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 the 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

NOEL A. GENCO, RICHARD A. PARTIS, AND HOWARD ALPER\*

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

### Received July 5, 1973

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 [Fe(CO)<sub>5</sub>] has recently been shown to be a useful reagent for converting  $\alpha$ -halo ketones to 1,4-diketones.<sup>1</sup> Also isolated in these reactions were monoketones and, in several instances,  $\beta$ -epoxy ketones. A mechanistic study of the reaction indicated initial oxidative addition to the  $\alpha$ -halo ketone 1 to give the iron tetracarbonyl halide 2.

$$\begin{array}{c} 0 & 0 \\ \parallel & & \\ \text{RCCH}_2 X \xrightarrow{\text{Fe}(\text{CO})_s} & \parallel \\ & & \\ & & \\ 1 & & \\ 1 & & 2 \end{array} \\ \begin{array}{c} 0 \\ \text{Fe}(\text{CO})_s \\ \parallel \\ \text{RCCH}_2 \text{Fe}(\text{CO})_4 + \text{CO} \\ & \\ & \\ X \\ 1 & & 2 \end{array}$$

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

$$\begin{array}{c} H \\ RC = NOH \\ 3 \end{array} \xrightarrow{Fe(CO)_{\delta}} RC = 0 \\ 3 \end{array}$$

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



H. Alper and E. C. H. Keung, J. Org. Chem., 37, 2566 (1972).
 H. Alper and J. T. Edward, J. Org. Chem., 32, 2938 (1967).

(3) H. Alper, unpublished results.

specifically chlorine (5), then oxidative addition may now occur to give 6 either directly or, more likely, via the  $\pi$  complex 7. Regarding the latter, irradiation of related vinyl halides with Fe(CO)<sub>5</sub> (or thermal reaction with diiron enneacarbonyl) has been reported to give iron tetracarbonyl complexes with  $\pi$  complexation to the double bond.<sup>4,5</sup> These mononuclear  $\pi$  complexes are convertible to binuclear complexes via analogs of 6. Such transformations can be effected thermally<sup>5</sup> or photolytically.<sup>4,5</sup> subject to the stereochemistry of the mononuclear  $\pi$ -complexed vinyl halides. This paper describes the reaction of benzohydroxamoyl chlorides with Fe(CO)<sub>5</sub>. 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.,  $8 \rightarrow 9$ ).<sup>6</sup> Several benzohydroxamoyl chlorides



were also exposed to the iron hydride in order to determine whether hydrogenation would occur here, as was observed for 8.

(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, "Proceedings of the

(5) F. W. Grevels, E. K. von Gustorf, and G. Bor, "Proceedings 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).

TABLE I
YIELDS OF NITRILES OBTAINED FROM REACTION OF BENZOHYDROXAMOYL CHLORIDES WITH
$Fe(CO)_{6}$ and with the <i>in situ</i> Generated $HFe_{3}(CO)_{11}$

<b>5</b> , R =	Registry no.	Product(s)	Registry no.	$Fe(CO)_{s}$ yield, $\%^{a}$	HFe₃(CO)11 - yield, %ª
$C_6H_5$	698-16-8	Benzonitrile	100-47-0	76	
$4-\mathrm{ClC}_6\mathrm{H}_4$	28123-63-9	4-Chlorobenzonitrile	623-03-0	60	86
$4-C_{\mathfrak{G}}H_{\mathfrak{z}}C_{\mathfrak{G}}H_{4}$	42202-94-8	4-Cyanobiphenyl	2920-38-9	33	76
$2,6-\mathrm{Cl}_2\mathrm{C}_6\mathrm{H}_3$	6579-27-7	2,6-Dichlorobenzonitrile	1194-65-6	62	90
$4-FC_6H_4$	42202-95-9	4-Fluorobenzonitrile	1194-02-1	67	
$2,4,6-(CH_{3}O)_{3}C_{6}H_{2}$	2904-65-6	2,4,6-Trimethoxybenzonitrile	2571 - 54 - 2	44	
$4-\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4$	1011-84-3	4-Nitrobenzonitrile	619-72-7	40	$58^{b}$
$4-\mathrm{NH}_2\mathrm{C}_6\mathrm{H}_4$	42202-97-1	4-Aminobenzonitrile	873-74-5	0	19
37111 0 131 1					

<sup>a</sup> Yields are of sublimed, recrystallized, or distilled material. The melting or boiling points and spectral data were in good agreement with data reported in the literature. <sup>b</sup> Use of a 2:1 mole ratio of  $Fe_3(CO)_{12}$  to 5,  $R = 4-NO_2C_6H_4$ , gave 4-aminobenzonitrile in 68% yield.

#### **Results and Discussion**

Treatment of benzohydroxamoyl chlorides (5, R = aryl) with  $Fe(CO)_5$  [2:1 mole ratio of  $Fe(CO)_5$ :5] in refluxing anhydrous tetrahydrofuran (THF) for 18-24 hr results in the formation of nitriles in 33-76% yields (Table I). This reaction is very simple both in execution and work-up, thus providing a convenient synthesis of nitriles under neutral conditions. The reaction is not catalytic in the metal carbonyl.



Nitriles were also formed when **5** was treated with an approximately equimolar amount of triiron dodecacarbonyl [Fe<sub>3</sub>(CO)<sub>12</sub>] and methanol in boiling benzene. As indicated in Table I, the yields of nitriles are superior using this reagent combination as compared with the results with Fe(CO)<sub>5</sub>. However, there are several differences between the two processes. First, Fe(CO)<sub>5</sub> is a more economical reagent than Fe<sub>3</sub>(CO)<sub>12</sub>. Secondly, while Fe(CO)<sub>5</sub> is uncharged, the iron hydride is anionic (and of moderate nucleophilicity).

The results for 4-nitrobenzohydroxamoyl chloride  $(5, R = 4-NO_2C_6H_4)$  are noteworthy. Iron pentacarbonyl is known to deoxygenate nitrobenzenes to azo, azoxy, and/or amino compounds, subject to the nature and position of substitution on the benzene ring.7 The formation of only 4-nitrobenzonitrile from treatment of 5,  $R = 4-NO_2C_6H_4$ , with  $Fe(CO)_5$  is indicative of the substantially greater reactivity of the CIC==NOH group as compared with the nitro function. In addition, Landesberg and coworkers<sup>8</sup> have reported that nitrobenzenes, bearing a variety of substituents, can be reduced to anilines with  $Fe_3(CO)_{12}$  and methanol in benzene. Here, however, reaction occurs primarily at the hydroxamic acid site of 5,  $R = 4-NO_2C_6H_4$ , when equimolar quantities of reactants are used. 4-Aminobenzonitrile was obtained in 68% yield using a 2:1 mole ratio of  $Fe_3(CO)_{12}$ :5,  $R = 4-NO_2C_6H_4$ .

Solid evidence for the intermediacy of nitrile oxides in the  $Fe(CO)_5$  reaction was obtained by conducting the reaction of benzohydroxamoyl chloride and the metal carbonyl in the presence of excess benzaldehyde. The 1,3-dipolar cycloaddition product, 2,5-diphenyl-1,3,4-dioxazole,<sup>9</sup> was isolated in 40% yield, along with some nitrile. In addition, treatment of 2,6-dichlorobenzohydroxamoyl chloride with Fe<sub>2</sub>(CO)<sub>9</sub> at room temperature for 2 hr afforded a mixture of an iron tetracarbonyl complex [6 or 7,  $\nu_{CO}$ (KBr) 2083 (w-m), 2036 (s), and 1982 cm<sup>-1</sup> (m-s) ], 2,6-dichlorobenzonitrile, and 2,6-dichlorobenzonitrile oxide (the infrared spectrum showed intense bands at 2294 and 1366 cm<sup>-1</sup> characteristic of nitrile oxides).<sup>10</sup>

The above results suggest the deoxygenation of nitrile oxides. Treatment of 2,4,6-trimethoxybenzonitrile oxide with an equimolar quantity of  $Fe(CO)_5$ gave 2,4,6-trimethoxybenzonitrile in 47% yield. Similarly, mesitonitrile was obtained in 64% yield from 2,4,6-trimethylbenzonitrile oxide and  $Fe(CO)_5$ . Therefore,  $Fe(CO)_5$  is capable of deoxygenating nitrile oxides to nitriles in moderate yields. The use of excess Fe- $(CO)_5$  in these deoxygenations should be avoided, since such conditions lead to the ligand substitution products  $(RCN)Fe(CO)_4$  and/or  $(RCN)_2Fe(CO)_3$ . The latter complexes, however, undergo partial or complete decomposition to nitriles after standing for 3–6 weeks.

It is not clear how the hydridoundecacarbonyltriferrate anion converts benzohydroxamoyl chlorides to nitriles. 2,6-Dichlorobenzaldoxime failed to react with  $Fe_3(CO)_{12}$  and methanol in benzene using identical reaction conditions with those for the 2,6-dichlorobenzohydroxamoyl chloride- $Fe_3(CO)_{12}$ -methanol reaction. Therefore, oximes are not involved in the benzohydroxamoyl- $HFe_3(CO)_{11}$ -reaction.

#### **Experimental Section**

Melting points were determined using a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Hoffmann-La Roche, Inc. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. Polystyrene was used for calibration. Nuclear magnetic resonance spectra were determined on Varian A-60 (TMS as internal standard) and/or HA-100 spectrometers.

Iron pentacarbonyl, diiron enneacarbonyl, and triiron dodecacarbonyl were purchased from Pressure Chemical Co. and used as received. Solvents were dried and purified by standard techniques. All reactions were run under an atmosphere of dry nitrogen.

**Benzohydroxamoyl Chlorides** (5).—Except for 5, R = 2,4,6-(CH<sub>3</sub>O)<sub>3</sub>C<sub>3</sub>H<sub>2</sub>, all of the benzohydroxamoyl chlorides were readily prepared by chlorination of the corresponding oxime in commercial chloroform. The following general procedure is a modification of that described by Chiang.<sup>11</sup> To commercial

<sup>(7)</sup> H. Alper and J. T. Edward, Can. J. Chem., 48, 1543 (1970).

<sup>(8)</sup> J. M. Landesberg, L. Katz, and C. Olsen, J. Org. Chem., 37, 930 (1972).

<sup>(9)</sup> R. Huisgen and W. Mack, Tetrahedron Lett., 583 (1961).

<sup>(10)</sup> R. H. Wiley and B. J. Wakefield, J. Org. Chem., 25, 546 (1960).

<sup>(11)</sup> Y. Chiang, J. Org. Chem., 36, 2146 (1971).

chloroform (225 ml) was added 15 drops of absolute ethanol. After the solution was cooled to -15 to  $-20^{\circ}$  (Dry Ice-CCl<sub>4</sub>) the oxime (2.8-4.0 g) was added and then chlorine gas was bubbled through the solution at a moderate rate for 25-35 min. The reaction mixture was allowed to stand at  $-20^{\circ}$  for 2 hr, and then at room temperature for 6-8 hr. The solution was flushed with nitrogen gas to remove excess chlorine. Filtration and subsequent evaporation of the filtrate gave an oil. The benzohydroxamoyl chloride was crystallized by adding pentane and immersing the solution in a Dry Ice-acetone bath for 15 min. The crystals were filtered and dried in a vacuum desiccator. Yields of pure 5 follow: R = C<sub>6</sub>H<sub>5</sub>, 56%; R = 4-ClC<sub>6</sub>H<sub>4</sub>, 79%; R = 4-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>, 42%; R = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 84%; R = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>8</sub>, 62% [mp 92-93° (lit.<sup>12</sup> mp 93-94°). Anal. Calcd for Cr<sub>7</sub>H<sub>4</sub>Cl<sub>5</sub>NO: C, 37.44; H, 1.80; N, 6.24. Found: C, 37.44; H, 1.76; N, 6.31 (Dondoni and coworkers<sup>12</sup> claimed that this compound could not be prepared by direct chlorination of the oxime)]; R = 4-FC<sub>6</sub>H<sub>4</sub>, 74% (mp 72-73°. Anal. Calcd for Cr<sub>7</sub>H<sub>6</sub>ClFNO: C, 48.44; H, 2.90; N, 8.07. Found: C, 48.09; H, 2.73; N, 8.29.).

Compound 5,  $R = 2,4,6-(CH_3O)_2C_6H_2$ , was prepared from the nitrile oxide following the procedure of Grundmann and Dean.<sup>18</sup>

General Procedures for Conversion of Benzohydroxamoyl Chlorides to Nitriles. A.  $Fe(CO)_{5}$ .—To a dried, deoxygenated solution to THF (40-50 ml) was added the benzohydroxamoyl chloride (5.0-8.7 mmol) followed by  $Fe(CO)_{5}$  [2:1 mole ratio of  $Fe(CO)_{5}$ :5]. The mixture was refluxed (expect for 5, R = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, where a reaction temperature of 60° was used) with stirring for 18-24 hr, cooled, and filtered, and pentane (100 ml) was then added to the filtrate. After standing in the refrigerator overnight, the solution was filtered, and the filtrate was flash evaporated. The residual nitrile (10) obtained from flash evaporation was then purified, if necessary, by sublimation, recrystallization (*n*-heptane), or distillation. The yields of nitrile are given in Table I.

**B.**  $Fe_3(CO)_{12}$ -CH<sub>3</sub>OH.—A mixture of  $Fe_3(CO)_{12}$  (2.92 g, 4.3 mmol) and methanol (1.0 ml) in benzene (55 ml) was refluxed with stirring for 8 hr. The solution was cooled, the benzohydroxamoyl chloride (4.52 mmol) was added, and the resulting mixture was refluxed for 17-22 hr. The solution was cooled and filtered, and the filtrate was evaporated to afford reasonably pure

(12) A. Dondoni, G. F. Pedulli, and G. Barbaro, J. Org. Chem., 37, 3564 (1972).

(13) C. Grundmann and J. M. Dean, J. Org. Chem., 30, 2809 (1965).

nitrile. Further purification, if required, could be effected as described in A. The two products obtained from 4-nitrobenzo-hydroxamoyl chloride were separated by chromatography on Florisil or by trituration with hexane. 2,6-Dichlorobenzaldoxime failed to react with  $Fe_8(CO)_{12}$ -methanol under these conditions.

Reaction of 2,6-Dichlorobenzohydroxamoyl Chloride with  $Fe_2(CO)_9$ .—A mixture of  $Fe_2(CO)_9$  (1.72 g, 4.72 mmol) and 2,6dichlorobenzohydroxamoyl chloride (0.825 g, 3.60 mmol) in benzene (50 ml) was stirred at room temperature for 2 hr. The solution was filtered and evaporation of the filtrate gave 2,6dichlorobenzonitrile and the nitrile oxide. The benzene-insoluble solid apparently was an iron tetracarbonyl complex (see Results and Discussion) but was of low stability and could not be isolated in analytically pure form. Reactant 5, R = 4- $C_6H_5C_6H_4$ , behaved similarly when treated with  $Fe_2(CO)_9$ .

**2,5-Diphenyl-1,3,4-dioxazole.**—The general procedure described for the reaction of 5 and  $Fe(CO)_5$  was repeated for 5,  $R = C_6H_5$ , in the presence of a fivefold excess of benzaldehyde. Work-up as above gave 2,5-diphenyl-1,3,4-dioxazole, mp 38-40° (lit.<sup>9</sup> mp 41-42°), in 40% yield and benzonitrile in 14% yield.

General Procedure for Deoxygenation of Nitrile Oxides by  $Fe(CO)_5$ .—An equimolar mixture of nitrile oxide<sup>13</sup> (0.5–4.0 mmol) and  $Fe(CO)_5$  in THF (20–50 ml) was refluxed with stirring for 1–2 hr. The reaction was worked up as described for the benzohydroxamoyl chloride– $Fe(CO)_5$  reaction. The nitriles were identified by comparison with authentic samples and by comparison with melting points and spectral data. Rearrangement of nitrile oxides to isocyanates<sup>13</sup> does not occur to a significant extent under these reaction conditions.

Acknowledgments.—Acknowledgment is made to the Research Foundation of the State University of New York, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Hoffmann-La Roche, Inc., for carrying out the microanalytical determinations. Ms. R. Cartmell was kind enough to run some nmr spectra on the HA-100 spectrometer.

**Registry No.**—Fe(CO)<sub>5</sub>, 13463-40-6; HFe<sub>3</sub>(CO)<sub>11</sub><sup>-</sup>, 25948-56-5.

## A New Method for the Conversion of Nitro Groups into Carbonyls

JOHN E. MCMURRY\* AND JACK MELTON

Thimann Laboratories, University of California, Santa Cruz, California 95064

Received July 16, 1973

When a primary or secondary nitro compound is treated with aqueous  $TiCl_3$ , reduction occurs yielding an imine which hydrolyzes to the corresponding ketone or aldehyde. A study of the scope and mechanism has been carried out. A variety of functional groups including ketone, ester, nitrile, ketal, and hydroxyl survive the reaction conditions. Yields range between 45 and 90%. The reaction probably proceeds through a nitroso intermediate which then tautomerizes to an oxime and is further reduced to imine. Evidence in support of this mechanism is presented. The use of the reaction in organic synthesis is illustrated by a synthesis of *cis*-jasmone.

The nitro group is a function of great synthetic potential in organic chemistry because of the versatility with which it may react.<sup>1</sup> Acting as a strong electron withdrawer, a nitro group can activate a neighboring C-H bond for aldol or Michael-type additions to suitable acceptors. Conversely, nitro olefins can themselves act as excellent Michael acceptors. Nitro groups  $\beta$  to carbonyls can also act as leaving groups in  $\beta$ -elimination reactions—a property which we recently took advantage of in our synthesis of  $\alpha$ -methylenebutyrolactones.<sup>2</sup> Acting in yet other ways, nitro groups can be converted into other useful functional groups such as amines or carbonyls. This latter conversion is of considerable interest and utility because it in effect reverses





<sup>(1)</sup> For a review of the chemistry of nitro groups, see H. Feuer, Ed., "The Chemistry of the Nitro and Nitroso Groups," Wiley-Interscience, New York, N. Y., 1969.