(2) Supported by the National Science Foundation, Grant MPS 75-02794, and the Robert A. Welch Foundation, Grant D-028.
(3) For details see (a) B. K. Bandlish, A. G. Padilla, and H. J. Shine, *J. Org. Chem.*, **40**, 2590 (1975); (b) S. R. Mani and H. J. Shine, *ibid.*, **40**, 2756 (1975), and earlier references cited therein.
(4) J. J. Silber and H. J. Shine, *J. Org. Chem.*, **36**, 2923 (1971).
(5) For example, see Y. Sato, S. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **40**, 2539 (1967); **42**, 548 (1969); I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).
(6) Unpublished work of Dr. T. Okuyama.
(7) W. Rundel and K. Scheffler, *Tetrahedron Lett.*, 993 (1963).
(8) Aldrich Chemical Co., Inc.
(9) N. G. Donnelly, Z. Demidowicz, and R. L. Kelly, *J. Chem. Soc., Dalton Trans.*, 2335 (1975).
(10) W. L. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976). We thank Professor Musker for additional information.
(11) B. K. Bandlish and H. J. Shine, *J. Heterocycl. Chem.*, **12**, 287 (1975).
(12) V. D. Pokhdenko, V. A. Khizhnyi, V. G. Koshechko, and I. Shkrebtii, *J. Org. Chem. USSR (Engl. Transl.)*, **11**, 1883 (1975).
(13) P. Collings, K. Al-Mallah, and G. Stedman, *J. Chem. Soc., Perkin Trans. 2*, 1734 (1975); K. Y. Al-Mallah, P. Collings, and G. Stedman, *J. Chem. Soc., Dalton Trans.*, 2469 (1974).
(14) A. V. Blom, *J. Prakt. Chem.*, **94**, 77 (1916).

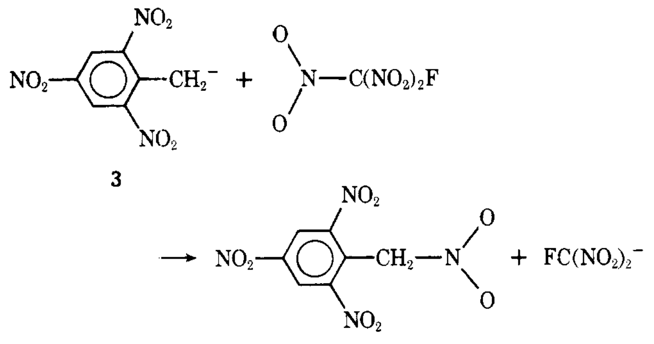
Fluorotrinitromethane as an Alkaline Nitrating Agent. Preparation of α,2,4,6-Tetranitrotoluene from 2,4,6-Trinitrotoluene

Michael E. Sitzmann,* Lloyd A. Kaplan,[1a] and Isaac Angres[1b]

Naval Surface Weapons Center,
White Oak, Silver Spring, Maryland 20910

Received August 4, 1976

Although alternative synthetic methods for α,2,4,6-tetranitrotoluene (**1**) have been reported,[2,3] they are relatively cumbersome. We have therefore investigated the possibility that alkaline nitration of 2,4,6-trinitrotoluene (**2**) might offer a more convenient route to **1**. In contrast with more usual alkaline nitrating agents (alkyl nitrates, tetranitromethane), which did not give the desired tetranitrotoluene, we found that **1** can be prepared in excellent yield by the reaction of **2** with fluorotrinitromethane in alkaline THF–methanol.


3

1

Alkaline nitration of **2** with fluorotrinitromethane apparently proceeds by nucleophilic attack of 2,4,6-trinitrobenzyl anion **3**[4] on a nitro nitrogen, resulting in displacement of fluorodinitromethide carbanion; the latter, however, was not isolated.[5] This is in marked contrast to the manner in which certain other nucleophiles ($OC_2H_5^-$, $OCH_2CF_3^-$, N_3^-, F^-) attack fluorotrinitromethane resulting in formal substitution on carbon, with displacement of one of the nitro groups.[6]

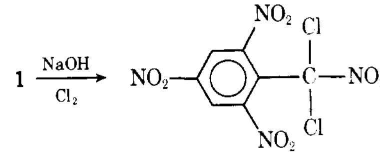
$$B^- + FC(NO_2)_3 \rightarrow FC(NO_2)_2B + NO_2^-$$

The fact that **3** attacks fluorotrinitromethane on nitrogen rather than carbon is probably due to the greater steric requirements of **3** over the other nucleophiles. The nitrogen atoms in fluorotrinitromethane are sterically more accessible than the carbon atom.

The reasons for failure with alkyl nitrates and tetranitromethane are not clear and cannot be rationalized on the basis of the relative stabilities of the leaving groups since fluorodinitromethide carbanion is very much less stable than trinitromethide carbanion.[6] Other factors to be considered are the relative rates of the competing reactions of tetranitromethane with **3** and the excess of hydroxide ion used to convert **2** to **3**. Another possibility is O-nitration as a competing reaction. However, by TLC analysis we detected no trinitrobenzyl alcohol, trinitrobenzyl nitrite, or trinitrobenzaldehyde, which would be likely products of O-nitration.

The pK_a of **1** in methanol–water (75:25) was found to be 5.93 (the midpoint in the titration with sodium hydroxide). The potassium salt of **1** can be formed from **1** and potassium hydroxide in tetrahydrofuran–methanol solution and precipitated by the addition of ether (Caution! The potassium salt is highly sensitive to impact and heat.) Addition of the deep red potassium salt to aqueous acid regenerates **1**.

Chlorination of **1** in the presence of sodium hydroxide yields α,α-dichloro-α,2,4,6-tetranitrotoluene (**4**).


4

Experimental Section[7]

General. (Caution!) The compounds described herein are explosives and should be handled with care. Fluorodinitro compounds show varying degrees of toxicity and may cause painful burns when brought into contact with the skin.

α,2,4,6-Tetranitrotoluene. A well-stirred solution of 11.5 g (0.05 mol) of 2,4,6-trinitrotoluene and 17 g (0.1 mol) of fluorotrinitromethane[8] in 150 ml of tetrahydrofuran and 75 ml of methanol was immersed in a dry ice–acetone bath. When the temperature of the solution reached 0 °C, an ice-cold solution of 9.6 g (0.15 mol) of potassium hydroxide (87%) in 50 ml of water and 75 ml of methanol was quickly added. The temperature immediately rose to about 5 °C and then began to fall. When the temperature of the deep red solution again reached 0 °C, the reaction was quenched by pouring the solution into 1500 ml of water containing 25 ml of concentrated hydrochloric acid. The total reaction time was approximately 1.5 min. The precipitated yellow solid was removed by filtration, washed well with water, and dried. The yellow solid (12.0 g, 89%) showed only one spot on a thin layer chromatogram (no starting TNT remained). Crystallization from benzene–hexane gave 10.0 g, mp 114–116 °C. An additional crystallization from methanol–water raised the melting point to 116.5–118 °C; NMR (CD_3COCD_3) δ 9.24 (s, 2, aromatic H), 6.30 (s, 2, CH_2); mass spectrum *m/e* 226 ($M^+ - NO_2$); mol wt calcd 272, found 270.

Anal. Calcd for $C_7H_4N_4O_8$: C, 30.89; H, 1.48; N, 20.58. Found: C, 30.76; H, 1.26; N, 20.45.

α,α-Dichloro-α,2,4,6-tetranitrotoluene. To a solution of 0.54 g (0.002 mol) of α,2,4,6-tetranitrotoluene in 15 ml of tetrahydrofuran and 5 ml of water was added 0.4 ml of 5 N sodium hydroxide. Chlorine gas was bubbled into the red solution until the solution was light yellow in color and then 50 ml of water containing 5 ml of concentrated hydrochloric acid was added. A yellow oil separated which solidified upon standing to give 0.65 g, mp 126–129 °C dec. Crystallization from methanol–water gave 0.5 g of pale yellow needles: mp 133–134 °C dec; NMR (CD_3COCD_3) δ 9.18 (s); mass spectrum *m/e* 294, 296, 298 ($M^+ - NO_2$, chlorine isotopes).

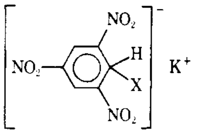
Anal. Calcd for $C_7H_2N_4O_8Cl_2$: C, 24.65; H, 0.59; N, 16.43; Cl, 20.79. Found: C, 24.45; H, 0.48; N, 16.25; Cl, 20.41.

Acknowledgment. This work was supported by NSWC Task IR-144. The authors are grateful to Dr. Mortimer J. Kamlet for his helpful suggestions and to Mr. Donald J. Glover for the pK_a determination. I.A. would like to thank the National Research Council and the Naval Surface Weapons Center for a postdoctoral associateship.

Registry No.—**1**, 35113-75-8; **2**, 118-96-7; **4**, 60789-52-8; fluorotrinitromethane, 1840-42-2.

References and Notes

(1) (a) Deceased. (b) NRC Postdoctoral Fellow.
(2) S. K. Yasuda, *J. Chromatog.*, **13,** 78 (1964). An immobile impurity (TLC analysis) present in 2,4,6-trinitrotoluene is assumed to be **1.**
(3) A. N. Parnes, S. M. Shein, M. I. Kalinkin, L. I. Sidelńikova, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10,** 2350 (1971). Chloranil oxidized I (X = CH_2NO_2) in 20 h at room temperature to give **1** in 12% yield. *Chemical Abstracts* [**76,** 59172e (1972)] indicates that **1** can be formed in 50% yield



I

from I (X = CH_2NO_2) and tropylium tetrafluoroborate. However, the original Russian article claims this reaction only for X = CH_2COCH_3. Analytical data and physical properties of **1** are not given.
(4) K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, **37,** 1966 (1972).
(5) L. V. Okhlobystina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10,** 2339 (1969), states that reaction of fluorotrinitromethane with reducing and nucleophilic reagents (KI, HI, $NaBH_4$, $FeCl_2$, SO_2, H_2O_2–$NaNO_2$) proceeds by a route involving radical intermediates. If radical intermediates are involved in the reaction of **2** with fluorotrinitromethane, one might expect formation of 2,2′,4,4′,6,6′-hexanitrobibenzyl from 2,4,6-trinitrobenzyl radical. However, no bibenzyl is produced in the reaction. In fact, no product other than **1** is detected by thin layer chromatography.
(6) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33,** 3073 (1968). However, the formation of fluorodinitromethane in the reaction of fluorotrinitromethane with hydroperoxide ion can be explained either by attack of hydroperoxide ion on carbon with displacement of a nitro group or by attack of hydroperoxide ion on oxygen or nitrogen of one of the nitro groups with displacement of fluorodinitromethide ion.
(7) NMR spectra were determined on a Varian HA-100 spectrometer and the chemical shifts are relative to tetramethylsilane. The melting points are uncorrected.
(8) Reference 6, p 3079.

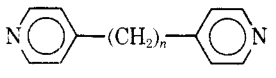
Synthesis of Bis(4-pyridyl)methane[1]

P. L. Gaus, Albert Haim,* and Francis Johnson

Departments of Chemistry and Pharmacology, State University of New York, Stony Brook, New York 11794

Received August 10, 1976

In connection with our studies of intramolecular electron transfer mediated by aromatic nitrogen heterocycles,[2,3] it became important to examine the role of the bridging ligands represented by 1.



1

Bis(4-pyridyl)methane (compound 1, where $n = 1$) is not available commercially, but its synthesis via the reaction of chloropyridine with 4-methylpyridine and potassium amide in liquid ammonia has been reported.[4] Unfortunately, repeated (18) attempts (under rigorous exclusion of water and oxygen) to synthesize this compound using the reported method yielded intractable oils, with properties unlike those described by Jampolsky et al.,[4] or those established in the present work for an authentic sample of the desired compound. Therefore, we designed an alternate synthesis of bis(4-pyridyl)methane, and report r results herein.

Bis(4-pyridyl) ketone was prepared using the method of Wibaut and Heeringa.[5] Conversion to the corresponding hydrocarbon was accomplished using the Huang-Minlon[6] modification of the Wolff–Kishner reduction, except that 1-butanol was used as the solvent.

The purified product is a white, crystalline, extremely hygroscopic solid,[7] and, therefore, must be handled by drybox techniques. Proof of the composition and structure of the compound is based on analytical and spectroscopic data reported in detail in the Experimental Section.

Experimental Section

4-Cyanopyridine (Aldrich) was recrystallized from ethanol. Diethyl ether was dried using calcium hydride, and was stored under dry nitrogen. 4-Bromopyridine hydrochloride (Pfaltz and Bauer) and *n*-butyllithium (2.9 M in hexane, Ventron) were used as received.

Visible and ultraviolet spectra were obtained using a Cary 118 spectrophotometer. Infrared spectra were obtained using a 567 Perkin-Elmer spectrophotometer using matched cells (Beckman-RIIC, Ltd). ^1H NMR spectra were obtained on a Varian CFT-20 instrument.[8] The mass spectrum (acetone solution) was obtained using a Hewlett-Packard 5980A mass spectrometer, preceded by a Hewlett-Packard 5710A gas chromatograph. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N.Y.

Bis(4-pyridyl) ketone was synthesized (nitrogen atmosphere) using the literature[5] method, with some modifications. 4-Bromopyridine hydrochloride was neutralized in aqueous solution at 0 °C, and the free base was extracted into ether. The ether solution was dried over magnesium sulfate for 12 h at 5 °C, and then the concentration of 4-bromopyridine was determined gravimetrically.[9] The reaction was allowed to proceed as described[5] and the reported quenching procedure was utilized. The product was isolated as described,[5] except that following the treatment with active carbon, neutralization of the final aqueous phase gave a precipitate of (mostly) potassium sulfate, which was removed by filtration. The faintly yellow filtrate was extracted with ether. Evaporation of the ether gave a white solid which was recrystallized three or four times from ethanol, mp 136–137 °C. The 45% yield of recrystallized product is somewhat higher than that reported.[5]

Bis(4-pyridyl)methane. Bis(4-pyridyl) ketone (4.0 g, 0.022 mol) was added to a solution of 4.0 g of potassium hydroxide in 40 ml of 1-butanol at 60 °C. After stirring for 15 min, 3.7 ml of 85% hydrazine hydrate was added. The solution was refluxed for 1.3 h. Then some solvent was removed by distillation until the temperature of the vapors immediately above the reactant solution had reached 110 °C. Heating was continued under reflux conditions for 8 h. The resulting clear yellow solution was allowed to cool at 60 °C, and then treated with 60 ml of water. The aqueous phase was acidified to pH ~2 by dropwise addition of 6 M hydrochloric acid. The aqueous phase was extracted four times with 50-ml portions of ether, basified to pH 10, and then extracted repeatedly with benzene. The benzene extracts were evaporated at 40 °C to ca. 20 ml in a flash evaporator. The resulting solution was placed on an alumina column (5 × 0.5 in., neutral, activity 1.0, 80–200 mesh), and the column was eluted with 300 ml of benzene. The benzene was removed by evaporation at 40 °C in a flash evaporator to yield a clear, colorless oil. The last traces of benzene were removed at room temperature on a vacuum line, resulting in the crystallization of small, white needles. Since the substance is quite volatile, as a further purification, it was subjected to a short path vacuum distillation at 40 °C onto a cold finger at 15 °C, yielding a white, crystalline solid. The apparatus was filled with dry nitrogen, and then transferred to a dry bag over phosphorus pentoxide. All subsequent manipulations were performed in a glove bag. Yield 3.3 g, 89%; mp 36–37 °C;[10] IR (C_6H_6) 2990 m, 2969 w, 2930 w, 1600 vs, 1565 m, 1420 vs, 1208 w, 1060 w, 982 m, 910 vw, 828 w, 785 m, 770 m, 610 s, 540 m, 475 cm^{-1} w; NMR (C_6D_6/Me_4Si) δ 3.19 (s, 2 H, $-CH_2-$), 6.46 (m, 4 H, aromatic H), 8.40 (m, 4 H, aromatic H); MS *m/e* 170 (P, base), 171 (11.6%) 169 (65%), 168 (11%), 143 (6%), 142 (11%), 141 (4%), 117 (5%), 115 (8%), 92 (3%), 89 (5%), 84 (3%), 65 (5%), 63 (4%), 51 (7%); UV λ_{max} (water) 256 nm.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.61; H, 5.93; N, 16.46. Found: C, 77.69; H, 6.10; N, 16.14.

Registry No.—Bis(4-pyridyl) ketone, 6918-15-6; 4-bromopyridine HCl, 19524-06-2; 4-bromopyridine, 1120-87-2; bis(4-pyridyl)methane, 60776-05-8.

References and Notes

(1) This work was supported by Grants GP-37057X and CHE 7610449 from the National Science Foundation.

(2) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96,** 7845 (1974).
(3) J. J. Jwo and A. Haim, *J. Am. Chem. Soc.*, **98,** 1172 (1976).
(4) L. M. Jampolsky, M. Baum, S. Kaiser, L. H. Sternbach, and M. W. Goldberg, *J. Am. Chem. Soc.*, **74,** 5222 (1952).
(5) J. P. Wibaut and L. G. Heeringa, *Recl. Trav. Chim. Pays-Bas*, **74,** 1003 (1955).