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PRELIMINARY NOTE

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# Trifluoromethylation of 1,3,5-Trinitrobenzene

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## SUMMARY

The trifluoromethyl anion was trapped as Meisenheimer complex **2** on heating a mixture of potassium trifluoroacetate and 1,3,5-trinitrobenzene (TNB) in DMF or DMSO. Treatment of **2** with *tert*-butylhypochlorite afforded 1-trifluoromethyl-2,4,6-trinitrobenzene (**3**).

The trichloromethyl anion is an intermediate in a number of processes. A convenient trap for this carbanion is 1,3,5-trinitrobenzene (TNB). Thus, the Meisenheimer salt **1** has been obtained by reaction of TNB with chloroform and base [1], trichloroacetic acid [2], tetrachloromethane and tin (II) salts [3], and hexachloroacetone [4].

On the other hand, the trifluoromethyl anion ($CF_3^-$) is extremely unstable. Early attempts to generate nucleophilic metal trifluoromethide compounds were unsuccessful [5], presumably due to the rapid dissociation of $CF_3^-$ into $CF_2$ and $F^-$ [6]. More recently, reports have appeared describing trifluoromethylcopper ($CF_3Cu$), which exhibits nucleophilic character [7]. One method of $CF_3Cu$ generation is the decomposition of metal trifluoroacetates in the presence of copper (I) iodide [8].

We now report the trapping of $CF_3K$ generated by thermal decomposition of potassium trifluoroacetate. When a mixture of $CF_3CO_2K$ (210 mg, 1.4 mmol) and TNB (100 mg, 0.47 mmol) in one mL of N,N-dimethylformamide (DMF) or dimethylsulfoxide (DMSO) was heated at 150°C for one hour, a deep red solution of Meisenheimer complex **2** was obtained. The structure of **2** was evident from the $^1H$ NMR spectrum in DMSO-$d_6$ : $\delta$ 5.78 (quartet of triplets, $J_{HF}$ = 7 Hz, $J_{\text{allylic HH}}$

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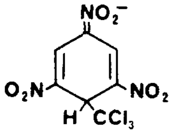
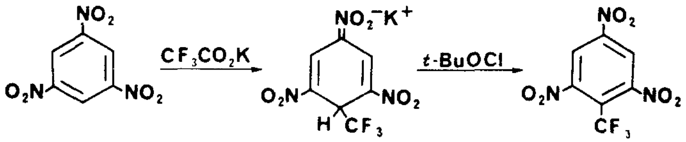
= 1 Hz), 8.46 (doublet, $J_{\text{allylic HH}} = 1$ Hz). This spectrum is consistent with that reported for analogous compound **1**, which consists of a 2 Hz doublet at δ 8.45 and a 2 Hz triplet at δ 6.32 [1].

Oxidation of a DMF solution of **2** by dropwise addition of *tert*-butylhypochlorite until the red color disappeared (about seven drops) followed by aqueous workup (10 mL of 1M HCl extracted with three portions of diethyl ether) afforded an oil. This was purified by preparative thin layer chromatography (one 2 mm silica gel plate eluted with 50 % petroleum ether / 50 % dichloromethane) to give 53 mg (40 % yield) of the known 1-trifluoromethyl-2,4,6-trinitrobenzene (**3**) [9].



**1**



**TNB** **2** **3**

The formation of complex **2** is the first example of the capture of $CF_3K$ by an organic electrophile without the involvement of a transition metal. Hine's kinetic study of haloform deprotonations suggested that $CF_2X^-$ ions have no finite existence [6], but subsequent work by Burton and coworkers revealed that both bromodifluoromethyl [10] and chlorodifluoromethyl [11] anions can be generated and trapped. Generation of trifluoromethyltransition metal compounds was reported [7] as well as capture of $CF_3K$ by protons [8].

The reaction of TNB with potassium trifluoroacetate also represents a potentially general method for syntheses of 1-perfluoroalkyl-2,4,6-trinitrobenzenes. We have successfully carried out the same sequence using potassium pentafluoropropionate and TNB. The only other known route to compound **3** is quite laborious, involving nitration, chlorination, and reduction of 3-trifluoromethylphenol [9].

1 S. M. Shein, A. D. Khmelinskaya, and V. V. Brovko, *Chem. Commun.*, (1969) 1043; S. M. Shein and A. D. Khmelinskaya, *Zh. Org. Khim.*, 8 (1972) 1237.

2 P. J. Atkins and V. Gold, *Chem. Commun.*, (1983) 140; P. J. Atkins, V. Gold, and R. Marsh, *J. Chem. Soc., Perkin Trans. 2*, (1984) 1239.

3 P. J. Atkins, V. Gold, and P. J. Routledge, *J. Chem. Soc., Perkin Trans. 2*, (1985) 1563.

4 V. Gold, G. L. Johnston, and W. N. Wassef, *J. Chem. Soc., Perkin Trans. 2*, (1986) 471.

5 R. N. Haszeldine, *J. Chem. Soc.*, (1954) 1273, O. R. Pierce, E. T. McBee, and G. F. Judd, *J. Am. Chem. Soc.*, 76 (1954) 474; E. Bergman, *J. Org. Chem.*, 23 (1958) 476; E. T. McBee, R. D. Battershell, and H. P. Braendlin, *J. Org. Chem.*, 28 (1963) 1131.

6 J. Hine, ' Physical Organic Chemistry ', McGraw - Hill, New York, 1962, p 486.

7 D. M. Wiemers and D. J. Burton, *J. Am. Chem. Soc.*, 108 (1986) 832 and references cited therein; J. H. Clark, M. A. McClinton, and R. J. Blade, *Chem. Commun.*, (1988) 638.

8 K. Matsui, E. Tobita, M. Ando, and K. Kondo, *Chem. Letters*, (1981) 1719; G. E. Carr, R. D. Chambers, T. F. Holmes, and D. G. Parker, *J. Chem. Soc., Perkin Trans. 2*, (1988) 921.

9 D. N. Gray, J. J. Schmidt - Collerus, and C. D. Smith, U. S. Pat. 3 417 153 (1968).

10 H. S. Kesling and D. J. Burton, *Tetrahedron Lett.*, (1975) 3355.

11 G. A. Wheaton and D. J. Burton, *J. Org. Chem.*, 43 (1978) 2643.