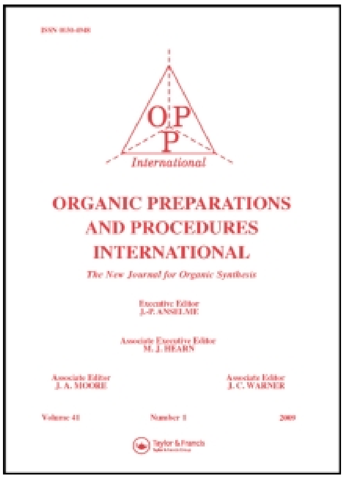


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED PREPARATION OF TRINITROPHLOROGLUCINOL

A. A. Defusco[a]; A. T. Nielsen[a]; R. L. Atkins[a]
[a] Code 3858, Chemistry Division, Research Department, Naval Weapons Center, China Lake, CA

To cite this Article Defusco, A. A. , Nielsen, A. T. and Atkins, R. L.(1982) 'AN IMPROVED PREPARATION OF TRINITROPHLOROGLUCINOL', Organic Preparations and Procedures International, 14: 6, 393 — 395
To link to this Article: DOI: 10.1080/00304948209354939
URL: http://dx.doi.org/10.1080/00304948209354939

ORGANIC PREPARATIONS AND PROCEDURES INT. 14(6), 393-424 (1982)

OPPI BRIEFS

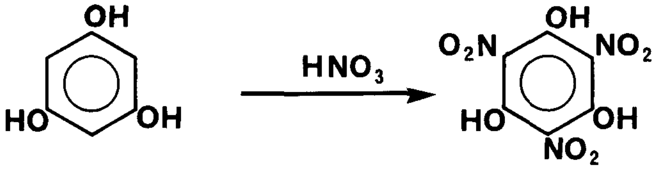
AN IMPROVED PREPARATION OF TRINITROPHLOROGLUCINOL

Submitted by (4/13/82) A. A. DeFusco,*† A. T. Nielsen and R. L. Atkins

Code 3858, Chemistry Division, Research Department,
Naval Weapons Center, China Lake, CA 93555

Trinitrophloroglucinol (II) and some of its derivatives have attracted the attention of both synthetic and theoretical chemists.[1,2] However, existing methods[3-6] for the preparation of II have limitations because multiple-step syntheses are required, overall yields are generally very poor, and immediate precursors to II in multiple-step syntheses often are very sensitive, highly-explosive compounds. Typical procedures include alkaline hydrolysis of precursors such as pentanitroaniline[3a] or 1,3,5-trichloro-2,4,6-trinitrobenzene.[3b] A procedure involving nitrolysis of the tripotassium salt of trinitrosophloroglucinol is quite hazardous.[4a]

The direct nitration of phloroglucinol (I) provides a simple, inexpensive and efficient one-pot synthetic route to II. There is one previous, but undetailed, report by Huntress and Mulliken[6] which describes the nitration of I. Unfortunately, using that procedure (which employs only 0.1 g of I as starting material) we could not scale to even 1 g of I. In fact, we were unable to isolate any product whatsoever by that route using 1 g of I. In our present work, we have found that by changing the order of addition (i.e., adding a nitric acid-sulfuric acid mixture to phloroglucinol in sulfuric acid solution) and using a



I II

stoichiometric amount of nitric acid excellent results could be achieved. An excess of nitric acid is to be avoided in the preparation of II.

Our improved procedure has been successfully scaled to 1 g, 10 g, or 25 g of reactant I leading to II in yields up to 70%. Note that the nitration of I must be performed in the minimum amount of time possible. The product II must also be quickly removed from, and washed free of, nitric acid to insure minimum loss of the product through oxidation. We found our procedure to be reproducible and the product to be very pure if the experimental procedure is followed carefully.

EXPERIMENTAL

Capillary melting points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Caution! Trinitrophloroglucinol is an explosive compound and should be handled with care. Its sensitivity to impact (hammer blow) is between that of RDX (hexogen, 1,3,5-trinitro-1,3,5-hexahydrotriazine) and TNT (2,4,6-trinitrotoluene). It is thermally stable and may be stored at ambient temperature, preferably in a desicator in the dark.

Preparation of Trinitrophloroglucinol (II).- A solution of 38 ml of 71% HNO_3 (0.608 mole) in 62 ml of 97% H_2SO_4 was added to a mechanically-stirred solution of 25.22 g (0.2 mole) of phloroglucinol (Matheson, Coleman and Bell, anhydrous, mp. 217-219°) in 500 ml of 97% H_2SO_4 over a 1-hour period with ice-bath cooling. During addition the temperature of the reaction mixture is maintained at 5-8° by adjusting the addition rate to maintain a slightly exothermic reaction. After addition is complete, stirring is continued for 9 minutes at which time a precipitate is present. The mixture is then poured over 1800 g of ice. The resulting precipitate is immediately filtered through a coarse sintered-glass funnel by gentle suction and then washed with two 125-ml portions of aqueous 3N HCl.

After drying in vacuo at 25°, 36.56 g (70%) of II is obtained (mp. 160-163°). The product is quite pure and suitable for many synthetic purposes; its IR spectrum is identical to high purity II. It may be recrystallized from hot dichloroethane (800 ml) which affords 25 g (70% recovery) of high purity II as long spear-like needles (mp. 164-165°, lit. 167°,[3a] 165-166°,[2b,6] 163-165°[3d]) and three subsequent crops, mp. 158-160° (96% total recovery). An IR (KBr) spectrum of pure II shows peaks at 3000 (br s), 1625, 1575, 1515, 1345, 1310, 1200, 1170, 915, 810, 788, 758 and 700 cm^{-1}.

Anal. Calcd. for $C_6H_3N_3O_9$: C, 27.60; H, 1.16; N, 16.09.

Found: C, 27.42; H, 1.38; N, 15.86.

A parallel experiment employing 10 g of phloroglucinol, afforded 11.1 g (54%) of II (mp. 160-163°). Recrystallization from 800 ml of boiling aqueous 3N HCl gave 10.07 g (90% recovery) of high purity II (mp. 163-165°).

REFERENCES

† National Research Council Postdoctoral Research Associate, 1981-1982.

1. a. F. W. Lichtenthaler and H. Leinhert, Chem. Ber., 99, 903 (1966).
   b. G. Quadbeck and E. Rohm, ibid., 89, 1645 (1956).

2. a. J. Ladik and J. Schawartz, Acta Chim. Sci. Hung., 5, 299 (1955); Chem. Abs., 49, 11583g (1955).
   b. S. V. Dubiel and S. Zuffanti, J. Org. Chem., 19, 1359 (1954).
   c. T. Urbanski, "Chemistry and Technology of Explosives," Vol. II, p. 542, Pergamon Press, Oxford, 1965.
   d. E. Hertel and K. Schneider, Z. Physik. Chem., B, 12, 139 (1931); Chem. Abs., 25, 2893 (1931).

3. a. B. Flürscheim and E. L. Holmes, J. Chem. Soc., 3044 (1928).
   b. F. Sorm and C. Z. Drapalova, Chem. Obzor., 12, 153 (1937); Chem. Zentralblatt, II, 4033 (1937); Chem. Abs., 31, 8520 (1937).
   c. G. C. Shaw and D. L. Seaton, J. Org. Chem., 26, 5227 (1961).
   d. A. T. Nielsen, R. L. Atkins and W. P. Norris, J. Org. Chem., 44, 1181 (1979).

4. a. K. Freudenberg, H. Fikentscher and W. Wenner, Ann., 442, 309 (1925).
   b. D. A. Salter and R. J. J. Simkins, Ger. Offen., 1,959,930, 25 June 1970; Chem. Abs., 73, P76860h (1970).
   c. G. Travagli, Atti Accad. Sci. Ferrara, 27, 3 pp. (1949-1950); Chem. Abs., 45, 7544 (1951).

5. G. P. Sharnin, V. V. Nurgatin, F. G. Khairutdinov and I. F. Falyakhov, USSR, 515,740, 30 May 1976; Chem. Abs., 85 P108416j (1976).

6. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," p. 248, John Wiley and Sons, Inc., New York, 1941.