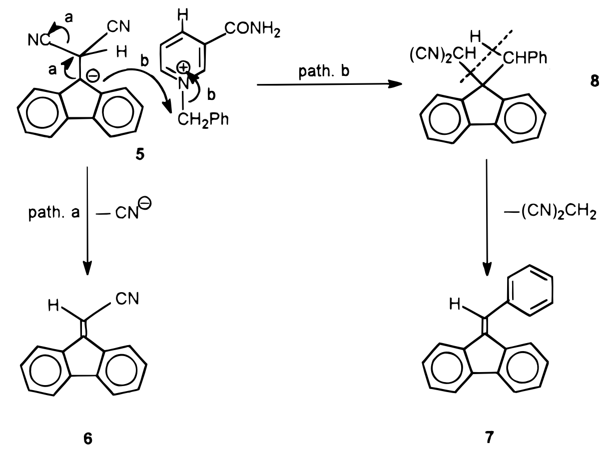
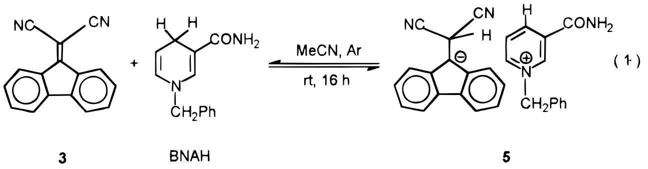
Scheme 1





salt solution formed upon the reaction of **3** with BNAH was heated to 60 °C and maintained for 60 h, two thermolytic products fluoren-9-ylideneacetonitrile (**6**)[11] and 9-benzylidenefluorene (**7**)[12] were obtained. The yields of **6** and **7** were crucially dependent on the reaction time, and the estimates at different times by GC are tabulated in Table 1. If 1-propyl-1,4-dihydronicotinamide was used as the reductant instead of BNAH for the thermolytic reaction, no corresponding propylidene product was generated. The reason could be that the stability of benzyl carbonium is much larger than that of the propyl one. The mechanism of thermolytic reaction of salt **5** is depicted in Scheme 1. Obviously, product **6** must be derived from carbanion **1** rather than carbanion **2** by removal of a cyanide, which also can be supported by Hoz and co-worker's work.[13] Product **7** could be obtained from intermediate **8** by removal of a malononitrile, which presumably resulted from the combination of carbanion **1** with a benzyl cation from BNA$^+$. These results further supported that the reduction of compound **3** by BNAH yielded carbanion **1** and BNA$^+$ cation.

Regarding to the mechanism by which carbanion **1** was formed during the hydride-transfer reaction, it may deal with the multistep hydride transfer initiated by one-electron transfer from BNAH (e$-$H$^+-$e transfer); the details are now under investigation.

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[12] Buu-Hoi, N. P.; Sait, G. *Bull. Soc. Chim. Fr.* **1967**, 10, 3738.
[13] Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904.