Reduction of Nitroaryls by Dodecacarbonyltriiron–Methanol[1]

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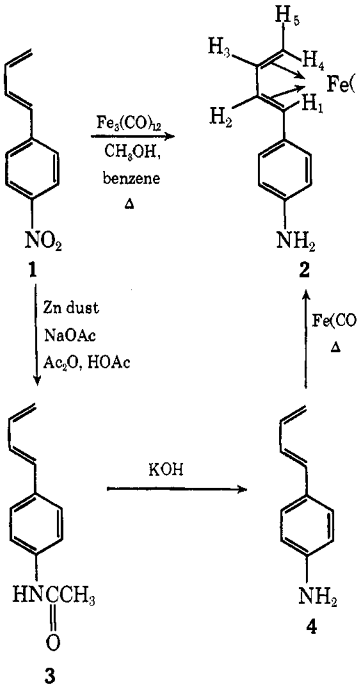
Received July 28, 1971

Methanolic solutions of dodecacarbonyltriiron [$Fe_3(CO)_{12}$] *specifically* reduce the nitro group of nitroaryls to a primary amine in the presence of functional groups often encountered in aromatic synthesis (*e.g.*, C=C, C=O, CO_2R, NHAc). High yields result. The effective reducing agent is the hydridoundecacarbonyltriferrate anion. Aspects of the synthetic scope and mechanistic pathway are discussed.

Our interest in the use of dodecacarbonyltriiron–methanol systems for the reduction of nitro groups arose from an attempt to prepare *p*-nitrophenylbutadienetricarbonyliron. Reaction of *p*-nitrophenylbutadiene (**1**) with a molar amount of dodecacarbonyltriiron [$Fe_3(CO)_{12}$] gave a mixture of amines **2** and **4**. With a two fold excess of $Fe_3(CO)_{12}$, an 80% yield of complex **2** was obtained; the structure was confirmed by the alternative synthesis outlined in Scheme I. The source of proton for the reduction was apparently the methanol included in the $Fe_3(CO)_{12}$ reagent as a stabilizer (*ca.* 10% by weight).[4] Without methanol no amine was obtained; instead the reaction yielded a complex (*vide infra*).

SCHEME I



Since **1** was reduced in high yield without loss of the sensitive functional group, other nitroaryls were tested in order to broaden the synthetic applicability. The conditions used are outlined in eq 1. The compounds reduced are listed in Table I. Conditions were not optimized for each compound. Yield analyses were carried out either using vapor phase chromatography (vpc) (internal standard) or by product isolation.

$$\underset{0.01\ M}{ArNO_2} + \underset{0.01\ M}{Fe_3(CO)_{12}} + \underset{(0.1\ M)}{\underset{2.5\ ml}{CH_3OH}} \xrightarrow[\text{10–17 hr}]{\text{excess benzene, reflux}} ArNH_2 \quad (1)$$

TABLE I

YIELDS OBTAINED FROM REACTION OF $ArNO_2$ AND $Fe_3(CO)_{12}$ WITH METHANOL IN BENZENE

$NO_2C_6H_4X$, X	$NH_2C_6H_4X$, Yield of amine, %
H	77^a
p-Cl	86^a
o-Cl	83^a
p-CH_3	73^a
o-CH_3	87^a
m-NH_2	95^a
p-NH_2	63^a
m-NO_2	$77^{a,c}$
p-CO_2Et	83^a
o-Br	86^a
p-OCH_3	84^a
p-OH	38^b
m-OH	66^b
p-$COCH_3$	91^b
p-$NHCOCH_3$	77^b
p-CH=CHCH=CH_2	$80^{b,d}$
o-Biphenyl	93^b

[a] Determined by vpc. [b] Isolated yield. [c] Using a twofold excess of reagent. [d] Isolated as the tricarbonyliron complex.

Reduction of the nitro group is specific and takes place in relatively high yields with a variety of substituents (Table I). Acid- or base-sensitive groups survive; carbonyl and olefin groups remain unaltered. Only amine results; no azo, azoxy, or carbonyl insertion products are formed.[5] Complete reduction takes place with less than a stoichiometric quantity of $Fe_3(CO)_{12}$ (Table IV); however, the reaction is not catalytic. Shorter reaction times may improve yields (Table V).

Several mechanistic questions required answers: What happens to the oxygens from the $-NO_2$ group? What is the role of the $Fe_3(CO)_{12}$ and the purpose of the methanol? Are intermediates such as polynuclear carbonyliron anions or organometallic complexes involved?

Results and Discussion

Some of the oxygen appears as carbon dioxide; only 1 mol of CO_2 is found (Table III). One of the oxygens of the $-NO_2$ function must be lost by oxidation of ligand carbon monoxide. The other oxygen is lost by another route. Insoluble iron residues result and appear to be iron oxides; loss of oxygen to iron may be involved.

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[1] This work was supported by the National Science Foundation. It was presented at Metrochem '71, San Juan, Puerto Rico, April 30–May 3, 1971, Abstracts of Papers, p 19.

[2] Abstracted in part from the Ph.D. Thesis of Lawrence Katz, Adelphi University, April 1971.

[3] Abstracted in part from the M.S. Thesis of Carol Olsen, Adelphi University, June 1971.

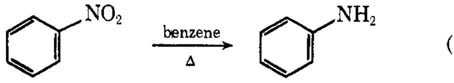
[4] $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ supplied by Alfa Inorganics, Beverly, Mass.

[5] (a) H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970); (b) Professor H. Alper, private communication.

Dodecacarbonyltriiron and methanol, in the absence of nitroaryl, gave an unstable, pyrophoric red solid (eq 2). An absorption maximum at 543 mμ (MeOH)

$$\underset{\lambda_{\max}\text{ (MeOH) 602 m}\mu}{Fe_3(CO)_{12} + CH_3OH} \xrightarrow[\text{benzene, 7.5 hr}]{\Delta} \underset{\lambda_{\max}\text{ (MeOH) 543 m}\mu}{\text{Red solid on filtration}} \qquad (2)$$

suggested the hydridoundecacarbonyltriferrate anion $[HFe_3(CO)_{11}^-]$ [$HFe_3(CO)_{11}^-$, $\lambda_{\max}$ 540 mμ;[6b] $Fe_3(CO)_{12}$, $\lambda_{\max}$ 605 mμ[6a]]. Two salts of this anion were brick red to black, pyrophoric crystalline solids; visible spectra corresponded to the isolated red solid {$Et_3NH[HFe_3(CO)_{11}]$ (**5**), $\lambda_{\max}$ 540 mμ;[6a] $Me_4N[HFe_3(CO)_{11}]$} (**6**), $\lambda_{\max}$ 540 mμ[6a]]. Thus, $Fe_3(CO)_{12}$ is converted into an active hydrido species which is the effective reducing agent. The reaction time is important; after 7.5 hr the 602-mμ absorption of the $Fe_3(CO)_{12}$ is lost and only the 543-mμ absorption remains. When nitrobenzene was introduced into the reducing system which showed absence of the $Fe_3(CO)_{12}$ (602 mμ) but presence of the suspected $HFe_3(CO)_{11}^-$ anion (543 mμ), aniline was formed. The salts **5**[6a] and **6**[7a] also reduce nitrobenzene to aniline (eq 3).



(3)

a. $Fe_3(CO)_{12}$ + CH_3OH reflux in benzene for 8 hr, then add $PhNO_2$	34% (37% $PhNO_2$)
b. $Et_3NH[HFe_3(CO)_{11}]$ (**5**)[6a]	62%
c. $Me_4N[HFe_3(CO)_{11}]$ (**6**)[7a]	32%
d. $Fe(CO)_5$ + CH_3OH	0

Differences in yield are noted. In system a (eq 3) not all of the nitrobenzene is reduced, and the yield of aniline is low; this is probably due to loss of $HFe_3(CO)_{11}^-$ anion through decomposition or conversion to less active polynuclear carbonyliron species. Salt **5** gave aniline in yields close to the optimum obtained in the original reaction medium (eq 1, Table I). However, salt **6** reproducibly gave half as much aniline as did **5**. The apparent difference is the proton in **5**. Thus, a proton source is required. In salt **6**, therefore, the hydrido species acts not only as a reducing agent but also as a proton source (eq 4).[7] The methanol

$$HFe_3(CO)_{11}^- \longrightarrow H^+ + Fe_3(CO)_{11}^{2-} \qquad (4)$$

reacts with the $Fe_3(CO)_{12}$ to form the hydrido species and acts as a proton source.

Pentacarbonyliron[4] and methanol did not reduce nitrobenzene. Alper[5] used these reagents to convert nitroaryls[5a] into azo, azoxy and/or amino compounds, and nitroalkyls[5b] into formamides and/or ureas. A key difference is the solvent and temperature for reaction: dry diglyme and 130° in his system *vs.* dry benzene and 80° in our system. Differences in the effective reagent and reaction pathway are apparent.

Hieber and Brendel[7] established the formation of the $HFe_3(CO)_{11}^-$ anion from methanol and $Fe_3(CO)_{12}$.

$$3Fe_3(CO)_{12} \xrightarrow{MeOH} Fe(MeOH)_n[Fe_3(CO)_{11}] + 5Fe(CO)_5$$

$$2Fe(MeOH)_n[Fe_3(CO)_{11}] \longrightarrow Fe(OMe)_2 + Fe(MeOH)_n[HFe_3(CO)_{11}]_2$$

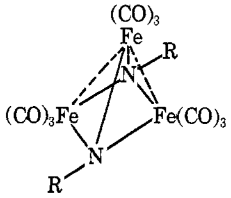
$$Fe(MeOH)_n[HFe_3(CO)_{11}]_2 \longrightarrow Fe(OMe)_2 + 2H_2Fe_3(CO)_{11}$$

Pentacarbonyliron can be detected in our product mixtures.

The nature of the intermediates remains. Since only one oxygen is lost by oxidation of ligand carbon monoxide to carbon dioxide, nitrosobenzene may be generated. This possibility was eliminated, since reduction of nitrosobenzene with **6** or with $Fe_3(CO)_{12}$ and methanol in benzene gave azobenzene, azoxybenzene, and a substantial quantity of CO_2 in addition to aniline. Since no azobenzene or azoxybenzene is observed in the reduction of nitrobenzene with either reagent, free nitrosobenzene is not involved.

When nitrobenzene was treated with methanol-free $Fe_3(CO)_{12}$[8] in anhydrous benzene, a complex (**7b**, 18%) and azobenzene (4%) resulted. The empirical formula of **7b** was established as $C_{21}H_{10}N_2O_9Fe_3$ by analysis. The mass spectrum had a parent peak at *m/e* 602 (±1) (2%) and showed successive loss of carbon monoxide units in the fragmentation pattern. The isotopic distribution of elements in the fragments agrees with the number of iron atoms (Table VI). The large peak at *m/e* 91 (±1) suggests that a Ph–N group might be present. The nuclear magnetic resonance spectrum of **7b** shows only an aromatic singlet and indicates only one type of aryl moiety.

Complex **7b** was compared spectrally to complex **7a** reported by Dekker and Knox.[9,10] The structure



7a, R = CH_3
b, R = Ph

of **7a** proposed by these workers[9] was confirmed by X-ray analysis.[11] Mössbauer spectra[12,13] showed identical oxidation states for the irons in both complexes. Thus, phenylnitrene or its complex **7b** may be intermediates.

A nitrobenzene reduction was stopped after 4 hr; work-up yielded no complex, only aniline and unreacted nitrobenzene. Should complex **7b** or free phenylnitrene be intermediates, their reduction must take place as fast as their formation. Dekker and Knox[9] proposed formation of **7a** through a triplet nitrene; complex **7b** might also arise in a similar way. However, reaction of nitrobenzene with methanol-free Fe_3-

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(6) (a) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960); these workers describe the reduction of nitromethane with ethanolic solutions of $KHFe(CO)_4$; methylamine and ferric hydroxide result after 12 hr. (b) W. Hieber and H. Beutner, *Z. Naturforsch.*, **17b**, 211 (1962).

(7) (a) W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.*, **289**, 324, 338 (1957); (b) F. Calderozzo, R. Ercoli, and G. Natta in "Organic Syntheses *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 101, 109.

(8) Dodecacarbonyltriiron[4] was made methanol free by keeping the reagent at 0.5 mm for at least 5 hr; the quantity of reagent (6–10 g) gave constant weight readings after 5 hr.

(9) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

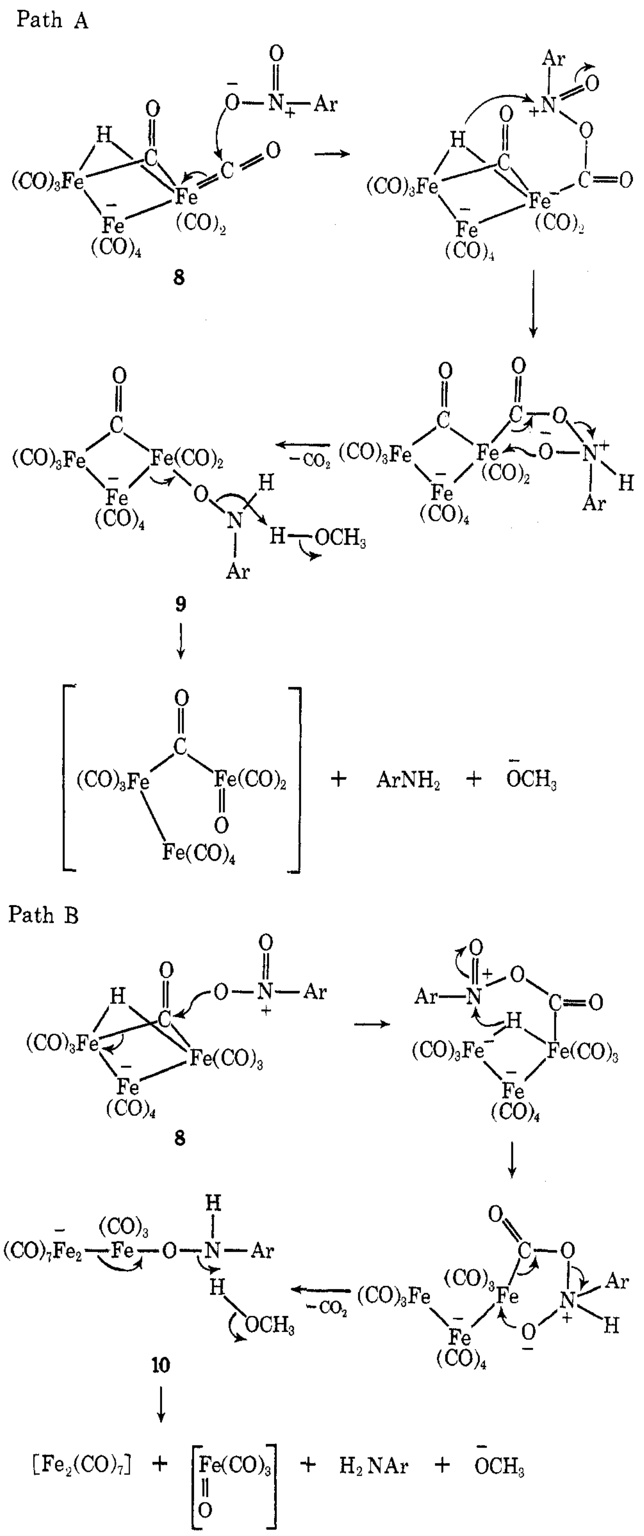
(10) We thank Professor G. R. Knox for kindly supplying a sample of **7a** and the spectra: $\lambda_{\max}$ (cyclohexane) ($\epsilon \times 10^3$) 311 (8.8), 356 (4.5), 410 (sh) (3.4), and 519 mμ (2.3); ν (CS_2) 2062 (vs), 2043 (vs), 2011 (s), 1979 (sh), 1960 cm^{-1} (sh) ($C\equiv O$).

(11) R. J. Doedens, *Inorg. Chem.*, **8**, 570 (1969).

(12) Mössbauer spectra of **7a** and **7b** were determined by Dr. F. Ross, Brookhaven National Laboratory, Brookhaven, N. Y.

(13) Professor R. Greatrex, The University of Newcastle upon Tyne, England, kindly provided data for Mössbauer spectrum of **7a**.

SCHEME II

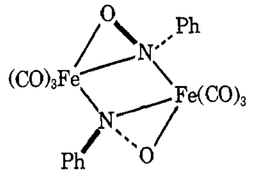


$(CO)_{12}$[8] in cyclohexane gave no *N*-phenylcyclohexylamine;[14,15] complex **7b** resulted (6%). A free nitrene appears unlikely.

Alper[5a] treated *o*-nitrobiphenyl with $Fe(CO)_5$ in hot butyl ether and found *o*-aminobiphenyl (58%) and carbazole (15%). Carbazole formation was taken as evidence for a nitrene intermediate.[5a,14] *o*-Nitrobiphenyl was treated with $Fe_3(CO)_{12}$. With methanol-free $Fe_3(CO)_{12}$[8] in anhydrous benzene, carbazole (1.3%) was found. Other products were isolated: *o*-aminobiphenyl (53%), *o*-hydrazobiphenyl (17%), and *o*-azobiphenyl (10%). Traces of a green complex were also found. In the presence of methanol, 1 mol of CO_2 was generated, but *only o-aminobiphenyl* (93%) was isolated; no carbazole was found. Therefore, though amine or coupling products may arise from a nitrene intermediate, either complexed or free,[5,9,14,15] a nitrene intermediate seems unlikely in the reduction of nitro groups to amines using methanol and $Fe_3(CO)_{12}$.

A rationalization for the reduction is presented in Scheme II. Attack of nitroxide oxygen on ligand carbon monoxide is the probable first step. This is similar to the proposal of Alper and Edward[5a] for the reduction of compounds with the N–O linkage. The site of attack could be either at a terminal carbonyl (path A) or at the bridging carbonyl (path B) of the $HFe_3(CO)_{11}^-$ anion (**8**).[16] A definitive choice between path A or path B cannot be made; however, the bridging carbonyl should be more susceptible to nucleophilic attack[17-19] and may account for the relative ease of the reaction [*vs.* $Fe(CO)_5$[5]]. Since nitroso intermediates have been discounted, transfer of the bridging hydrogen as a hydride ion[20] must follow and takes place before CO_2 loss. The complexed *N*-oxide can then decompose by attack on iron[21] with loss of 1 mol of CO_2. The new complex (**9** or **10**) can decompose by abstraction of a proton from methanol or from the $HFe_3(CO)_{11}^-$ anion,[7,20] if no other proton source is available; a nitrene or nitrene complex is never passed through.

The closest model for complexes of type **9** and **10** is bis(phenylnitroso)hexacarbonyldiiron (**11**) prepared by



11

Koerner von Gustorff and Jun.[22] Reduction of **11** gives aniline and small amounts of nitrosobenzene. The presence of aniline suggests that complexes of this type may be involved.

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[14] J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965), and references cited therein.

[15] J. H. Hall, J. W. Hill, and H. Tsai, *Tetrahedron Lett.*, 2211 (1965), and references cited therein; phenylnitrene inserts into cyclohexane to give *N*-phenylcyclohexylamine.

[16] The structure of the hydrodoundecacarbonyltriferrate anion has been determined: (a) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965); (b) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).

[17] A bridging CO is more like an organic carbonyl group than is a terminal CO. It has also been noted that Lewis basicity may be a general property of the bridging carbonyl ligand.[18]

[18] N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969).

[19] See also (a) Sr. A. Alich, N. J. Nelson, and D. F. Shriver, *Chem. Commun.*, 254 (1971); (b) J. C. Katz and C. D. Turnipseed, *ibid.*, 41 (1970).

[20] P. L. Pausen, "Organometallic Chemistry," St. Martins Press, New York, N. Y., 1967, pp 91, 92.

[21] Ligand displacement on iron by $M^+{-}O^-$ (where M is N, S, P, As) is known; see (a) W. Strohmeier, J. F. Guttenberger, and G. Popp, *Chem. Ber.*, **98**, 2248 (1965); (b) W. Hieber and A. Lipp, *ibid.*, **92**, 2085 (1959); (c) W. Hubel in "Organic Syntheses *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, p 322. (d) See also H. Alper, *Organometal. Chem. Syn.*, **1**, 69 (1970).

[22] (a) E. Koerner von Gustorf and M. J. Jun, *Z. Naturforsch.*, **20B**, 521 (1965); prepared photochemically from $Fe(CO)_5$ and nitrobenzene. (b) E. Koerner von Gustorf, M. C. Henry, R. E. Sacher, and C. DiPietro, *ibid.*, **21B**, 1152 (1966).

The carbonyliron fragments[23] which remain would undergo further decomposition and/or regeneration of the starting reagent, $Fe_3(CO)_{12}$; the latter is likely since a less than molar ratio of reagent brings about reduction. We hope to obtain more information on this reaction from further experiments.

Experimental Section

General.—Capillary melting points were taken with a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared (ir) spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer, calibrated with the 1944 and the 1601 cm^{-1} bands of polystyrene. Nuclear magnetic resonance (nmr) spectra were determined with a Varian A-60 spectrometer; the chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane used as internal standard; coupling constants (J) are accurate to ± 0.5 Hz. Vapor phase chromatography (vpc) was carried out isothermally on an F & M Model 720 thermal conductivity gas chromatograph using the following aluminum columns: A, 2 ft × 0.25 in., 10% UCW98 on Chromosorb P 60/80 mesh; B, 4 ft × 0.25 in., similarly packed; C, 2 ft × 0.25 in., 10% Carbowax 1540 on Chromosorb W, acid washed, 60/80 mesh. The reaction products were determined quantitatively by the internal standardization method.[24] Relative percentages were calculated with a Disc integrator, made by Disc Instruments, Inc. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6D mass spectrometer. Ultraviolet (uv) and visible spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer and standardized using holmium oxide glass. Mössbauer spectra were recorded at Brookhaven National Laboratory.[12] Analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y., or Spang Microanalytical Laboratory, Ann Arbor, Mich. Column chromatography was carried out using the "Dry Column" method of Loev[25] on silica gel approximately grade III (60–200 mesh). The commercial nitroaryls were purified by recrystallization or distillation. The standards were commercial samples or material isolated from the reduction reactions.

1-(*p*-Acetamidophenyl)-1,3-butadiene (3).—To a stirred solution of 35.04 g (0.20 mol) of 1-(*p*-nitrophenyl)-1,3-butadiene (1)[26] in 850 ml of glacial acetic acid, 850 ml of acetic anhydride, and 60 g of sodium acetate was added 100 g (1.53 g-atoms) of zinc dust over 20 min. The solution was stirred for an additional 2 hr at room temperature. Excess zinc and sodium acetate were removed by suction filtration, and the yellow solution was concentrated under reduced pressure. The yellow solid was allowed to stand overnight in contact with 1 l. of dilute ammonium hydroxide; the solid was broken up, placed in a Büchner funnel, and washed with several liters of water. The air-dry solid was dissolved in 800 ml of benzene, filtered, decolorized with Norit, and cooled in a refrigerator. The yellow crystals were dried on a Büchner funnel and washed with water. The yield was 20.5 g (55%) of yellow solid, mp 139–145°. The analytical sample was recrystallized twice from benzene as a very light yellow powder: mp 161–163° (corrected) (sealed evacuated tube); ir ν ($CHCl_3$) 3434 (NH), 1690 (C=O), 1601, 1588, and 1514 cm^{-1}; nmr δ (DMSO-d_6) 9.94 (broad s, 1, -NHAc), 7.25–7.80 [$(AB)_2$ q, d at 7.64, J = 9 Hz, d at 7.40, J = 9 Hz, 4, ArH), 6.20–6.90 (m, 3, -HC=CHCH=), 5.03–5.57 (m, 2, $=CH_2$), and 2.10 (s, 3, $-COCH_3$).

Anal. Calcd for $C_{12}H_{13}NO$: C, 77.00; H, 7.00; N, 7.47. Found: C, 77.09; H, 7.13; N, 7.24.

1-(*p*-Aminophenyl)-1,3-butadiene (4).—A solution of 17.6 g of potassium hydroxide in 12.6 ml of water was diluted to 50 ml with methanol before adding 7.70 g (41.0 mmol) of 1-(*p*-acetamidophenyl)-1,3-butadiene (3). The mixture was heated for 15 min on a steam bath, with stirring; 5 ml of water was added; and heating was continued for 15 min. Ether extraction yielded 4.22 g of a red liquid which was distilled to yield 2.22 g (37%) of colorless liquid, bp 84–86° (0.04–0.05 mm). The analytical sample of 4 was redistilled: ir ν (CCl_4) 3477 and 3392 (NH_2), 1621, 1601, and 1516 cm^{-1}; nmr δ (CCl_4) 6.17–7.12 [$(AB)_2$ q, d at 6.98, J = 8 Hz, d at 6.33, J = 8 Hz, 4, ArH), 5.92–6.49 (m, 3, -CH=CH=CH=), 4.79–5.27 (m, 2, $=CH_2$), and 3.43 (broad s, 2, $ArNH_2$).

Anal. Calcd for $C_{10}H_{11}N$: C, 82.75; H, 7.63; N, 9.65. Found: C, 82.60; H, 7.50; N, 9.71.

Its phenylthiourea derivative was prepared by heating with an excess of phenyl isothiocyanate. Several recrystallizations from aqueous ethanol gave an off-white solid, mp 137–140° dec.

Anal. Calcd for $C_{17}H_{16}N_2S \cdot H_2O$: C, 68.55; H, 6.08. Found: C, 68.66; H, 5.73.

1-(*p*-Aminophenyl)-1,3-butadienetricarbonyliron (2). A.—A mixture of 2.18 g (15.0 mmol) of 1-(*p*-aminophenyl)-1,3-butadiene (4) and 15 ml (23 g, 0.11 mol) of pentacarbonyliron[4] was heated under nitrogen, with stirring, at 110–115° for 24 hr. Removal of excess $Fe(CO)_5$ yielded a yellow solid. Its acetone solution was filtered, and upon solvent removal a tarry solid remained. This solid was heated with four 125-ml portions of ligroin (bp 60–90°) and the combined solutions were cooled to −78°. The yellow crystals weighed 0.38 g. The filtrate was concentrated to yield an additional 0.49 g. Evaporation to dryness followed by recrystallization of the residue from petroleum ether (bp 30–60°) yielded an additional 0.53 g. The total yield was 1.40 g (33%), mp 77.5–78.5°. The analytical sample was recrystallized from petroleum ether as golden crystals: mp 95.5–96° (corrected); ir ν (CCl_4) 3482 and 3402 (NH_2), 2047, 1980, and 1973 (C≡O), and 1257 cm^{-1} (CN); nmr δ ($CDCl_3$) 6.16–7.35 [$(AB)_2$ q, d at 8.05, J = 8 Hz, d at 6.49, J = 8 Hz, 4, ArH), 5.75 (dd, 1, J = 10 Hz, H_2, complexed vinyl proton), 5.05–5.54 (m, 1, H_3, complexed vinyl proton), 3.48 (broad s, 2, $ArNH_2$), 2.10 (d, 1, J = 9.5 Hz, H_1, complexed vinyl proton), 1.77 (dd, 1, J = 7.5 Hz, H_5, complexed vinyl proton), and 0.52 (dd, 1, J = 9.5, 2.5 Hz, H_4, complexed terminal vinyl proton).

Anal. Calcd for $C_{13}H_{11}FeNO_3$: C, 54.80; H, 3.89; N, 4.92. Found: C, 55.08; H, 3.68; N, 5.21.

B.—A mixture of 1.75 g (10.0 mmol) of 1-(*p*-nitrophenyl)-1,3-butadiene (1), 12.0 g of dodecacarbonyltriiron[4] (containing *ca.* 10% methanol), and 2.5 ml of methanol in 100 ml of benzene was stirred at 70° for 15 hr. The mixture was filtered, decolorized with charcoal, and evaporated. The residue was triturated with pentane and filtered to give 2.27 g (80%) of yellow-gold solid, mp 80–86°. Two recrystallizations from petroleum ether gave a pure sample, mp 95.5–96.5° (corrected), no depression by mixture melting point with previously obtained material.

General Reaction Procedure for the Reduction of Nitroaryls. A.—The nitroaryl (10 mmol) was refluxed overnight with either 5.0 g (methanol free)[8] or with 6.0 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol) (*ca.* 10 mmol) and 2.5 ml of absolute methanol in 100 ml of benzene under nitrogen. The reaction mixture was filtered, and the collected residue was washed with 100–200 ml of a solvent for the amino product. The filtrate was then concentrated to *ca.* 25 ml on a rotary evaporator. An internal standard (equivalent to 10 mmol of arylamine) was added. Product identification and relative percentages were determined by vpc, calibrating with authentic mixtures. Details are presented in Table II and yields are summarized in Table I.

B.—For certain arylamines, the product was isolated by evaporating a filtered solution to dryness. *p*-Aminophenyl gave a solid from benzene, 0.42 g (38%), mp 160–180° dec (lit.[27] mp 186°). *m*-Aminophenol yielded crystals from benzene, 0.72 g (66%), mp 120.5–121.5° (lit.[27] mp 123°). *p*-Aminoacetophenone was recrystallized from ligroin (bp 90–120°), 1.23 g (91%), mp 104–105° (lit.[27] mp 106°). *p*-Aminoacetanilide gave crystals from benzene, 1.16 g (77%), mp 158–160° (lit.[27] mp 162–162.5°).

Determination of Evolved Carbon Dioxide.—Escaping CO_2 gas was trapped in a moisture-protected tube of Ascarite[28] connected to the top of the reflux condenser. A positive stream of dry, CO_2-free nitrogen gas was bubbled through the reaction mixture. The results are given in Table III.

Reduction of Nitrobenzene.—Nitrobenzene was reduced using general reaction procedure A and varying the quantity of $Fe_3(CO)_{12}$. The results are presented in Table IV.

Time Study of the Reduction of Nitrobenzene with Dodeca-

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[23] The chemistry of such species is unknown; however, organometallic oxo metal complexes are known; see M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1567 (1964).

[24] (a) L. Szepesey, "Gas Chromatography," English translation by E. D. Morgan, Iliffe Books, London, 1970, pp 133, 134, 266. (b) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[25] B. Loev and M. M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

[26] G. A. Ropp and E. C. Coyner in "Organic Syntheses," Collect. Vol., IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 727.

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TABLE II

CONDITIONS FOR REDUCTION OF NITROARYLS

X	Reaction conditions	Vpc analysis Column and column temp, °C	 Internal standard	 Amine, %
H	*a*	A, 100	Nitrobenzene[e]	77
	b	A, 100	Nitrobenzene[e]	76
p-Cl	*a*	A, 162	Biphenyl[e]	89
	b	A, 160	Biphenyl[e]	82
o-Cl	*a*	A, 125	Biphenyl[e]	89
	b	A, 122	Biphenyl[e]	84
p-CH_3	*a*	A, 125	Biphenyl[e]	73
	b	A, 125	Biphenyl[e]	73
o-CH_3	*a*	A, 120	Biphenyl[e]	87
m-NH_2	*a*	C, 170	*p*-Bromoaniline[f]	95
p-NH_2	*a*	C, 150	*p*-Bromoaniline[f]	63
m-NO_2	*c*	C, 170	*p*-Bromoaniline[f]	77
p-CO_2Et	*b*	C, 170	*p*-Bromoaniline[f]	83
o-Br	*b*	A, 125	Biphenyl[e]	86
p-OCH_3	*b*	C, 140	*p*-Bromoaniline[e]	84
p-OH	*b, d*			38[d]
m-OH	*b, d*			66[d]
p-$COCH_3$	*b, d*			91[d]
p-$NHCOCH_3$	*b, d*			77[d]

[a] General reaction A using 5.0 g of methanol-free $Fe_3(CO)_{12}$. [b] General reaction A using 6.0 g of $Fe_3(CO)_{12}$ containing *ca.* 10% CH_3OH. [c] General reaction A using 10.0 g of $Fe_3(CO)_{12}$ containing *ca.* 10% CH_3OH and 5.0 ml of CH_3OH. [d] Product isolated. [e] 0.01 mol of standard added. [f] 0.005 mol of standard added.

TABLE III

EVOLVED CARBON DIOXIDE DURING REDUCTION

X	Avg CO_2, %
H	101
p-Cl	95
o-Cl	84
p-CH_3	106
p-OCH_3	104
o-Br	84
p-$COCH_3$	85
p-$NHCOCH_3$	103
p-$CO_2CH_2CH_3$	87
o-Biphenyl	99

TABLE IV

STUDY OF THE RELATIONSHIP OF THE REACTANTS IN NITROBENZENE REDUCTION

Mole ratio[a]	Vpc column[b,c]	Yield of aniline, %	Yield of nitrobenzene, %
1:3	A	75	0
1:2	A	77	0
1:1	A	77	0
1:0.8	B	70	0
1:0.75	A	75	16
1:0.7	B	66	5
1:0.6	B	64	18
1:0.5	B	46	30
1:0.4	B	37	42
1:0.2	B	22	69

[a] $C_6H_5NO_2$:$Fe_3(CO)_{12}$ (methanol-free). [b] Column temperature maintained at 100°. [c] Internal standard, *p*-dibromobenzene.

TABLE V

RELATIVE PER CENT OF ANILINE AND NITROBENZENE WITH TIME

Time, hr	Nitrobenzene, %	Aniline, %
0.5	80	6
1.0	65	16
1.5	59	20
2.0	47	27
2.5	42	47
3.0	19	60
3.5	7	65
4.0	4	73
5.0	0	79
5.5	0	80
6.5	0	78
7.0	0	84
7.5	0	84
17	0	76

carbonyltriiron[4]-Methanol.—A mixture containing 1.23 g (10.0 mmol) of nitrobenzene, 5.03 g (10.0 mmol) of methanol-free $Fe_3(CO)_{12}$[8], 2.5 ml of methanol, and 2.35 g (10.0 mmol) of *p*-dibromobenzene was refluxed, with stirring, under nitrogen. At 0.5-hr intervals 0.5-ml aliquots were removed, filtered, and analyzed by vpc (column A, 74°). The results are presented in Table V. A control showed no loss of *p*-dibromobenzene under reaction conditions.

Further Studies on the Reduction of Nitrobenzene to Aniline with Dodecacarbonyltriiron-Methanol. A.—A mixture containing 6.0 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol) and 2.5 ml of methanol in 100 ml of benzene was refluxed, with stirring, under nitrogen. After 5 hr, 0.25-ml aliquots were removed at 15-min intervals.[29] Filtration of these aliquots yielded a red solid (kept under nitrogen) (*vide infra*) and a green solution. The filtrates were volumetrically diluted with cyclohexane and the absorbance at 602 mμ was monitored. The $Fe_3(CO)_{12}$ was consumed after 7.5 hr.

After 8 hr, 1.23 g (10.0 mmol) of nitrobenzene in 5 ml of benzene was added and the mixture was refluxed for an additional 16 hr. The solution was filtered and 2.36 g (10.0 mmol) of *p*-dibromobenzene was added. The yield of aniline (column A, 74°), was 37%; in addition, unreacted nitrobenzene (34%) was present.

B.—A mixture containing 0.62 g (5.0 mmol) of nitrobenzene, 3.20 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol), and 1.5 ml of methanol in 50 ml of benzene was refluxed for 4 hr, with stirring, under nitrogen. The green filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in a minimum quantity of methylene chloride, a small amount of silica gel was added, and the solvent was removed *in vacuo*. The dried mixture of silica gel and residue was added to the top of a column containing 70 g of silica gel.

The first fraction, eluted with petroleum ether, contained $Fe_3(CO)_{12}$. The second fraction, eluted with benzene, contained traces of a yellow solid: ir ν (CS_2) 2084 (mw), 2050 (s), and 2043 cm^{-1} (vs) (C≡O); the material rapidly deteriorated. Other fractions eluted with more polar solvents, contained only nitrobenzene and aniline.

Reaction of Dodecacarbonyltriiron and Methanol in Benzene.—A mixture containing 6.0 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol), 2.5 ml of methanol, and 100 ml of benzene was refluxed under nitrogen with stirring. After 5 hr,[29] samples were filtered. The red solid formed a red solution in methanol: visible max 543 mμ; ir ν (DMF) 2040 (sh), 1998, 1964 (C≡O), and 1829 cm^{-1} (w) (bridging C═O); ν (cyclohexane) 2043, 1999, 1953 (C≡O), and 1812 cm^{-1} (bridging C═O).

Preparation of Hydridoundecacarbonyltriferrate Salts. A. Triethylammonium Hydridoundecacarbonyltriferrate (5).—This complex was prepared from pentacarbonyliron[4] and triethylamine as described by Case and Whiting.[6a] The impure material was usually pyrophoric. The recrystallized material (aqueous methanol) was obtained as large, dark red needles (stable for several weeks at 0°): visible max (MeOH) 545 mμ (ε 2.4 × 10^3); ir ν (DMF) 3540 (broad) (NH), 1947 (sh), 1975 (s), 1999 (vs), and 2062 cm^{-1} (vw) (C≡O) {lit.[6a] visible max (EtOH) 540 mμ (ε 3.06 × 10^3); lit.[30] ir [for unspecified salt of $HFe_3(CO)_{11}^-$] ν (DMF) 1950 (w), 1980 (m), 2004 (s), and 2070 cm^{-1} (vw) (C≡O)}.

B. Tetramethylammonium Hydridoundecacarbonyltriferrate (6).—This complex was prepared from dodecacarbonyltriiron[4] in

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(29) Up to 5 hr the solution is heterogeneous. After 5 hr the solution is homogeneous.

(30) W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 3080 (1965).

alkaline methanol by neutralization and treatment with tetramethylammonium iodide as described by Heiber and Brendel.[7a] This salt was always *pyrophoric* when impure. The dark red crystals from acetone were dried *in vacuo:* visible max (MeOH) 545 mμ (ϵ 2.7 × 10^3); ir ν (DMF) 1962 (sh) and 1973 (m), 1997 (vs) and 2066 cm^{-1} (w) (C≡O) [lit.[6a] visible max (aqueous MeOH) 540 mμ (ϵ 3.09 × 10^3); lit.[30] ir, see A].

Reduction of Nitrobenzene with Hydridoundecacarbonyltriferrate Salts. A. Reduction with 5.—A mixture containing 1.23 g (10.0 mmol) of nitrobenzene, 5.79 g (10.0 mmol) of **5**, and 100 ml of dry benzene was refluxed for 15 hr under nitrogen. The reaction was worked up as in general reaction procedure A. The yield of aniline (column A, 74°) was 62%. A second reaction was carried out using 5.0 mmol of **5**. The yield of aniline (column A, 74°) was 38%.

B. Reduction with 6.—A mixture containing 551 mg (1.00 mmol) of **6** and 123 mg (1.00 mmol) of nitrobenzene in 10 ml of dry benzene was refluxed for 15 hr under nitrogen. The solution was worked up as above. The yield of aniline (column A, 74°) was 34%.

Reaction of Nitrobenzene with Dodecacarbonyltriiron in the Absence of Methanol. Formation of Bis(phenylnitrino)enneacarbonyltriiron (7b). A.—A mixture containing 2.46 g (20.0 mmol) of nitrobenzene and 10.1 g (20.0 mmol) of methanol-free $Fe_3(CO)_{12}$[8] in 200 ml of dry benzene was refluxed for 15 hr under nitrogen. The solution was filtered, the residue was washed with dichloromethane, and the combined solutions were evaporated *in vacuo*. The red-purple residue was taken up in a minimum amount of dichloromethane, mixed with a small amount of silica gel, and evaporated to dryness *in vacuo*. This silica gel was added to the top of a column containing 200 g of silica gel. The first fraction, a diffuse green band eluted with petroleum ether, was $Fe_3(CO)_{12}$. The second fraction, a purple-red band eluted with petroleum ether, yielded 1.19 g of black crystals, mp 143–145° (corrected) (18%). The analytical sample was recrystallized from pentane, black crystals: mp 143° (corrected); λ_{max} (cyclohexane) (ϵ × 10^4) 330 (1.17), 365 (1.02), and 553 mμ (0.31); ir ν (CS_2) 2067 (vs), 2043 (s), 2022 (s), 1972 (vw), and 1956 cm^{-1} (vw) (C≡O); nmr δ ($CDCl_3$) 6.96 (s, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 602 (2), 574 (90), 546 (97), 518 (5), 490 (49), 462 (81), 434 (97), 406 (86), 378 (39), 166 (24), 91 (93), 77 (99), 65 (95), 64 (50), 40 (45), 32 (46), and 28 (100); mol wt calcd for $C_{21}H_{10}N_2Fe_3O_9$, 602. The isotope distributions for four principle fragments are given in Table VI.

TABLE VI

MASS SPECTRA OF ISOTOPE PEAKS OF **7b**

Peak	Found, %	Calcd, %
+1	31.9	29.7
574		assuming 100
−2	19.5	19.1
+1	28.0	28.6
546		assuming 100
−2	19.1	19.1
+1	26.8	26.4
490		assuming 100
−2	21.4	19.1
+1	25.2	24.2
462		assuming 100
−2	19.6	19.1

Anal. Calcd for $C_{21}H_{10}N_2Fe_3O_9$: C, 41.85; H, 1.80; N, 4.65. Found: C, 41.64; H, 1.77; N, 4.60.

The third fraction, eluted with petroleum ether, gave azobenzene, 38 mg (4%) of orange needles, mp 66–67° (corrected), no depression by mixture melting point with authentic material.

B.—A refluxing mixture containing 11.02 g (21.90 mmol) of methanol-free $Fe_3(CO)_{12}$[8] and 4.37 g (35.4 mmol) of nitrobenzene in 219 ml of dry benzene generated 98% of theoretical carbon dioxide. Column chromatography as described in A yielded 860 mg (8%) of **7b** and 840 mg (26%) of azobenzene.

C.—A mixture containing 615 mg (5.00 mmol) of nitrobenzene and 2.52 g (5.00 mmol) of methanol-free $Fe_3(CO)_{12}$[8] in 50 ml of cyclohexane was refluxed for 15.5 hr under nitrogen. Vpc[31] of the filtrate showed no detectable *N*-phenylcyclohexylamine. Column chromatography of the filtrate as described in A, using 42 g of silica gel, yielded 173 mg (6%) of **7b**.

Reduction of *o*-Nitrobiphenyl with Dodecacarbonyltriiron–Methanol.—*o*-Nitrobiphenyl, 1.99 g (10.0 mmol), when treated with 6.0 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol) according to general reaction procedure A, generated 436 mg (9.90 mmol, 99%) of carbon dioxide. After filtering, the filtrate was reduced in volume, a small amount of silica gel was added, and the solvent was evaporated *in vacuo*. This silica gel was added to the top of a column containing 100 g of silica gel. *o*-Aminobiphenyl, 1.57 g (92.5%), mp 46.5–47.5 (corrected) (lit.[27] mp 49–50°), was eluted with benzene.

Reaction of *o*-Nitrobiphenyl with Dodecacarbonyltriiron.—*o*-Nitrobiphenyl, 1.99 g (10.0 mmol), was treated with 5.03 g (10.0 mmol) of methanol-free $Fe_3(CO)_{12}$[8] in 100 ml of dry benzene as above. Carbon dioxide, 220 mg (5.0 mmol, 50%), was trapped. A similar work-up and column chromatography were carried out. Elution with petroleum ether removed $Fe_3(CO)_{12}$ and unidentified trace solids. Elution with carbon tetrachloride yielded 180 mg (10%) of *o*-azobiphenyl, orange needles from hexane, mp 138–140° (corrected) (lit.[27] mp 145°); its spectral characteristics were identical with those of authentic material.

Prior to recrystallization, solid from the above fraction was taken up in petroleum ether; 15 mg of an insoluble white solid remained, mp 239.5–242° (corrected). An additional 7 mg of insoluble white solid was obtained from the column by further elution with carbon tetrachloride. The combined 22 mg (1.3%) of material was carbazole (lit.[27] mp 247°), no depression on mixture melting point with authentic material. Elution with benzene yielded 900 mg (54%) of *o*-aminobiphenyl, mp 42–45° (corrected) (lit.[27] mp 49–50°). The solid was converted into the acetamide and gave a white solid from ligroin (bp 90–120°), mp 119–120° (corrected) (lit.[27] mp 121°). Elution with chloroform yielded 280 mg (17%) of *o*-hydrazobiphenyl, crystals from alcohol, mp 183.5–184.5° (corrected) (lit.[27] mp 182°).

Elution with more polar solvents yielded trace amounts of uncomplexed materials which were not characterized.

Repetition of this experiment with a different batch of methanol-free $Fe_3(CO)_{12}$[8,32] and carefully dried solvents gave similar results.

Reduction of Nitrosobenzene. A. With Dodecacarbonyltriiron–Methanol.—Nitrosobenzene, 1.07 g (10.0 mmol), $Fe_3(CO)_{12}$, 6.0 g (containing *ca.* 10% methanol), and methanol, 2.5 ml, when refluxed for 16 hr in 100 ml of benzene, with stirring and under nitrogen, yielded aniline (55%).[33] Azobenzene and azoxybenzene were detected, although the yields were not determined.[34]

B. With 6.—Nitrosobenzene, 96.3 mg (0.900 mmol), and **6**, 495 mg (0.900 mmol), in 9 ml of benzene were refluxed for 17 hr, with stirring, under nitrogen. Carbon dioxide, 36 mg (0.83 mmol, 92%), was trapped. The yield of aniline was 26%.[33] In addition, azobenzene (22%) and azoxybenzene (31%) were found.[35]

Reactions of Bis(phenylnitroso)hexacarbonyldiiron (11).[22] **A. With Dodecacarbonyltriiron–Methanol.**—A mixture containing 494 mg (1.00 mmol) of **11**, 1.25 g of $Fe_3(CO)_{12}$[4] (containing *ca.* 10% methanol, *ca.* 2 mmol), and 0.5 ml of methanol in 20 ml of benzene was refluxed for 16.5 hr, with stirring, under nitrogen. The yield of aniline was 55%.[33]

B. With 5.—A mixture containing 494 mg (1.00 mmol) of **11** and 579 mg (1.00 mmol) of **5** in 20 ml of dry benzene was refluxed for 15.5 hr, with stirring, under nitrogen. Trapped carbon dioxide totaled 15%. The yield of aniline was 21%;[33] a 2% yield of nitrosobenzene was also detected.[36] With 2.0 mmol

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[31] Aniline detected, column B, 74°; the column was cleaned by raising the temperature to 160°. A sample was analyzed at 160° for *N*-phenylcyclohexylamine against prepared samples of known composition.

[32] Complex **7b** formed in a reaction using reagent from the same batch without aniline formation.

[33] Aniline analysis was carried out as previously described (column B, 80°; *p*-dibromobenzene).

[34] The oven temperature was raised to 185° removing azobenzene and azoxybenzene. These compounds were collected and compared to authentic samples: identical infrared spectra, no depressions on mixture melting point.

[35] Yields of azobenzene and azoxybenzene were determined against prepared samples of known composition (column B, 185°; *p*-dibromobenzene).

[36] Presence and yield of nitrosobenzene was determined by comparison to prepared samples of known composition (column B, 80°; *p*-dibromobenzene).

of **5**, the carbon dioxide trapped amounted to 17%, the aniline found was 44%,[33] and the nitrosobenzene detected[36] was 4%. A third reaction with 4.0 mmol of **5** also gave carbon dioxide (11%), aniline (44%),[33] and nitrosobenzene (4%).[36]

Registry No.—**2**, 33479-92-4; **3**, 33482-90-5; **4**, 33537-34-7; **4** (phenylthiourea derivative), 33482-91-6; **5**, 18129-63-0; **6**, 33479-90-2; **7b**, 33519-79-8; **11**, 33479-91-3; dodecacarbonyltriiron, 15444-70-9; methanol, 67-56-1; nitrobenzene, 98-95-3; aniline, 62-53-3; *o*-nitrobiphenyl, 86-00-0; nitrosobenzene, 586-96-9.

The Isomerization and Disproportionation of Acylcobalt Carbonyls

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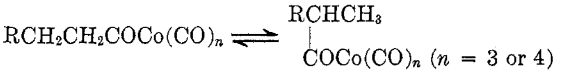
Received August 27, 1971

When acylcobalt carbonyls, $RCOCo(CO)_4$, are left standing under a nitrogen atmosphere, they not only slowly isomerize but disproportionate irreversibly to yield a mixture of aldehydes and olefins. Thus when R is n-C_3H_7, the products are n- and isobutyraldehyde and propylene, formed in accordance with the reaction scheme shown in Chart I. The report that nonpolar solvents inhibit the isomerization of acylcobalt carbonyls is confirmed, but this failure is now shown to arise because of the competing disproportionation reaction. In nonpolar solvents the olefin–metal hydride π complex required as an intermediate for the isomerization reacts with the acyl compounds to produce the aldehyde and olefin. With polar solvents, however, the π complex is rapidly converted to the σ complex and thence to the isomerized acylcobalt compound. The implications of these reactions for the mechanism of the oxo reaction in which the acylcobalt carbonyls play a vital role are discussed.

Although the room temperature, spontaneous interconversion of branched and straight chain acylcobalt carbonyls (eq 1) is well documented,[1-6] certain features



$$\mathrm{RCH_2CH_2COCo(CO)_n} \rightleftharpoons \underset{\displaystyle \mathrm{COCo(CO)_n}\ (n = 3 \text{ or } 4)}{\overset{\displaystyle \mathrm{RCHCH_3}}{|}} \qquad (1)$$

of the isomerization are difficult to explain. Furthermore, these acyl compounds are intermediates in the oxo reaction and whether such interconversions affect the product distribution of the aldehydes, especially in the stoichiometric hydroformylation, has not been explicitly ascertained. Accordingly we undertook an investigation of this reaction in an effort to elaborate the details of the interconversion.

In our initial experiments we planned to prepare the acylcobalt carbonyls by the published procedure (eq 2)

$$\mathrm{RCOX + NaCo(CO)_4 \longrightarrow RCOCo(CO)_4 + NaX} \qquad (2)$$

and, after a lapse of time during which interconversion of the acyl compounds would be permitted to proceed, we planned to hydrogenolyze the resulting mixture with $HCo(CO)_4$ (eq 3) in order to duplicate the last step of the stoichiometric hydroformylation.

$$\mathrm{RCOCo(CO)_n + HCo(CO)_4 \longrightarrow RCHO + Co_2(CO)_{4+n}} \qquad (3)$$

In the course of studying this reaction, we found, much to our surprise, that aldehydes were formed even before the $HCo(CO)_4$ was added, and that in addition, olefins possessing one carbon less than the starting acyl compound were also formed. This observation indicated that not only were the acylcobalt carbonyls undergoing isomerization but they were disproportionating as well.

Results and Discussion

Treatment of n- and isobutyrylcobalt tetracarbonyl under three different sets of conditions gave the results shown in Table I. These results are most conveniently discussed in terms of the reaction scheme shown in Chart I.

TABLE I

ISOMERIZATION AND DISPROPORTIONATION OF n- AND ISOBUTYRYLCOBALT CARBONYL[a]

Butyryl-cobalt carbonyl	Atm	Solvent	Butyraldehydes Yield, mmol[b]	Butyraldehydes n, %	Butyraldehydes Iso, %
n	CO	Pentane	0.15	95	5
Iso	CO	Pentane	0.08	0	100
n	N_2	Pentane	0.55	77	23
Iso	N_2	Pentane	0.55	8	92
n	N_2	Ethyl ether	0.27	51	49
Iso	N_2	Ethyl ether	0.07	21	79

[a] 2.6 mmol of $NaCo(CO)_4$, 2 mmol of acyl chloride in 10 ml of solvent for 24 hr. [b] The yields of propylene were proportional to the yields of aldehydes.

Under 1 atm of CO, relatively little of anything happens in 24 hr to either of the acylcobalt carbonyls, probably because the first steps in the reaction sequence involve the loss of CO and hence the reaction is inhibited. However, when the reaction is repeated under N_2 rather than under CO, extensive isomerization and disproportionation occurs. The total yield of aldehydes is the same (perhaps fortuitously, exactly the same, 55%) regardless of the structure of the starting isomer. The yield is based on the stoichiometry

$$\mathrm{2RCOCo(CO)_n \longrightarrow RCHO + R_{-H} + Co_2(CO)_{2n}} \qquad (4)$$

Under our conditions, the reaction does not go to completion because of the self-inhibiting effect of the CO liberated during the reaction. When ethyl ether rather than pentane is used as a solvent, there is much more extensive interconversion of isomers but appreciably less disproportionation; with isobutyrylcobalt carbonyl, practically no disproportionation occurs.

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