

Safer and Convenient Synthesis of 3,4-Dicyanofuroxan

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S Supporting Information

ABSTRACT: A safer, convenient, cost-effective, and scalable synthesis for 3,4-dicyanofuroxan $(C_4N_4O_2)$ is described. Dropwise treatment of a well-stirred suspension of cyanoacetic acid in dichloromethane with concentrated mixed acid (HNO₃/H₂SO₄) affords dicyanofuroxan in 72% yield and in 84% purity after liquid chromatography analysis. Single crystal X-ray diffraction studies further confirm the product and yield its molecular conformation and crystal packing. During the dropwise addition of mixed acid, self-heating occurs, and this event is necessary for the reaction to adequately proceed. However, such self-heating is limited to the refluxing temperature of dichloromethane. This new method supersedes the previous methods used to synthesize dicyanofuroxan, which were low-yielding and of significantly lower purity, irreproducible, relied on expensive reagents, and suffered from dangerous exothermic profiles.

KEYWORDS: synthesis, energetic materials, explosives, propellants, process chemistry

INTRODUCTION

3,4-Dicyanofuroxan (DCFO) is a common intermediate in the synthesis of a host of energetic materials. It has been used to make energetic heterocyclic compounds in which the cyano moieties are derivatized to the 1H-tetrazole,¹ 1-hydroxytetrazole,² and 1,2,4-oxadiazole³ moieties. DCFO is a known hypergolic material,⁴ and while first prepared by Weiland in 1925,⁵ the most reliable synthesis was reported by Parker et al. in 1962.⁶ Despite other reports in the literature by Grundmann, Nickel, and Bansal in 1975⁷ and Mel'nikova et al. in 2001⁸ concerning the synthesis of DCFO, the aforementioned route by Parker has remained the current method of choice. The Grundmann, Nickel, and Bansal route to DCFO involves a lengthy four-step synthetic process from glyoxal, with yields being \sim 30%, while the route reported by Mel'nikova et al. is also a low-yielding four-step sequence, which was irreproducible in our hands. Unfortunately, the reliable synthesis method of Parker et al. is expensive, suffers from low yields, and contains a significant exothermic profile. Because DCFO is a popular intermediate in the synthesis of energetic materials, a reproducible, cost-effective, safer, and higher-yielding method pertaining to the synthesis of this material is of high interest. In this paper, we report such a procedure and confirm the product by single crystal X-ray diffraction.

RESULTS AND DISCUSSION

The most widely accepted synthesis of dicyanofuroxan, reported by Parker et al.,⁶ is summarized in Scheme 1. The



NCCOOH	100% HNO ₃ (1.1 eq) 20% Oleum (cat.),	
	TFA, 40 ºC, 2-3 h	^N ´ _O ´ ^N [→] O ⁻ 1 (25-40% yield, 59% purity)

synthesis features a reaction of cyanoacetic acid with 100% HNO₃ in the presence of catalytic oleum performed in a solvent medium of trifluoracetic acid. This reaction occurs via the dimerization of the dinitroacetonitrile intermediate. According to Parker et al., oleum is critical to the success of this reaction, as the absence of this sulfuric acid-containing catalyst does not yield any product. The reaction is heated to 40 °C, and the nitric acid is added dropwise to the mixture. When the reaction is completed, it is poured onto crushed ice and is extracted with dichloromethane. These extracts are then washed with water until a pH of 6-7 is reached. Evaporation of the solvent affords DCFO in a low purity of just 59% (See Supporting Information). Parker et al. report that a clean product can be obtained upon recrystallization from carbon tetrachloride. Use of this solvent today, however, is discouraged for environmental and human health reasons.

When performing the procedure described by Parker et al., significant care must be taken during the dropwise addition of HNO_3 , as this reaction is prone to violent exotherms under these conditions. On larger scales, we have observed that even multihour dropwise addition of HNO_3 still results in a steep temperature increase, in which the solution refluxes violently (75–80 °C), producing a significant volume of NOx gases in the process. For these reasons, the Parker et al. synthesis of DCFO is typically done only on the small-scale. Our laboratories have limited the synthesis of DCFO by the Parker method to 5 g, and large-scale reactions using this process are certainly not advised.

Thirteen years after Parker et al. reported the synthesis of DCFO, Grundmann, Nickel, and Bansal disclosed the synthesis of this material from glyoxal, which involved the treatment of dicyanoglyoxime (4) with nitrous oxide to induce ring closure to form DCFO (1) (Scheme 2).⁷ Although this synthetic sequence has been found to be reproducible,⁹ it suffers from a lengthy synthesis compared to the Parker et al.

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Scheme 2. Grundmann, Nickel, and Bansal Synthesis of DCFO



synthesis as well as relatively low yields in the final two reactions of the synthetic sequence. As a result, the Grundmann, Nickel, and Bansal synthesis results in just a 30% yield of product.

In 2001, Mel'nikova et al. reported a synthesis of DCFO via the diazotization of nitrosoaminofurazan (7) through the supposed elimination of a cationic species produced during the course of the reaction (Scheme 3).⁸ Unfortunately, attempts to synthesize DCFO in our laboratories using this method failed to yield any product. In addition, this pathway has limited scalability due to the low overall yield (ca. 16%), the lengthy synthesis to obtain this intermediate, and the potential issues associated with large-scale diazotizations of energetic furazan intermediates.

Because of the synthetic utility of DCFO to the energetic materials community, we sought to develop a safer, scalable, and higher-yielding process for making this material. We reasoned that a variation of the Parker et al. synthesis would be ideal, as DCFO could be obtained in a single step from cyanoacetic acid. We reasoned that employing dichloromethane in place of trifluoroacetic acid as the solvent in this reaction was advantageous for various reasons. The refluxing temperature of dichloromethane (39.6 °C) is much lower than trifluoroacetic acid (72.4 °C), and it was believed that the lower refluxing temperature would improve the safety margin, minimize byproducts, and thus improve scalability, yields, and purity. Dichloromethane was much cheaper than trifluoroacetic acid and was already shown to be an optimal extraction solvent of DCFO when the reaction reached the workup stage (Scheme 4). Knowing that the Parker et al. synthesis of DCFO required the use of oleum, we decided to employ a premixed acid (1:2 mixture of 100% HNO₃/98% H₂SO₄) to the suspension of cyanoacetic acid in dichloromethane, thus eliminating the need for oleum in the reaction. We report only the optimized mixed acid ratio required, as altering this ratio significantly leads to an extensive loss of product.



Scheme 4. Optimized Synthesis of DCFO



Our process in synthesizing DCFO is given in Scheme 4. Upon suspending cyanoacetic acid in dichloromethane with vigorous stirring, we opted to not chill the reaction but instead immersed the reaction vessel in a water bath at 27 °C. Mixed acid was then added over a 3 h period, during which time the reaction slowly self-heated and a gentle reflux with minimal NOx gases was observed. During the addition process, the water bath reached a maximum of 32 °C. When addition of the mixed acid was completed, the reaction mixture was stirred for an additional hour, during which time the temperature of the water bath cooled to 25 °C. This gentle self-heating event appears to be critical for the reaction to proceed and to obtain good yields. The reaction mixture was then poured onto crushed ice, warmed to ambient temperature, and extracted with dichloromethane. The combined organic extracts were then washed with water until a pH of 6-7 was achieved. Removal of the solvent afforded DCFO as a white/pale yellow solid.

With DCFO in hand, we then assessed its purity by liquid chromatography analysis. According to our analysis, DCFO synthesized by the Parker et al. method was obtained in a purity of just 59%, whereas DCFO synthesized by the method outlined in Scheme 4 was obtained in a much improved purity of 84% (see Supporting Information). The safer process in Scheme 4 has been scaled-up numerous times in our laboratories to afford DCFO in about 60 g quantities with a high degree of reproducibility. Although the identities of the impurities present in DCFO are not clear at this time, they have been determined not to negatively influence further reactions in our laboratories. Although attempts at recrystallizing DCFO in 84% purity from solvents other than carbon tetrachloride failed to yield a more pure product, we have successfully converted the crude DCFO to its bis-amidoxime derivative by employing 50% aqueous hydroxylamine, and this bis-amidoxime is isolated in very high purity (see Supporting Information) and a reasonable yield of 68%.

Further confirming the validity of our synthesis, we determined a crystal structure for DCFO by single crystal X-ray diffractometry. The details of the data acquisition and structure solution and refinement are provided in the Supporting Information.^{11–14} DCFO crystallizes in the orthorhombic $Pna2_1$ space group with eighth molecules in its unit cell. Its asymmetric unit comprises two independent







Figure 1. Molecular conformation and atom-numbering schemes of compounds 1, comprising two distinct molecules (1 and 1A) in its asymmetric unit. All of the atoms are shown as 50% probability displacement ellipsoids.

molecules (1 and 1A, see Figure 1). Each molecule adopts a near planar conformation [C1/C2/C3/C4/N1/N1/N3/N4/O1/O2; r.m.s. deviation = 0.019 Å (1) and 0.025 Å (1A)], with the largest deviation resulting from the C1/C1A atoms [distances of C1/C1A atoms to their respective plane = <math>-0.030 (2) and -0.044 (2) Å]. Their bond lengths and angles are in the usual ranges of typical furoxan derivatives,^{3,15-21} and they are in excellent agreement with those reported by Pasinszki et al.²² The molecular planes subtend a dihedral angle of 65.43 (4)° and exhibit a plane centroid-to-plane centroid distance of 5.358 (1) Å. A superimposition of the two structures yields a r.m.s. deviation of 0.030 Å.

Intermolecular interactions play a key role in the crystal packing of molecules. Figure 2A shows the interactions for 1, whose contact distances range between 2.96 (4) and 3.195 (3) Å. The shortest contact length results from the N1A ring atom interacting with the N3A atom of adjacent molecules [N1A··· N3Aⁱ = 2.961 (4) Å; symmetry code (i) 2 - x, 1 - y, -1/2 + yz], whereas the longest contact length involves the C3 and N2A atoms of the asymmetric unit molecules 1 and 1A, respectively, $[C3 \cdot \cdot \cdot N4A = 3.185 (3) \text{ Å}]$ (see Figure 1). Figure 2B reveals the molecular stacking for 1 along the b-axis direction. On the basis of the molecular mass and lattice constants of a = 10.18098 (5) Å, b = 10.8181 (4) Å, c =10.1946 (4) Å, and $\alpha = \beta = \gamma = 90^{\circ}$, we obtain a density of 1.610 g/cm³ at -23 °C. A similar analysis yields a value of 1.594 g/cm³ at 22 $^{\circ}$ C, in excellent agreement with the reported value of 1.584 g/cm³ obtained at the same temperature.²²

It should be worth noting that we felt the need to publish our optimized procedure described in Scheme 4 because of the inability to reproduce experimental procedures in the Chinese patent literature.²³ For example, this patent claims that altering the mixed acid ratio still results in DCFO being obtained in significant yields and purities. We found this not to be the case, as the mixed acid ratio provided in Scheme 4 is critical for good yields to be obtained. Furthermore, the Chinese patent claims that replacing 100% HNO₃ with 90% or even 70% HNO₃ in the mixed acid system still gives high yields and purities of DCFO. However, we observed that replacing 100% HNO₃ with 70–90% HNO₃ yields significantly lower quantities of DCFO. Perhaps most importantly from the safety standpoint, the Chinese patent claims that addition of mixed acid to the stirring suspension of cyanoacetic acid in dichloromethane must be done cold (i.e., 0-5 °C) to obtain a reasonable amount of product. When we attempted to reproduce this portion of the procedure, it was found that no reaction occurred at cold temperatures. Upon warming the reaction mixture, however, the reaction spontaneously selfheated, which produced a spirited refluxing event, along with a significant formation of NOx gases. Clearly, following the experimental procedural guidelines of the aforementioned patent is not recommended for anyone who is cognizant of their own safety.

CONCLUSIONS

In summary, we have developed a scalable and reproducible method for the synthesis of DCFO in 72% yield and 84% purity and have found that it can be used in further reactions without further purification. Our process relies on the dropwise addition of mixed acid to a suspension of cyanoacetic acid in dichloromethane. We have found that a controlled self-heating event, in which the reaction mixture refluxes gently as opposed to violently, is critical for obtaining high yields in this reaction. Our process removes the need to use expensive trifluoroacetic acid, oleum, and does not employ toxic carbon tetrachloride as a recrystallization solvent. This new route confirmed in part by X-ray crystallography represents a more scalable, reliable, and reproducible synthesis as compared to those reported previously.

EXPERIMENTAL SECTION

Chemicals and solvents were used as received from Sigma-Aldrich. 13 C NMR spectra were recorded using a Bruker 101 MHz instrument. The chemical shifts quoted in parts per million in the text refer to typical standard tetramethylsilane in CDCl₃ as the solvent. Infrared spectra were measured with a Bruker Alpha-P FTIR instrument. Melting and decomposition temperatures were measured at a heating rate of 5 °C/min using a TA Instruments Q10 DSC instrument. Liquid chromatography analysis of DCFO samples were obtained using an Agilent 1200 series instrument. Single crystal X-ray diffraction studies were performed with a SuperNova Dualflex



Figure 2. (A) Atom-atom intermolecular contacts and (B) crystal packing for 1 viewed along the *b*-axis direction. Dashed lines represent intermolecular interactions.

diffractometer containing an EosS2 charge-couple device detector and a molybdenum Mo- $K\alpha$ ($\lambda = 0.71073$ Å) radiation source. The crystal was kept at -23.0 (1) °C during data collection. CCDC number 1912929 (for 1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/ steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

3,4-Dicyanofuroxan (1). In a 2 L three-neck roundbottom flask equipped with a stirbar, cyanoacetic acid (100 g, 1.18 mol, 1.00 equiv) was suspended in 400 mL of CH_2Cl_2 with vigorous stirring. The flask was then fitted with a reflux condenser and a 500 mL liquid addition funnel, and was

immersed in a 27 °C water bath, which was not heated externally throughout the course of the reaction. In a separate 600 mL beaker, 98% concentrated H₂SO₄ (368 g, 200 mL, 3.75 mol, 3.18 equiv) was stirred and cooled to 0 °C. Then 100% HNO₃ (151 g, 100 mL, 2.40 mol, 2.03 equiv) was added at such a rate that the temperature of the mixture did not rise above 25 °C. The mixed acid solution was stirred for 10 min and was then poured into the addition funnel. The mixed acid solution was added to the reaction mixture over a 3 h period. During this addition period, the cyanoacetic acid was drawn into solution, and self-heating occurred that resulted in the reaction mixture achieving a gentle reflux, while the temperature of the water bath reached a peak temperature of 32 °C. Because the reaction mixture became biphasic as the mixed acid was added, vigorous stirring was continued throughout the course of the reaction to ensure optimal yields were obtained. After addition of the mixed acid was complete, the reaction mixture was stirred for 1 h.

The reaction mixture was then poured onto 1 kg of crushed ice with vigorous stirring, and this mixture was stirred until the ice melted and the solution had achieved ambient temperature. The solution was then transferred to a 3 L separatory funnel, and the CH₂Cl₂ layer was drained. The solution in the separatory funnel was then extracted three more times with 500 mL portions of CH_2Cl_2 . At this stage, the aqueous layer was discarded, and the combined organic extracts were returned to the separatory funnel. The combined organic extracts were washed five times with 500 mL portions of distilled water until a pH of 6-7 was reached, during which time the CH₂Cl₂ phase had become colorless. The organic phase was dried over MgSO4, filtered, and concentrated in vacuo (water bath temperature = 30 °C) to afford a yellow liquid, which crystallized when residual CH₂Cl₂ was removed by means of a vacuum pump. The resulting light yellow/white crystalline solid was identified as DCFO (57.6 g, 72%, 84% purity); $T_{\text{melt}} = 30.4 - 37.7 \text{ °C}$; T_{dec} (onset) = 228.1 °C; $T_{\text{peak}} = 265.1 \text{ °C}$; IR (neat) cm⁻¹ 2255.13 (w), 1628.36 (s), 1460.73 (s), 1306.96 (m), 1099.99 (m), 1038.43 (s); ¹³C NMR (101 MHz, CDCl₃) δ 131.73, 104.97, 102.76, 95.50.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.9b00186.

¹³C and ¹H spectra for compound **2** (PDF)

¹³C spectrum, DSC trace, IR spectrum, and X-ray crystallographic data for compound **1** (PDF)

Liquid chromatography analysis of compound 1 (CIF)

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Author Contributions

E.C.J., E.J.B., and J.J.S. performed the synthesis reactions. E.C.J. and E.J.B. conducted the analytical analysis. R.C.S. performed the X-ray experiments and analysis. J.J.S. wrote the bulk of the paper.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DCFO = dicyanofuroxan; HNO_3 = nitric acid; H_2SO_4 = sulfuric acid; TFA = trifluoroacetic acid; CH_2Cl_2 = dichloromethane

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(9) In a communication with T. M. Klapötke, he has indicated that the Grundmann synthesis detailed in Scheme 2 is reproducible, and has been used in his laboratories to synthesize DCFO.

(10) For crude DCFO samples of 59% or 84% purity, we have been able to produce pure samples of the *bis*-amidoxime furoxan intermediate following the procedure detailed in ref 2. Purification of DCFO is not necessary, as the impurities present do not carry over in the preparation of its *bis*-amidoxime intermediate.

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