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Extreme thermal stability of disodium 9-fluorenone dianion as a practical indicator for the preparation of absolute THF

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Abstract

The fact that the lifetime of the disodium 9-fluorenone dianion is longer than that of the corresponding benzophenone dianion in refluxing THF for more than several months, which was proved by their ^1H NMR analyses and also by the isolated yields of their oxidation products (parent ketones), strongly suggests using 9-fluorenone as an excellent indicator for the preparation of absolute THF. © 1999 Elsevier Science Ltd. All rights reserved.

Sodium and potassium benzophenone ketyls are popularly used in many laboratories as an indicator for the preparation of absolute THF.¹ Recently, we had a chance to investigate the results of the reactions of diaryl ketones with alkali metals in refluxing THF and found a novel alkali metal-induced H-D atom-exchange reaction between the hydrogens of the diaryl ketones and α -deuteriums of the THF- d_8 oxygen.² The reaction was found to proceed through the formation of diaryl ketone dianions. In this paper, we wish to disclose the extreme stability of the disodium 9-fluorenone dianion and to recommend it as a superior indicator over that of the benzophenone dianion for the preparation of absolute THF.

When a mixture of benzophenone and lithium, sodium, or potassium was heated in THF, the initially formed deep-blue color of the benzophenone ketyls gradually or rapidly turned to red-purple indicating the formation of the corresponding dianion species.³ However, the lifetimes of these dianions in refluxing THF are highly counter cation-dependent. As shown in Table 1, the stabilities of the dilithium salts of the benzophenone dianion⁴ and 9-fluorenone dianion are particularly low because they easily cause alkylative opening of THF⁵ affording the corresponding diol (C)^{6,7} (entries 1 and 4). Although the disodium and dipotassium benzophenone dianions afforded, after oxidative work-up, benzophenone in 48% and 70% yields, respectively, a considerable amount of by-products (B⁶ and C) was still produced (entries 2 and 3). On the other hand, the disodium 9-fluorenone dianion was found to be extraordinarily stable under these conditions; it remained intact even after ten months thus maintaining its dark-green color, and the parent 9-fluorenone could be recovered in 96% yield (entry 6).

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Table 1
Stability of diaryl ketone dianions in refluxing THF- d_8 ^a

$$\text{Ar-C(=O)-Ar} \xrightarrow[\text{reflux, 240 h}]{\text{Metal / THF-}d_8} \text{O}_2 \rightarrow \text{A} + \text{Ar-}\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{-Ar} + \text{Ar-}\overset{\text{OH}}{\underset{\text{Ar}}{\text{C}}}\text{-(CD}_2\text{)}_4\text{OH}$$

A
B
C

Entry	Dianion	Counter cation	Product / % ^b		
			A	B	C
1	benzophenone	Li	1	—	75
2		Na	48 ^c	23 ^c	15 ^c
3		K	70	18	10
4	9-fluorenone	Li	6 ^c	—	55
5		Na	96 ^c	—	—
6 ^d		Na	96 ^c	—	—
7		K	61 ^c	20 ^c	10 ^c

a) The reaction was carried out in a sealed tube. b) Isolated yield. c) Aromatic hydrogens are partially deuterated. d) Reaction time: 10 months.

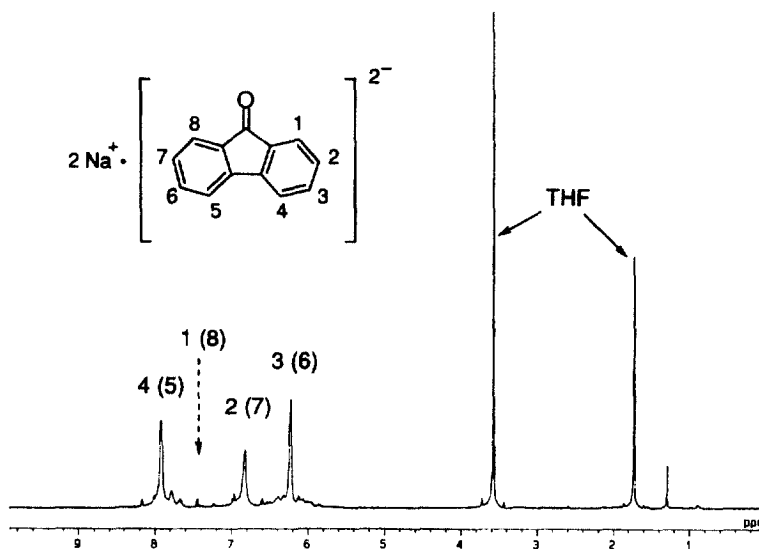


Figure 1. ¹H NMR spectrum of the partially deuterated disodium 9-fluorenone dianion in THF- d_8 (99.5 atom% D) after refluxing at 66°C for half a year

Fig. 1 shows the ¹H NMR spectrum of the disodium 9-fluorenone dianion in THF- d_8 after refluxing for half a year. As indicated by a dotted arrow, the 1,8-hydrogen atoms have been almost completely exchanged by deuteriums during the reaction,² however, all the other peaks are essentially the same as those of the authentic dianion.^{3a}

Different from the above case, the disodium benzophenone dianion generated in a sealed NMR tube completely decomposed within one week, which could be traced by the color change (red-

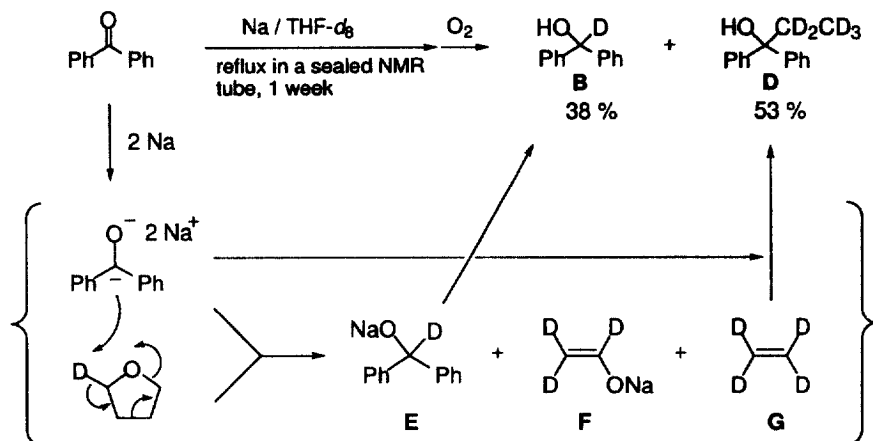


Figure 2. Main decomposition path of disodium benzophenone dianion in refluxing THF in a sealed NMR tube

purple→colorless). Oxidative work-up of the reaction mixture afforded a deuterated benzhydrol (**B**) and 1,1-diphenyl-1-propan-*d*₅-ol (**D**)^{6,8} in 38% and 53% yields, respectively. As shown in Fig. 2, the main reaction of the disodium benzophenone dianion is α -dedeuteration from THF-*d*₈ leading to the production of the diphenylmethoxide anion (**E**) and the fragmentation products of THF-*d*₈, an enolate anion (**F**) and ethylene-*d*₄ (**G**).⁹ A relatively high ethylene pressure in a sealed NMR tube, which is smaller than the sealed tube used in the experiment of entry 2 in Table 1, might be responsible for such a high yield of the ethylated product (**D**).

In conclusion, it was revealed that the benzophenone dianion is gradually decomposed in refluxing THF to give the diphenylmethoxide anion and the corresponding THF-adduct, but the disodium 9-fluorenone dianion is exceptionally stable. Therefore, we strongly recommend that chemists who manage absolute THF use sodium as a drying agent and 9-fluorenone as the source of a long term indicator.¹⁰

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5. For the alkylative opening of THF, see: Moret, E.; Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1991**, *409*, 83 and references cited therein.
6. Satisfactory GC–MS and ¹H NMR spectra were obtained.
7. Alternatively, 1,1-diphenylpentane-1,5-diol was prepared in a similar manner using THF instead of THF-*d*₈ and fully identified with an authentic sample which was prepared according to a literature method: Lehmann, J.; Marquardt, N. *Liebigs Ann. Chem.* **1988**, 827.

8. The corresponding nondeuterated compound of **D** was also obtained when THF was used in place of THF- d_8 and its structure was fully characterized.
9. When a mixed solvent, THF:THF- d_8 =3:1, was used for the NMR experiment, new triplet signals at around 1.1 ppm, which are assignable to the methyl protons of 1,1-diphenyl-1-propoxide anion, and a new singlet at around 5.3 ppm, which can be assigned to the ethylene protons, were observed.
10. Purification of tetrahydrofuran. The KOH-treated THF¹ (1.5 L) is transferred into an inert-atmosphere still. Sodium (ca. 1.5 g) and 9-fluorenone (ca. 0.5 g) were added and the THF was heated to reflux for a few hours. The resulting dark-green color of the 9-fluorenone dianion indicated that the THF was dry and peroxide-free.