Formation of 2,4,6-Trinitrobenzonitrile and 4-Chloro-5,7-dinitro-2-(2,4,6-trinitrophenyl)quinazoline 1-Oxide by the Action of Nitrosyl Chloride on 2,4,6-Trinitrotoluene

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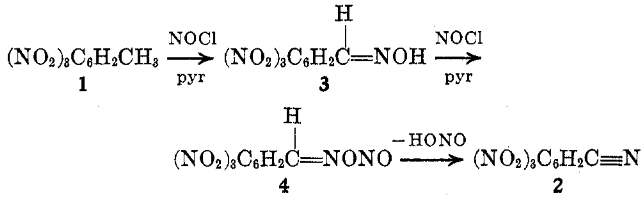
During an attempt to prepare 2,4,6-trinitrobenzonitrile by the action of nitrosyl chloride on 2,4,6-trinitrotoluene, the unexpected formation of the by-product 4-chloro-5,7-dinitro-2-(2,4,6-trinitrophenyl)quinazoline 1-oxide occurred. However, reaction conditions were found that gave the trinitrobenzonitrile free of the quinazoline. Mechanisms that account for the formation of the nitrile and the quinazoline are given.

The reaction of nitrosyl chloride with hydrocarbons is well established in the literature:[1] at low temperatures the products are nitroso compounds which often rearrange to oximes; at elevated temperatures, 100° and above, chlorinated products usually result. Heretofore, there has been no report in the literature of a nitrile isolated as a major product from nitrosyl chloride and a hydrocarbon.[2]

The action of nitrosyl chloride on 2,4,6-trinitrotoluene (**1**) in pyridine solution was investigated as a convenient method for the preparation of 2,4,6-trinitrobenzonitrile[3] (**2**). The nitrile **2** is obtained as the major product of the reaction *via* the intermediate 2,4,6-trinitrobenzaldoxime (**3**).



$$\underset{\mathbf{1}}{(NO_2)_3C_6H_2CH_3} \xrightarrow[\text{pyr}]{\text{NOCl}} \underset{\mathbf{3}}{(NO_2)_3C_6H_2\overset{H}{\overset{|}{C}}{=}NOH} \xrightarrow[\text{pyr}]{\text{NOCl}}$$

$$\underset{\mathbf{4}}{(NO_2)_3C_6H_2\overset{H}{\overset{|}{C}}{=}NONO} \xrightarrow{-\text{HONO}} \underset{\mathbf{2}}{(NO_2)_3C_6H_2C{\equiv}N}$$

A pyridine solution of **1** and nitrosyl chloride would be expected to first give α-nitroso-2,4,6-trinitrotoluene. Loss of a proton forms 2,4,6-trinitrobenzaldoxime anion, which upon reaction with nitrosyl chloride yields the oxime nitrite **4**. Elimination of the elements of nitrous acid from the oxime nitrite produces the nitrile **2**.

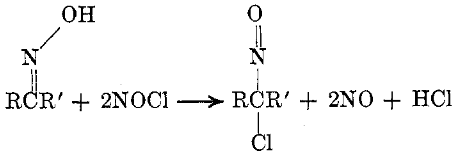
As evidence for this reaction sequence, authentic **3** gave the same products (see Experimental Section) as obtained from **1**. The conversion of **3** to **2** *via* the oxime nitrite seems logical in view of the fact that **3** in pyridine solution without nitrosyl chloride does not produce **2**. The considerable gas evolution that occurs during the course of the reaction results from the reaction of nitrous acid (eliminated from **4**) with nitrosyl chloride. The production of nitrous acid (pyridine salt) by addition of pyridine containing a small amount of water to a nitrosyl chloride–pyridine solution is accompanied by gas evolution. The unstable nitrous anhydride formed from nitrous acid and nitrosyl chloride decomposes to a mixture of nitric oxide and nitrogen dioxide.

$$\text{Pyr HONO} + \text{NOCl} \longrightarrow N_2O_3 + \text{Pyr HCl}$$

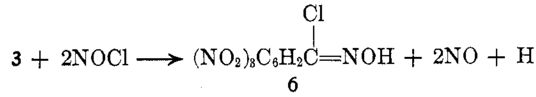
$$N_2O_3 \longrightarrow NO + NO_2$$

When the reaction was run by adding **1** to a solution of nitrosyl chloride in pyridine at 0° and slowly allowing the mixture to warm to 20-25°, 4-chloro-5,7-dinitro-2-(2,4,6-trinitrophenyl)quinazoline 1-oxide (**5**) was formed in addition to **2**. This made the isolation of pure **2** too difficult for a practical synthesis. At −10 to −5° the reaction gave no **5**, but gave 2,4,6-trinitrobenzohydroximoyl chloride (**6**) as a by-product from which a 60% yield of pure **2** could readily be separated.

The formation of **6** can occur by reaction of **3** with nitrosyl chloride. Nitrosyl chloride reacts with ketoximes[4] and onimino esters[5] to give chloro nitroso compounds. Aliphatic aldoximes with nitrosyl chloride give chloro nitroso compounds which can be converted by heating to the corresponding hydroximoyl chlorides, whereas aromatic aldoximes yield the hydroximoyl chlorides directly.[4] Thus **6** can be formed from the oxime **3** as shown. The reaction of **3** with nitrosyl chloride in pyridine did give **6** together with **2**.



$$R\overset{\overset{\diagup OH}{N}}{\overset{\|}{C}}R' + 2NOCl \longrightarrow R\overset{\overset{O}{\|}}{\overset{N}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}}R' + 2NO + HCl$$

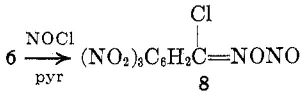


$$\mathbf{3} + 2NOCl \longrightarrow \underset{\mathbf{6}}{(NO_2)_3C_6H_2\overset{Cl}{\overset{|}{C}}{=}NOH} + 2NO + HCl$$

There is also the possibility that **6** produced from **1** results from nitrosation of 2,4,6-trinitrobenzyl chloride (**7**). Authentic **7** with nitrosyl chloride in pyridine did give **6**. The formation of **7** would have to result from chlorination rather than nitrosation of **1** by nitrosyl chloride.

$$\underset{\mathbf{7}}{(NO_2)_3C_6H_2CH_2Cl} \xrightarrow[\text{pyr}]{\text{NOCl}} \mathbf{6}$$

It is likely that **6** exists in the pyridine reaction mixture as the nitrite derivative **8**. The fact that **6** rather than **8** is isolated as a product from the reaction at −5 to −10° is probably due to hydrolysis of **8** during the



$$\mathbf{6} \xrightarrow[\text{pyr}]{\text{NOCl}} \underset{\mathbf{8}}{(NO_2)_3C_6H_2\overset{Cl}{\overset{|}{C}}{=}NONO}$$

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(1) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 354 (1951).

(2) A small amount of benzoyl cyanide from the reaction of nitrosyl chloride with acetophenone in ethanol-pyridine was the result of thermal dehydration of phenylglyoxal aldoxime during the work-up distillation: D. T. Manning and H. A. Standbury, Jr., *J. Amer. Chem. Soc.*, **81**, 4885 (1959).

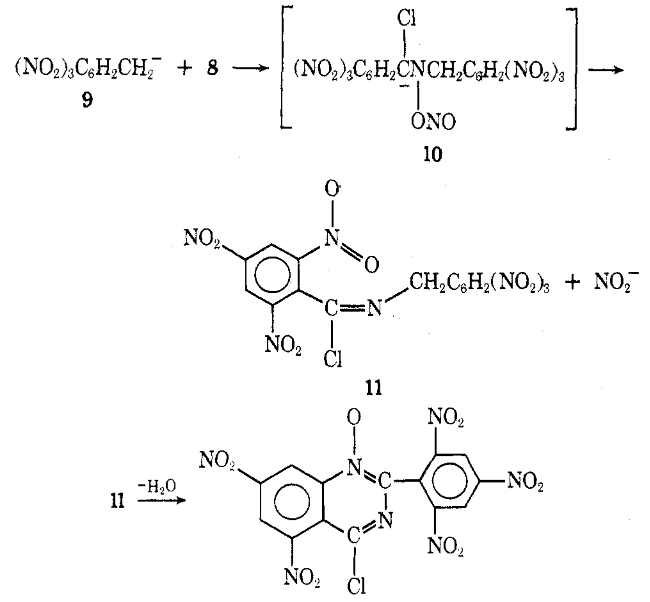
(3) Dr. Mortimer J. Kamlet of these laboratories obtained 2,4,6-trinitrobenzonitrile by dehydration of trinitrobenzaldoxime. Dehydration of 2,4,6-trinitrobenzamide also gives the trinitrobenzonitrile. Recently, Konarski and Graczyk described the preparation of 2,4,6-trinitrobenzonitrile in 60% yield by the reaction of picryl chloride with cuprous cyanide in nitrobenzene at 200°: J. Konarski and A. Graczyk, *Rocz. Chem.*, **46**, 745 (1972).

(4) Reference 1, pp 358–360.

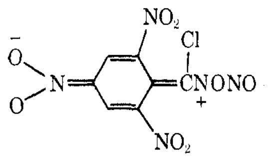
(5) L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **23**, 1517 (1958).

work-up procedure (the pyridine reaction mixture is poured into dilute hydrochloric acid).

The formation of the quinazoline **5** when the reaction temperature is allowed to rise above 0° can be rationalized as follows. The addition of 2,4,6-trinitrobenzyl anion[6] (**9**) to **8** gives the intermediate carbanion **10**; loss of nitrite ion from **10** produces **11**; the cyclization of **11** by the addition of the methylene carbon to the nitro group followed by dehydration yields **5**.



The apparent attack of **9** on the nitrogen of **8** is contrary to the usual mode of reaction of hydroximoyl chlorides.[7] This could be accounted for by resonance structures such as **12**, which show a positive charge on



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the nitrogen atom bearing the ONO group. Nucleophilic attack on this electron-deficient nitrogen atom by **9** produces the resonance-stabilized carbanion **10**.

The structure for **5** is consistent with all the analytical data obtained (elemental analysis, molecular weight, and nmr).[8] Hydrolysis products of **5** with refluxing 50% sulfuric acid included 2,4,6-trinitrobenzamide and 2,4,6-trinitrobenzoic acid. The trinitrobenzamide would be expected along with 2,4-dinitro-5-hydroxylaminobenzoic acid as products from hydrolytic cleavage of the bonds between positions 1 and 2 and 3 and 4 of the quinazoline ring. The trinitrobenzoic acid can arise from hydrolysis of the trinitrobenzamide.

Experimental Section

General.—Caution! The compounds described herein are explosives and should be handled with care. Melting points were taken on a Thomas-Hoover apparatus and are corrected. Silica gel HF-254 was used for tlc and the spots were visualized with uv light. Nmr spectra were determined on a Varian HA-100 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Work-up of the pyridine reaction mixtures was accomplished by pouring them into a stirred mixture of methylene chloride, dilute hydrochloric acid, and ice. The methylene chloride extract was dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure or in a current of air in the hood to give the product residue.

4-Chloro-5,7-dinitro-2-(2,4,6-trinitrophenyl)quinazoline 1-Oxide.—Six grams of 2,4,6-trinitrotoluene was added all at once to a solution of 7.5 g of nitrosyl chloride in 25 ml of pyridine cooled to 0°. The temperature was slowly allowed to rise to 15–18° to maintain a moderate rate of gas evolution. After *ca.* 45 min at 15–18°, the rate of gas evolution slowed considerably and the temperature was then maintained at 20–25° for 4 hr. Work-up (see above) gave a red oil which was stirred with 60 ml of methanol at 25°. The yellow solid (2.05 g, mp 182–188° dec) that formed was removed by filtration. Crystallization from acetone–methanol gave 1.75 g of the quinazoline: mp 198–199° dec; nmr (acetone-d_6) δ 9.45 (s, 2), 8.80 (d, 1), 8.54 (d, 1).

Anal. Calcd for $C_{14}H_4N_7O_{11}Cl$: C, 34.90; H, 0.84; N, 20.35; Cl, 7.36; mol wt, 481.67. Found: C, 34.85; H, 0.73; N, 20.14; Cl, 7.50; mol wt, 484, 482.

The methanol filtrate (60 ml of methanol above) was concentrated to 10 ml, after which 20 ml of benzene was added. Cooling gave 1.8 g of product, mp 115–127°. The product was mainly 2,4,6-trinitrobenzonitrile with a small amount of the quinazoline (as analyzed by tlc). Pure trinitrobenzonitrile was not obtained by repeated crystallizations.

2,4,6-Trinitrobenzonitrile from 2,4,6-Trinitrotoluene.—To a solution of 18.7 g of nitrosyl chloride in 55 ml of pyridine cooled to −10° was added 18 g of 2,4,6-trinitrotoluene. The dark mixture was stirred at −10 to −5° (evolution of gas occurs) for 6 hr. Work-up (see above) gave 19.8 g of residue which was crystallized from methanol–benzene to give 11.5 g (60.9%) of 2,4,6-trinitrobenzonitrile, mp 132–135°. Recrystallization from methanol–benzene raised the melting point to 134–135°. The trinitrobenzonitrile separates as solvates; drying for several hours at 60° removed the benzene of solvation. Nmr (acetone-d_6) showed δ 9.38 (s).

2,4,6-Trinitrobenzohydroximoyl Chloride. A. From 2,4,6-Trinitrotoluene.—In a parallel run at −10 to −5° as above, the residue from the methylene chloride extract was stirred with 60 ml of benzene at 25°. The insoluble solid (2,4,6-trinitrobenzonitrile containing a small amount of the hydroximoyl chloride) was removed by filtration. The benzene filtrate was treated with charcoal and filtered. Removal of the solvent under reduced pressure left a residual oil, which after two crystallizations from methylene chloride gave 1.0 g of crystals, mp 145–147° dec. A final crystallization (charcoal) from benzene by slow addition of hexane gave 0.75 g of 2,4,6-trinitrobenzohydroximoyl chloride: mp 151–152° dec; ir (film) 3525 cm^{-1} (OH); nmr (acetone-d_6) δ 9.21 (s), 12.30 (s, disappears with D_2O).

Anal. Calcd for $C_7H_3N_4O_7Cl$: C, 28.93; H, 1.04; N, 19.28; Cl, 12.20. Found: C, 29.06; H, 0.95; N, 19.11; Cl, 12.01.

B. From 2,4,6-Trinitrobenzaldoxime.—To a solution of 2.0 g of nitrosyl chloride in 5 ml of pyridine cooled to −30° was added 0.5 g of 2,4,6-trinitrobenzaldoxime. After the solution was stirred for 5 hr at −30 to −20°, work-up gave an oil which was shown by tlc (benzene) to be a mixture of the trinitrobenzohydroximoyl chloride and trinitrobenzonitrile. Separation of the products as before yielded 75 mg of the hydroximoyl chloride, mp 148–150° dec. Mixture with the hydroximoyl chloride from trinitrotoluene did not depress the melting point.

C. From 2,4,6-Trinitrobenzyl Chloride.—A solution of 1 g of nitrosyl chloride in 5 ml of pyridine was cooled to 0° before the addition of 0.5 g of 2,4,6-trinitrobenzyl chloride. After the mixture was stirred at 0–5° for 2 hr, work-up gave an oil which

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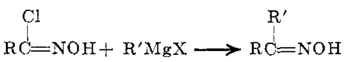
[6] *The use of 2,4,6-trinitrobenzyl anion as a nucleophile has been described in the literature:* K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, **37**, 1966 (1972).

[7] Hydroximoyl chlorides normally react with carbanions to give ketoximes.



$$\overset{\text{Cl}}{\text{RC}}\text{=NOH} + \text{R'MgX} \longrightarrow \overset{\text{R'}}{\text{RC}}\text{=NOH}$$

Alkoximoyl chlorides (RClC=NOR) react similarly. P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 87.

[8] There are a number of positional isomers (heteroring) of **5** which are entirely consistent with the nmr, molecular weight, elemental analysis, etc. Mechanistically, however, **5** is the most likely product. The authors wish to thank a referee for suggesting these possibilities.

tlc (benzene) showed to be mostly hydroximoyl chloride along with some origin material. The oil was crystallized twice by solution in benzene (charcoal) and precipitation by the slow addition of hexane to give 125 mg, mp 147–148° dec. A third crystallization yielded 100 mg, mp 150–152° dec. The melting point was not depressed by mixture with the product from trinitrotoluene.

Hydrolysis of 4-Chloro-5,7-dinitro-2-(2,4,6-trinitrophenyl)quinazoline 1-Oxide.—The quinazoline (0.3 g) was stirred at reflux temperature (*ca.* 160°) with 15 ml of 50% sulfuric acid for 2 hr before all the solid dissolved. The solution was heated at reflux temperature for an additional 1 hr, then was cooled and diluted with water. The small amount of dark solid that precipitated was removed by filtration, and the filtrate was extracted with ether. The ether solution, after extraction with aqueous sodium bicarbonate, was concentrated and hexane was added to precipitate the 2,4,6-trinitrobenzamide (identified by tlc and mixture melting point with an authentic sample). The bicarbonate extract contained 2,4,6-trinitrobenzoic acid which was identified by decarboxylation to 1,3,5-trinitrobenzene, mp 119–122°. Mixture with authentic trinitrobenzene did not depress the melting point.

Registry No.—**1**, 118-96-7; **2**, 37841-25-1; **3**, 42449-44-5; **5**, 42449-45-6; **6**, 42449-46-7; **7**, 7176-28-5.

Iron Pentacarbonyl and the Hydridoundecacarbonyltriferrate Anion as Reagents for Converting Benzohydroxamoyl Chlorides to Nitriles. The Deoxygenation of Nitrile Oxides

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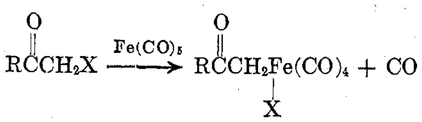
Several new convenient syntheses of nitriles are described. Reaction of benzohydroxamoyl chlorides with iron pentacarbonyl in refluxing tetrahydrofuran affords nitriles in moderate yields. Higher yields of nitriles can be realized by treating the organic reactant with triiron dodecacarbonyl and methanol in hot benzene. The *in situ* generated hydridoundecacarbonyltriferrate anion is the active species in the latter reaction. Iron pentacarbonyl can also deoxygenate nitrile oxides to nitriles.

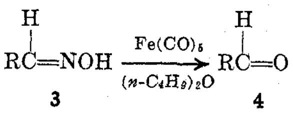
Iron pentacarbonyl [$\mathrm{Fe(CO)_5}$] has recently been shown to be a useful reagent for converting α-halo ketones to 1,4-diketones.[1] Also isolated in these reactions were monoketones and, in several instances, β-epoxy ketones. A mechanistic study of the reaction indicated initial oxidative addition to the α-halo ketone **1** to give the iron tetracarbonyl halide **2**.



$$\mathrm{R\overset{\overset{O}{\|}}{C}CH_2X \xrightarrow{Fe(CO)_5} R\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{X}{|}}{Fe}(CO)_4 + CO}$$

1 **2**

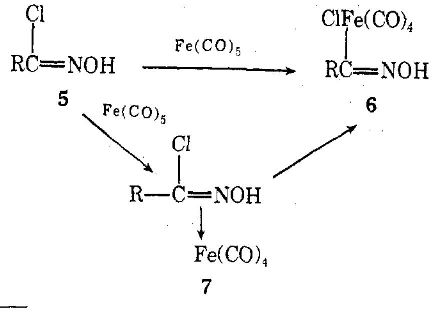
Treatment of oximes with the same metal carbonyl in di-*n*-butyl ether results in the regeneration of the corresponding carbonyl compound (*e.g.*, **3** → **4**) in



$$\mathrm{R\overset{\overset{H}{|}}{C}{=}NOH \xrightarrow[(\mathit{n}\text{-}C_4H_9)_2O]{Fe(CO)_5} R\overset{\overset{H}{|}}{C}{=}O}$$

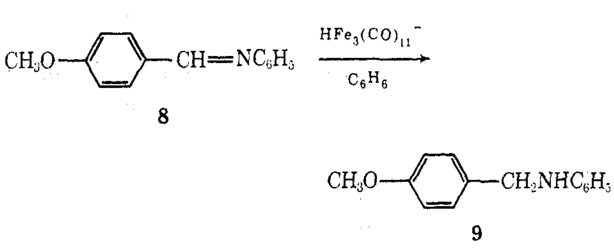
3 **4**

reasonable yields.[2] Although the mechanism of this reaction has yet to be fully elucidated,[3] it clearly does not involve initial oxidative addition. If, however, the vinylic hydrogen of **3** was replaced by a halogen,



specifically chlorine (**5**), then oxidative addition may now occur to give **6** either directly or, more likely, *via* the π complex **7**. Regarding the latter, irradiation of related vinyl halides with $\mathrm{Fe(CO)_5}$ (or thermal reaction with diiron enneacarbonyl) has been reported to give iron tetracarbonyl complexes with π complexation to the double bond.[4,5] These mononuclear π complexes are convertible to binuclear complexes *via* analogs of **6**. Such transformations can be effected thermally[5] or photolytically,[4,5] subject to the stereochemistry of the mononuclear π-complexed vinyl halides. This paper describes the reaction of benzohydroxamoyl chlorides with $\mathrm{Fe(CO)_5}$. It was of considerable interest to learn the fate of **6**, if formed, in these reactions.

One of us has demonstrated the utility of the hydridoundecacarbonyltriferrate anion (generated from triiron dodecacarbonyl and methanol in benzene) as a reagent for reducing the carbon–nitrogen double bond in heterocycles (*e.g.*, phthalazine) and in Schiff bases (*e.g.*, **8** → **9**).[6] Several benzohydroxamoyl chlorides were also exposed to the iron hydride in order to determine whether hydrogenation would occur here, as was observed for **8**.



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(1) H. Alper and E. C. H. Keung, *J. Org. Chem.*, **37**, 2566 (1972).

(2) H. Alper and J. T. Edward, *J. Org. Chem.*, **32**, 2938 (1967).

(3) H. Alper, unpublished results.

(4) C. Kruger, Y. H. Tsay, F. W. Grevels, and E. K. von Gustorf, *Israel J. Chem.*, **10**, 201 (1972), and references cited therein.

(5) F. W. Grevels, E. K. von Gustorf, and G. Bor, "Procedings of the Third International Symposium on Reactivity and Bonding in Transition Organometallic Compounds, Venice, 1970," Inorganica Chimica Acta, E4.

(6) H. Alper, *J. Org. Chem.*, **37**, 3972 (1972).