Journal of Organometallic Chemistry, 368 (1989) 83–101
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09801

Metathesis and reduction reactions of nitroso compounds with metal carbenes and metal carbonyls

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(Received February 22nd, 1988; in revised form October 4th, 1988)

Abstract

Reaction of nitroso compounds with metal-carbene complexes and metal carbonyls has been investigated. These reactions lead to reduction of the nitroso compounds, primarily to the corresponding azo- and azoxy compounds. Metal-nitrene complexes have been proposed as intermediates in these reactions. These intermediates couple rapidly with the unreacted nitroso compound, or enter into nitrene-like reactions with external or internal trapping agents. Reaction of metal carbonyls with nitrosoarenes and photolysis has been found to be an effective method for the reduction of nitrosoarenes to azoxyarenes, with few problems resulting from overreduction to amines or azo compounds.

Introduction

Recently, chromium(0) and iron(0) carbene complexes have emerged as valuable reagents for organic synthesis [1*]. The analogous mononuclear metal-nitrene complexes, in which the metal exists in a low oxidation state, have never been synthesized [2*], but have been suggested as intermediates in various metal carbonyl-induced processes [3*,4*]. The metathesis reaction between azoarenes and chromium- or tungsten-carbene complexes has recently been shown to produce compounds derived from metal-nitrene complexes [3a,b*]. Metal-nitrene complexes could not be isolated from these reactions due to coupling with the imino ether byproducts. We envisaged that the analogous reaction with nitrosoarenes could potentially give rise to metal-nitrene complexes, with less complications from coupling with the byproduct esters (Scheme 1). We herein report our studies of the reaction of chromium carbene and chromium or iron carbonyl complexes with nitroso compounds, leading to reduction products of the nitroso compounds. The

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* Reference number with asterisk indicates a note in the list of references.

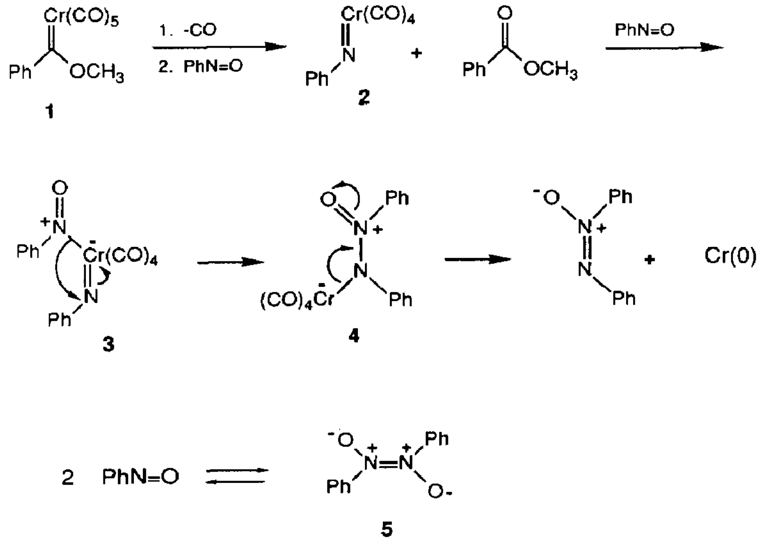
Scheme 1

reaction of nitroso compounds with tungsten carbene complexes has recently been reported [5]. While metal-nitrene complexes could not be isolated from these reactions, they were proposed as intermediates in the reaction.

Reaction of nitroso compounds with metal carbenes

Reaction of nitrosobenzene with carbene complex **1** (Scheme 2) at 65 °C in tetrahydrofuran (THF) solvent for a period of 5 h led to a mixture of azoxybenzene (42%), azobenzene (24%), benzanilide (6%), and methyl benzoate (76%). The reaction did not proceed at lower temperatures, and similar results were obtained if the reaction was performed in the presence of UV-visible irradiation (Table 1). Similarly, reaction of 2-nitroso-2-methylpropane with carbene complex **1** led to a low yield of azoxy-t-butane (20%) and methyl benzoate (66%).

We propose the mechanism in Scheme 2 to explain the formation of azoxybenzene and methyl benzoate. First, a metathesis reaction [6*] occurs between nitrosobenzene and carbene complex **1** [7*] to give methyl benzoate and metal-nitrene complex **2**. Next the metal-nitrene complex combines with unreacted nitrosobenzene, ultimately giving azoxybenzene. A possible mechanism for this process involves coordination of nitrosobenzene to the nitrene complex giving metal-nitrene complex **3**, which undergoes a migratory insertion reaction [8*] to give azoxybenzene after loss of the metal. Alternatively, azoxybenzene could arise via a deoxygenation of the nitrosobenzene dimer **5**, giving methyl benzoate as a



Scheme 2

Table 1

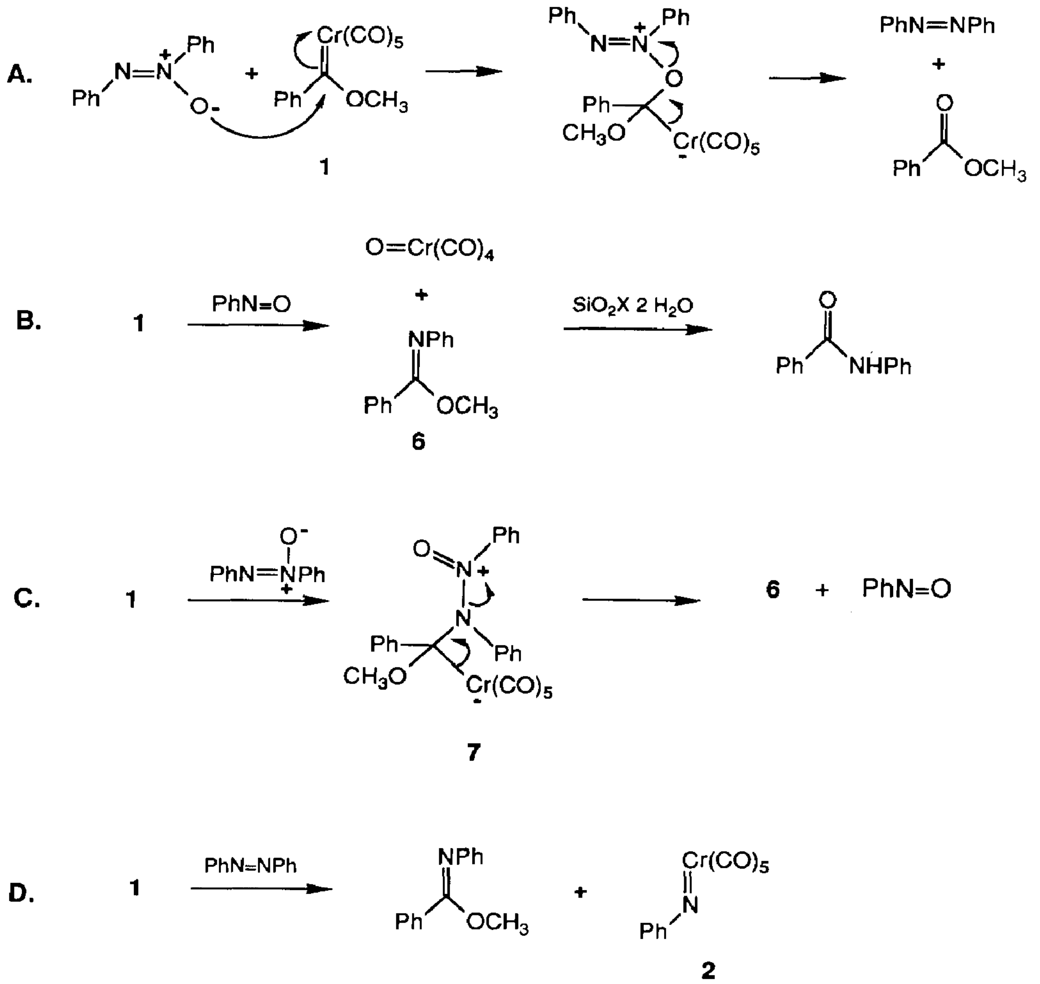
Reaction of nitroso compounds with metal carbonyls

Entry	R	Metal carbonyl	Conditions	Yield A (%) [a]	Yield B (%) [a]
1	Ph	$Cr(CO)_6$	Sunlamp through pyrex at 30 °C	46 [c]	0
2	Ph	$Cr(CO)_6$	THF reflux	5 [c]	0
3	Ph	none	Sunlamp through pyrex at 30 °C	0	0
4	Ph	$Fe(CO)_5$	n-butyl ether at 138 °C	0	14
5	Ph	$Fe(CO)_5$	450W Hg lamp through pyrex at 4 °C	80 [c]	0
6	Ph	$Fe(CO)_5$	Sunlamp through pyrex at 30 °C	96 [c]	4 [c]
7	Ph	$Fe(CO)_5$	30 °C (dark)	2	1
8	Ph	$Fe(CO)_5$	65 °C (dark)	87	5
9	Ph	$Fe(CO)_5$	450W Hg lamp through pyrex at 30 °C	86	14
10	Ph	$Fe(CO)_5$	*N*-methylmorpholine-*N*-oxide at 30 °C	76	2
11	p-$CH_3OC_6H_4$	$Fe(CO)_5$	Sunlamp through pyrex at 30 °C	70	17
12	p-$(CH_3)_2NC_6H_4$	$Fe(CO)_5$	450W Hg lamp through pyrex at 30 °C	50 [c]	0
13 [b]	$(CH_3)_3C$	$Fe(CO)_5$	Sunlamp through pyrex at 30 °C	4	1
14	p-IC_6H_4	$Fe(CO)_5$	Sunlamp through pyrex at 30 °C	60	36
15	p-NCC_6H_4	$Fe(CO)_5$	Sunlamp through pyrex at 30 °C	85 [c]	0

[a] Yields were determined by gas chromatographic analysis unless otherwise noted. All reactions were allowed to continue until the starting nitroso compound had disappeared or until no further change was noted. [b] Also t-butylcarbodiimide (1%) and *N*,*N*′-di-t-butylurea (13%) were obtained. [c] Isolated yields.

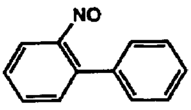
byproduct. Since these reactions were typically performed at 0.04 *M* concentration of nitrosobenzene, the concentration of nitrosobenzene dimer should be minimal [9]. However, since there is an equilibrium between monomer and dimer, we can not rule out this alternative mechanism for the formation of azoxybenzene.

Azobenzene can arise from deoxygenation of azoxybenzene by carbene complex **1** according to the mechanism in Scheme 3A [10*]. We propose three possible mechanisms to explain the formation of benzanilide, all involving hydrolysis of the imino ether **6** as the penultimate step of the reaction. The imino ether **6** could indeed be quantitatively converted to benzanilide by simple filtration through silica gel. Since **6** had a GC retention time very similar to that of azobenzene, the crude reaction mixture was filtered through silica gel before analysis. In the mechanism in Scheme 3B, the initial metathesis reaction proceeds with the opposite regiochemistry of that observed in Scheme 2 to give the imino ether **6** and a chromium oxo compound. In the mechanism in Scheme 3C, the nitrogen of the azoxy compound attacks the electrophilic carbene carbon of complex **1** to generate **7**, which fragments with loss of nitrosobenzene to give the imino ether **6**. In the mechanism in Scheme 3D, a metathesis reaction occurs between azobenzene and carbene complex **1** [3a,b*], giving the imino ether **6** and the nitrene complex **2**. If the reaction between



Scheme 3

complex **1** and nitrosobenzene was allowed to proceed to partial completion, only azoxybenzene (35%) and methyl benzoate were obtained; no azobenzene or benzanilide were formed under these conditions. This suggests that azobenzene and compound **6** are not formed in the initial reaction of nitrosobenzene with complex **1**, but rather in side reactions involving one of the products (azoxybenzene) and complex **1**. Indeed, when azoxybenzene was treated with carbene complex **1** (5 h, 65 ° C, THF), then azobenzene (45%) and benzanilide (30%) were produced. When azobenzene was treated with carbene complex **1** (5 h, 65 ° C, THF), then benzanilide was produced in 11% yield, and azobenzene was recovered in 45% yield. These results confirm that azobenzene and azoxybenzene are both potential sources of benzanilide. Since benzanilide was produced more efficiently from azoxybenzene than from azobenzene, and since azoxybenzene is formed before azobenzene during the reaction, the mechanism in Scheme 3C is probably responsible for the formation of imino ether **6**.



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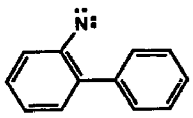

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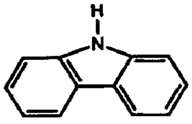

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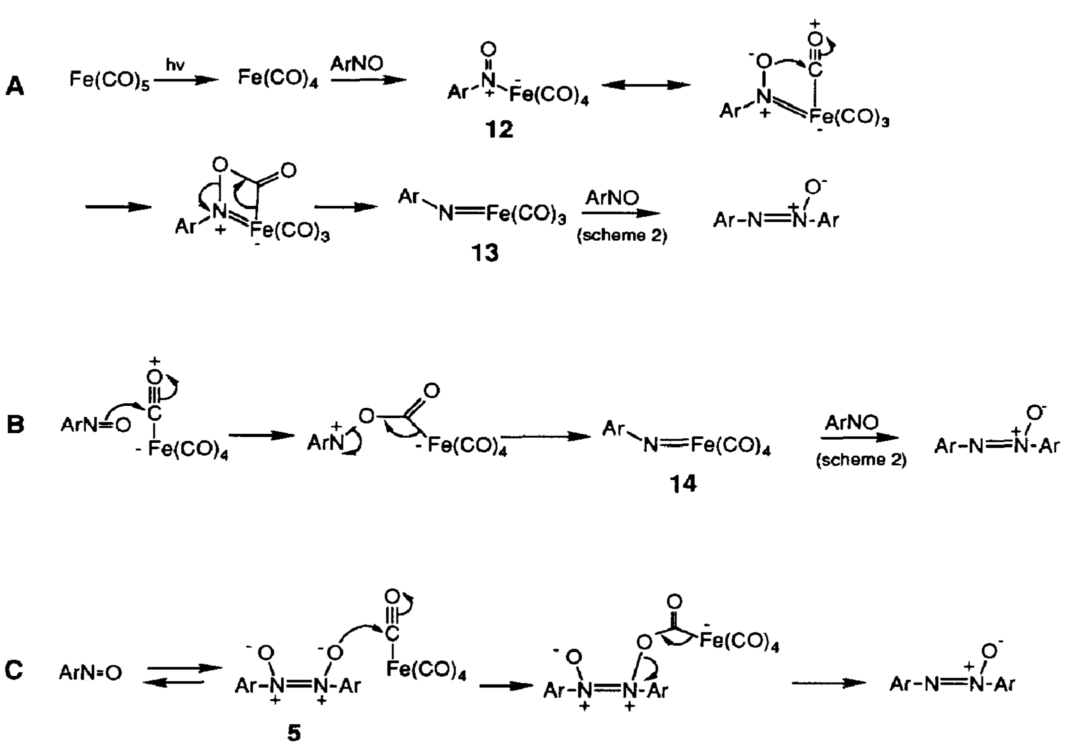
If a metal-nitrene complex is formed in these metathesis reactions, it could not be isolated due to complications from coupling with unreacted nitrosobenzene. These side reactions could not be suppressed even if the reaction was performed with a deficiency (0.5 equivalents) of nitrosobenzene. The reaction could not be performed at lower temperatures, except when induced by photolysis. As a test for the intermediacy of nitrene-like intermediates in these reduction reactions, we allowed 2-nitrosobiphenyl to react with carbene complex **1**. Nitrene **10** [11] and metal-complexed analogs [12] are known to cyclize to carbazole (**11**). When 2-nitrosobiphenyl was treated with complex **1** at 30 °C and under photolysis, carbazole (36%), 2-aminobiphenyl (31%), 2-azobiphenyl (14%), and methyl benzoate (71%) were produced. The formation of carbazole [11] and 2-aminobiphenyl [13*] is highly suggestive of nitrene-like intermediates. The formation of metal-nitrene complexes as intermediates implies that monomeric nitroso compounds and not their dimers are involved in the initial reaction with the carbene complex.

The reaction of metal-carbene complexes with nitroso compounds is complicated by coupling of the nitrene intermediates with the starting nitroso compounds, and also by coupling of the byproducts with the starting carbene complexes. Even when an excess of nitrosobenzene was used in the reaction, azobenzene and benzanilide were still produced in significant amounts. We undertook an investigation of the reaction of metal carbonyls with nitroso compounds as a route to the elusive metal-nitrene complexes (see below). Since metal carbonyls are typically less reactive than Fischer Carbene Complexes, there should be less complications from coupling of the byproducts with metal carbonyls.

Reaction of nitroso compounds with metal carbonyls

The reaction of nitro and nitroso compounds with metal carbonyls has been studied extensively [3*,4*]. To date, these reactions have usually been performed at high temperatures. To isolate metal-nitrene complexes from a reaction such as this will require much milder conditions. Chromium hexacarbonyl and nitrosobenzene did not react significantly with each other even in refluxing THF solution, however if this solution was photolyzed via a sunlamp through pyrex glass, azoxybenzene was produced in 46% yield. A much more facile reaction occurred between nitrosobenzene and iron pentacarbonyl, where photolysis at 4 °C via a Hg vapor lamp led to the production of azoxybenzene (80%). Carbon dioxide was also evolved during these reactions [14*], suggesting that carbon monoxide is involved in the deoxygenation process. Use of excess iron pentacarbonyl led to the formation of more azobenzene at the expense of azoxybenzene. In subsequent studies, the reactions were typically performed using 0.5–1.0 equiv. of iron pentacarbonyl relative to nitroso compound.

Three mechanistic schemes have been proposed by others [3c*,15,16] to explain the conversion of nitrosoarenes to azoxyarenes by low oxidation state metal carbonyls (Scheme 4) [17*]. Mechanisms A and B proceed via the intermediacy of metal-nitrene



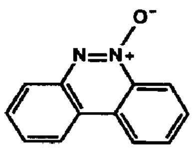
Scheme 4

complexes or free nitrenes. Mechanisms A and B are similar, differing only in the timing of the CO loss. In mechanism C, the nitrosobenzene dimer **10** is deoxygenated by iron pentacarbonyl in a manner similar to an amine oxide [18*].

Mechanism B has been proposed for the reaction of nitrosobenzene with iron pentacarbonyl at 138 ° C in n-butyl ether [3c*]. Our results suggest that the reaction requires a vacant coordination site at iron, presumably created by the dissociation of a CO ligand. Irradiation of iron pentacarbonyl with ultraviolet light or thermolysis is well-known to induce CO dissociation [19*]. Additional support for mechanism A comes from the reaction of nitrosobenzene with iron pentacarbonyl in the presence of *N*-methylmorpholine-*N*-oxide. This compound induces the reaction to go at or below room temperature. The ability of amine oxides to induce the dissociation of CO ligands from iron is well-documented [18*]. In mechanism A, the iron-nitrosobenzene complex **12** is formed, which can undergo intramolecular deoxygenation and loss of CO_2 to give the coordinatively unsaturated nitrene complex **13**. A similar intramolecular deoxygenation of a nitrosobenzene ligand by a carbonyl ligand has been suggested in the iridium(I) and rhodium(I) catalyzed reduction of nitrosobenzene by CO [15]. Unreacted nitrosobenzene then complexes with iron to eventually give azoxybenzene by a mechanism similar to that outlined in Scheme 2. Azoxybenzene can slowly be reduced with azobenzene under the conditions of the reaction; presumably through a mechanism analogous to C, using an azoxy compound rather than a nitroso dimer as substrate. The coupling of free phenylnitrene with nitrosobenzene is not an efficient process [20], suggesting that as predicted the iron-nitrene complex intermediate has substantially different properties from free nitrenes [4*].

Mechanism C has been suggested for the decacarbonyl dichromate dianion reduction of nitrosobenzene [16]. Since there is an equilibrium between monomer and dimer forms of nitroso compounds in solution, this mechanism could be operative in our system [9]. Since we performed the reactions at relatively high dilution (0.04 *M*), the concentration of dimeric forms of nitrosobenzene should be minimal. Further support for the involvement of monomers can be found in Table 1: for example, the reaction also provided similar products using *p*-nitrosoanisole, *p*-nitroso-*N*,*N*-dimethylaniline, and *p*-nitrosoiodobenzene. These compounds are monomeric even in the solid state [21*] and like nitrosobenzene do not form detectable amounts of dimers in solution. The reaction was considerably slower when *p*-nitroso-*N*,*N*-dimethylaniline was used as a substrate in the reaction. The reaction proceeded equally well for *p*-nitrosobenzonitrile, a compound which is more prone to dimer formation than is nitrosobenzene [22]. If benzo[*c*]cinnoline-*N*,*N*′-dioxide (**15**), a nitroso compound in which there is a high concentration of the dimeric form [23], is employed in the reaction with iron pentacarbonyl, it is reduced to benzo[*c*]cinnoline-*N*-oxide (**17**). However, in this reaction, photolysis is not required, suggesting that mechanism C can be operative if there is a high concentration of dimer.

15 **16**



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According to the mechanism in Scheme 4, the metal-nitrene complex **13** is obtained coordinatively unsaturated, and thus it should be very reactive and difficult to isolate. As a further test for the intermediacy of metal-nitrene complex intermediates in these processes, we ran the reaction between nitrosobenzene and iron pentacarbonyl in the presence of potential nitrene trapping agents. Previous studies with alleged chromium-nitrene complexes [3a*] showed that protonation of the nitrene-chromium complexes would lead to amine derivatives [24*]. Protonation of the iron residue from our reactions with hydrochloric acid led to the formation of no organic products. If the reaction between nitrosobenzene and iron pentacarbonyl was performed in the presence of acetic acid, then primarily azobenzene (15%) and azoxybenzene (75%) were formed, along with a small amount of aniline (9%). If the same reaction was performed with the nitrosobenzene being added via a syringe pump over a period of 1 h to a solution of iron pentacarbonyl and acetic acid, then aniline (38%) was formed along with azobenzene (9%) and azoxybenzene (16%). In a control experiment, reaction of azoxybenzene with iron pentacarbonyl and acetic acid provided only azo- and azoxybenzene. This suggests that the metal-nitrene complex forms, but couples very rapidly with nitrosobenzene; only when the nitrosobenzene concentration was kept low could the nitrenoid intermediate be intercepted. We also attempted the reaction of 2-nitrosobiphenyl with iron pentacarbonyl and photolysis. This led to a mixture of 2,2′-azobiphenyl (15%) and 2-aminobiphenyl (22%). The corresponding thermal reaction at 65 °C led to formation of carbazole (10%), azobiphenyl (44%), and 2-aminobiphenyl (35%). Carbazole formation is considerably more efficient in the chromium-carbene induced reactions than in the iron pentacarbonyl-induced reactions, suggesting that the iron-nitrene complex has substantially different reactivity from the chromium-nitrene complex mentioned previously.

Reaction of 2-nitroso-2-methylpropane with iron pentacarbonyl was less efficient than the corresponding reaction involving nitrosoarenes, leading to a low yield of a mixture of azoxy-t-butane, *N*,*N*′-di-t-butylurea, and *N*,*N*′-t-butylcarbodiimide. The course of this reaction is far different from that observed for nitrosoarenes, giving products derived from CO-insertion into the metal-nitrene complex. Ureas and/or iron-ureate complexes have also been obtained from the reaction of organic azides with diiron nonacarbonyl [25*], and are presumably derived from carbonylation of the metal-nitrene complex intermediates.

Conclusion

Reaction of nitroso compounds with metal carbenes and metal carbonyls leads to products resulting from reduction of the nitroso compounds. Mononuclear metal-nitrene complexes could not be isolated from these reactions; in all cases, the conditions required to initiate the reactions caused formation of byproducts which are suggestive of metal-nitrene complexes or free nitrenes as intermediates. In addition, we have presented a method to reduce nitrosoarenes to azoxyarenes, with few problems resulting from overreduction to the azoarene.

Experimental

General. Nuclear magnetic resonance (^1H and ^{13}C) spectra were recorded on Bruker AF200 (200 MHz) or Bruker AF400 (400 MHz) spectrometers. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Perkin–Elmer model 281 diffraction grating spectrometer. Band positions are reported in reciprocal centimeters: C–H stretching frequencies (2800–3100 cm^{-1}) are not reported. Band intensities are reported relative to the most intense band and are listed as: br (broad), s (strong), m (medium), w (weak). Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact ionization or on a Hewlett–Packard GC-Mass Spec 5970B with Mass Selection Detector; m/e values are reported, followed by the relative intensity in parentheses. Melting points were taken on a Fisher–Johns melting point apparatus (model 12–144) equipped with a calibrated thermometer. Gas chromatography (GC) was performed on a Hewlett–Packard, model 5890A, gas chromatograph equipped with a flame ionization detector and Hewlett–Packard integrator, model 3390A. All runs were made using a variable temperature program. The column used in all runs was a 3% OV-17 on Chromosorb W, 6′ × 1/8″ stainless steel column. In all runs helium was used as the carrier gas.Where GC yields were indicated, a known amount of an internal standard was included in the reaction solution after completion of the reaction; in all cases yields were corrected for detector response factors. The identities of the compounds were determined by coinjection with authentic samples and/or isolation and spectral identification. Flash column chromatography [26] was performed using thick-walled glass columns and "flash grade" silica (Bodman 230–400 mesh). Routine thin layer chromatography was effected by using precoated 0.25 mm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. Irradiations were performed using either a Sunlamp (GE time-a-tan, 275 W, 110 V) or a mercury vapor lamp (Hanovia, 450 W, 110 V). Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl prior to use.

Materials. 2-Aminobiphenyl, aniline, 4,4′-azoanisole, azobenzene, benzanilide, *p*-bromoanisole, carbazole, *m*-chloroperbenzoic acid, *N*,*N*′-di-t-butylcarbodiimide, *N*,*N*′-di-t-butylurea, 2,2′-dinitrobiphenyl, ferric chloride, *p*-iodonitrobenzene, iron pentacarbonyl, methyl benzoate, *p*-nitrobenzonitrile, nitrosobenzene, nitrosonium tetrafluoroborate, *p*-nitroso-*N*,*N*-dimethylaniline, phenyllithium, tributylphosphine, trimethyltin chloride, and zinc were purchased from Aldrich Chemical Company and used without further purification. *N*-methylmorpholine-*N*-oxide was purchased from Aldrich Chemical Company and dried by azeotropic removal of water (using benzene) before use. Methyl fluorosulfonate was purchased from Columbia Organic Chemical Company. Azo-t-butane was purchased from Fairfield Chemical Company. Azoxybenzene, benzo[*c*]cinnoline-*N*-oxide, and 2-nitroso-2-methylpropane were purchased from Lancaster Synthesis Company. Chromium hexacarbonyl was purchased from Pressure Chemical Company. 2,2′-Azobiphenyl [27], azoxy-t-butane [28], *p*-nitrosoanisole [29], 2-nitrosobiphenyl [30*], *p*-nitrosoiodobenzene [27], and *N*-phenylbenzimino methyl ether [31] were synthesized according to literature procedures. Benzo[*c*]cinnoline-*N*,*N*′-dioxide, *p*-nitrosobenzonitrile, and pentacarbonyl(methoxyphenylmethylene)chromium(0) (**1**) were synthesized as described in the experimental.

Reaction of nitrosobenzene with carbene complex 1. To a 50 ml round bottom flask equipped with condenser and rubber septum, under nitrogen, was added nitrosobenzene (0.100 g, 0.935 mmol) and tetrahydrofuran (25 ml). The solution was stirred at 25 °C until it was light blue in color and homogeneous. To this solution was added via syringe a solution of carbene complex **1** (0.152 g, 0.487 mmol) in tetrahydrofuran. The solution was heated under reflux until the starting carbene complex had disappeared according to TLC analysis. The resulting olive green solution was cooled to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and filtered through Celite. The solvent was removed from the orange-colored filtrate on a rotary evaporator. The residue was dissolved in a solution of 19:1 hexane/ethyl acetate and purified by flash column chromatography on silica gel. A gradient type solvent system was employed to elute the products. The first fraction was eluted with hexane and was orange in color. The second fraction was eluted with 19/1 hexane/ethyl acetate and was yellow in color. The last fraction was eluted with 1/1 hexane/ethyl acetate and was colorless. The purity of each fraction was confirmed by TLC analysis. The products were isolated and identified. The first fraction gave azobenzene (0.020 g, 24%); m.p. 65–67 °C (lit. [32] m.p. 71 °C). ^{1}H NMR ($CDCl_3$): 7.90 (dd, 4H, *J* 8.0, 3.1 Hz); 7.50 (m, 6H). IR (CCl_4): 1485 (m); 1455 (w); 1150 (w); 1070 (w); 1020 (w); 690 (s) cm^{-1}. The spectral data were consistent with those previously reported for azobenzene [33*]. The second fraction gave azoxybenzene (0.039 g, 42%); m.p. 27–30 °C (lit. [32] m.p. 36 °C for the pure *trans* isomer). ^{1}H NMR ($CDCl_3$): 8.30 (dd, 2H, *J* 9.0, 2.5 Hz); 8.15 (dd, 2H, *J* 8.9, 1.3 Hz); 7.45 (m, 6H). IR (neat): 1480 (s); 1440 (s); 1330 (m); 1300 (m); 1275 (m); 1165 (m); 1070 (m); 1025 (m); 760 (s);

680 (s) cm^{-1}. The spectral data were consistent with those previously reported for azoxybenzene [33*]. The third fraction gave benzanilide (0.011 g, 6%); m.p. 163–165 °C (lit. [32] m.p. 163° C). ^1H NMR ($CDCl_3$): 7.95 (br s, 1H); 7.85 (dd, 2H, *J* 8.3, 1.5 Hz); 7.64 (dd, 2H, *J* 7.9, 1.5 Hz); 7.40 (m, 5H); 7.10 (dt, 1H, *J* 7.4, 1.3 Hz). IR ($CDCl_3$): 3450 (w); 1675 (m); 1600 (m); 1520 (s); 1500 (m); 1450 (m); 1320 (m); 1250 (w) cm^{-1}. The spectral data were consistent with those previously reported for benzanilide [33*].

In subsequent experiments, the product distribution was determined by GC analysis. After the reaction mixture had cooled to 25 °C, biphenyl was added to the mixture as an internal standard. The product identities were determined by comparison of retention times.The yields and product identities were as follows: methyl benzoate 76%, azoxybenzene 44%. Since azobenzene and the imino ether **6** had very similar retention times, the yields for these species could not be determined accurately by GC analysis.

Reaction of 2-nitroso-2-methylpropane with carbene complex 1. To a 50 ml round bottom flask equipped with condenser and rubber septum, under nitrogen, was added a solution of 2-nitroso-2-methylpropane (0.084 g, 0.97 mmol) in tetrahydrofuran (15 ml). The solution was stirred at 25 °C until it was dark blue and homogeneous (5 min). A solution of carbene complex **1** (0.156 g , 0.500 mmol) in tetrahydrofuran (5 ml) was added all at once by syringe. The solution was then heated under reflux for a period of 6 h, after which time the reaction mixture was cooled to 25 °C and naphthalene (0.012 g) and biphenyl (0.014 g) were added as internal standards. An aliquot was taken from the solution and subjected to GC and GC-MS analysis. The identity of the products was determined by retention time comparison and by mass spectra. The major products of the reaction were determined to be methyl benzoate (66%) and azoxy-t-butane (20%); mass spectrum (EI): 102 (*M*, 10); 87 (15); 57 (100). The mass spectrum and GC retention time were similar to that for an authentic sample of this compound.

Reaction of azoxybenzene with carbene complex 1. To a 50 ml round bottom flask equipped with condenser and rubber septum, under nitrogen, was added azoxybenzene (0.100 g, 0.505 mmol) and tetrahydrofuran (25 ml). To this solution was added via syringe a solution of carbene complex **1** (0.165 g, 0.529 mmol) in tetrahydrofuran (1.0 ml). The solution was heated under reflux for a period of 5 h. The resulting dark green solution was allowed to cool to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane, filtered through Celite, and the solvent was removed from the orange colored filtrate on a rotary evaporator. The residue was dissolved in hexane and final purification was achieved by flash chromatography on silica gel. The first fraction was eluted with 19/1 hexane/ethyl acetate, and was identified as azobenzene (0.040 g, 40%). The second fraction was eluted with 1/1 hexane/ethyl acetate and identified as benzanilide (0.030 g, 30%).

Reaction of azobenzene with carbene complex 1. To a 50 ml round bottom flask equipped with condenser and rubber septum, under nitrogen, was added azobenzene (0.142 g, 0.780 mmol) and tetrahydrofuran (25 ml). To this solution was added via syringe a solution of carbene complex **1** (0.231 g, 0.740 mmol) in tetrahydrofuran (1 ml). The solution was heated under reflux for a period of 5 h. The resulting dark green solution was allowed to cool to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane, filtered through

Celite, and the solvent was removed from the orange colored filtrate on a rotary evaporator. The residue was dissolved in hexane and final purification was achieved by flash chromatography on silica gel. The first fraction was eluted with 19/1 hexane/ethyl acetate, and was identified as azobenzene (0.061 g, 43%). The second fraction was eluted with 1/1 hexane/ethyl acetate and identified as benzanilide (0.032 g, 11%).

Reaction of 2-nitrosobiphenyl with carbene complex 1. To a 50 ml round bottom flask equipped with condenser and rubber septum, under nitrogen, was added 2-nitrosobiphenyl (0.060 g, 0.328 mmol) and tetrahydrofuran (25 ml). The solution was stirred at 25 ° C until it was light green in color and homogeneous (5 min). To this solution was added via syringe a solution of carbene complex **1** (0.202 g, 0.647 mmol) in tetrahydrofuran (1.0 ml). The solution was then heated under reflux for a period of 5 h. The resulting olive green solution was cooled to 25 ° C, and the solvent was removed on a rotary evaporator. The residue was dissolved in a solution of 19/1 hexane/ethyl acetate and purified by flash column chromatography on silica gel. A gradient type solvent system was employed to elute the products. The first fraction was eluted with 19/1 hexane/ethyl acetate and was orange in color. Two fractions were eluted with 1/1 hexane/ethyl acetate and were yellow in color. The purity of each fraction was confirmed by TLC analysis. The products were isolated and identified. The first fraction gave 2,2'-azobiphenyl. ^{1}H NMR ($CDCl_3$): 7.3–7.5 (m). IR ($CDCl_3$): 1470 (w); 1430 (w); 1235 (s); 1185 (s); 1160 (w); 1010 (w); 815 (w) cm^{-1}. Mass spectrum (EI): 334 (*M*, 9); 183 (19); 167 (100); 152 (36); 139 (10); 127 (12). The spectral data were consistent with those previously reported for this compound [27]; the product also coinjected with an authentic sample of 2,2'-azobiphenyl. The second fraction gave 2-aminobiphenyl; m.p. 46–49 ° C (lit. [32] m.p. 51–53 ° C). ^{1}H NMR ($CDCl_3$): 7.45 (dd, 4H, *J* 7.0, 1.0 Hz); 7.32 (m, 1H); 7.15 (d, 2H, *J* 8.0 Hz); 6.85 (dd, 1H, *J* 8.2, 1.2 Hz); 6.75 (dd, 1H, *J* 8.4, 1.0 Hz); 3.55 (br s, 2H). IR ($CDCl_3$): 3450 (br,m); 3365 (br,m); 1600(s); 1575 (m); 1490 (m); 1470 (s); 1425 (s); 1285 (s); 1275 (s); 1235 (m); 1170 (m); 1145 (m); 1130 (m); 990 (m) cm^{-1}. The spectral data were consistent with those previously reported for this compound [33*]; the product also coinjected with an authentic sample of 2-aminobiphenyl. The compound in the third fraction was identified as carbazole; m.p. 246–249 ° C (lit. [32] m.p. 247–248 ° C). ^{1}H NMR ($CDCl_3$): 8.05 (d, 2H, *J* 10.2 Hz); 7.35 (m, 4H); 7.2 (m, 2H); 1.50 (s, 1H). IR ($CDCl_3$): 3460 (m); 1595 (w); 1490 (w); 1460 (s); 1445 (m); 1375 (m); 1320 (m); 1260 (s); 1235 (m); 1085 (m); 1020 (m); 900 (m) cm^{-1}. The spectral data were consistent with those previously reported for this compound [33*]; the product also coinjected with an authentic sample of carbazole. Complete separation of carbazole from 2-aminobiphenyl could not be achieved. Yield determinations were made by GC using biphenyl as an internal standard. The yields were as follows: methyl benzoate 71%; carbazole 36%; 2-aminobiphenyl 31%; 2,2'-azobiphenyl (14%).

General procedure for the reaction of nitroso compounds with metal carbonyls. To a 50 ml round bottom flask equipped with condenser, rubber septum, and thermometer, under nitrogen, was added a solution of the nitroso compound in tetrahydrofuran. This solution was stirred until it became light blue in color and homogeneous. To this solution was added 0.5–1.0 equiv. of the metal carbonyl. The reaction was performed using the conditions described in Table 1. When sunlamp photolysis was used the lamp was placed 20 cm from the reaction flask, and an electric fan was used to circulate the air around the reaction flask. The reaction was allowed to proceed until all the nitroso compound had disappeared or until there was no further change as noted by TLC analysis. The reaction mixture was then cooled to 25 ° C, the solvent was removed on a rotary evaporator, and the residue after evaporation was treated as outlined in subsequent sections.

Reaction of nitrosobenzene with chromium hexacarbonyl. The general procedure was followed using chromium hexacarbonyl (0.220 g, 1.00 mmol) and nitrosobenzene (0.214 g, 2.00 mmol) in tetrahydrofuran (25 ml). The solution was heated under reflux for a period of 6 h. Final purification was achieved by flash chromatography on silica gel, using 19/1 hexane/ethyl acetate as eluent. The only product was determined to be azoxybenzene (0.011 g, 5%).

Reaction of nitrosobenzene with chromium hexacarbonyl and photolysis. The general procedure was followed using chromium hexacarbonyl (0.223 g, 1.01 mmol) and nitrosobenzene (0.211 g, 1.97 mmol) in tetrahydrofuran (25 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 4 h. Final purification was achieved by flash chromatography on silica gel, using 19/1 hexane/ethyl acetate as eluent. The only product was determined to be azoxybenzene (0.090 g, 46%).

Reaction of nitrosobenzene with iron pentacarbonyl and photolysis. The general procedure was followed using nitrosobenzene (0.215 g, 2.01 mmol) and iron pentacarbonyl (0.13 ml, 0.98 mmol) in tetrahydrofuran (25 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 1 h. Final purification was achieved by flash chromatography on silica gel. The first fraction was eluted with hexane and was assigned as azobenzene (0.007 g, 4%). The second fraction was eluted with 19/1 hexane/ethyl acetate and was assigned as azoxybenzene (0.190 g, 96%).

Reaction of nitrosobenzene with iron pentacarbonyl and photolysis (Hg lamp). A solution of nitrosobenzene (1.60 g, 15.0 mmol) in tetrahydrofuran (50 ml) was prepared, and was stirred until it was light blue in color and homogeneous. The solution was placed in a 500 ml Ace-Thred photochemical apparatus (Ace glass, model 7868), and additional tetrahydrofuran (130 ml) was added to the solution. A 450W Hg vapor lamp, fitted with a pyrex glass sleeve filter, served as the light source. Before photolysis, a 0 ° C ice bath was placed around the external surface of the apparatus and the temperature was allowed to equilibrate for 30 min. A nitrogen inlet was placed at the bottom of the reaction chamber, and nitrogen was bubbled through the system for a period of 5 min. Iron pentacarbonyl (1.00 ml, 7.60 mmol) was then added to the solution and the lamp was turned on. During the photolysis, the lamp was cooled by continuous circulation of 0 ° C water through the lamp holder. The solution was irradiated for a period of 15 min. The lamp was turned off, the solution was allowed to warm to 25 ° C, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and the resulting solution was filtered through Celite. The solvent was removed from the filtrate on a rotary evaporator, and the residue after evaporation was dissolved in 19/1 hexane/ethyl acetate. This solution was subjected to flash chromatography on silica gel. Elution with 19/1 hexane/ethyl acetate provided a single compound which was identified as azoxybenzene (1.20 g, 81%).

Reaction of nitrosobenzene with iron pentacarbonyl and N-methylmorpholine-N-oxide. To a 50 ml round bottom flask containing anhydrous *N*-methylmorpholine-

N-oxide (0.085 g, 0.74 mmol), equipped with rubber septum and a nitrogen inlet, at 0° C, was added a solution of nitrosobenzene (0.157 g, 1.47 mmol) and iron pentacarbonyl (0.10 ml, 0.76 mmol) in tetrahydrofuran (25 ml) by syringe over a period of 30 min. The solution was stirred an additional 5 min. Biphenyl (0.073 g) was then added to the solution as an internal standard and the mixture was subjected to GC analysis. The yields and product identities were concluded to be as follows; azoxybenzene 76%, azobenzene 2%.

Reaction of nitrosobenzene and iron pentacarbonyl in the dark at 30° C. The general procedure was followed using nitrosobenzene (0.210 g, 1.96 mmol) and iron pentacarbonyl (0.13 ml, 1.00 mmol) in tetrahydrofuran (25 ml). A dark environment was provided by placement of a cardboard box over the reaction apparatus. The solution was stirred for a period of 2 h at 30° C, after which time biphenyl (0.069 g) was added to the reaction as an internal standard. The product yields were determined by GC analysis. The identity of the products was confirmed by co-injection with authentic samples of the known compounds. The yields and product identities were concluded to be as follows: azoxybenzene 2%, azobenzene 1%.

Reaction of nitrosobenzene with iron pentacarbonyl at 65° C. The general procedure was followed using nitrosobenzene (0.250 g, 2.34 mmol) and iron pentacarbonyl (0.31 ml, 2.4 mmol) in tetrahydrofuran (40 ml). The reaction mixture was heated under reflux for a period of 2.5 h. Final purification was achieved by flash chromatography on silica gel. The first fraction was eluted with hexane and was assigned as azobenzene (0.017 g, 8%) (see above). The second fraction was eluted with 19/1 hexane/ethyl acetate and was assigned as azoxybenzene (0.210 g, 91%) (see above).

Reaction of p-nitrosoanisole and iron pentacarbonyl with photolysis. The general procedure was followed using *p*-nitrosoanisole (0.050 g, 0.36 mmol), iron pentacarbonyl (0.050 ml, 0.38 mmol), in tetrahydrofuran (10 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 1 h. Final purification was achieved by flash chromatography on silica gel. Elution with 9/1 hexane/ethyl acetate provided two fractions. The first fraction was identified as azoanisole (0.0075 g, 17%); m.p. 163–166° C (lit. [32] m.p. 165–166° C). ^{1}H NMR ($CDCl_3$): 7.80 (d, 4H, J 8.3 Hz); 6.95 (d, 4H, J 8.3 Hz); 3.8 (s, 6H). IR ($CDCl_3$): 1600 (w); 1585 (w); 1500 (m); 1295 (w); 1250 (s); 1180 (m) cm^{-1}. The second fraction was assigned as azoxyanisole (0.033 g, 70%); m.p. 120–122° C (lit. [32] m.p. 119–121° C). ^{1}H NMR ($CDCl_3$): 8.25 (d, 2H, J 9.9 Hz); 8.19 (d, 2H, J 9.9 Hz); 6.95 (d, 2H, J 9.9 Hz); 6.90 (d, 2H, J 9.9 Hz); 3.85 (s, 6H). IR ($CDCl_3$): 1600 (s); 1575 (w); 1500 (s); 1470 (s); 1285 (m); 1260 (s); 1190 (m) cm^{-1}. The spectral data were consistent with those previously reported for these compounds [33*].

Reaction of p-nitroso-N,N-dimethylaniline with iron pentacarbonyl and photolysis. A solution of *p*-nitroso-*N*,*N*-dimethylaniline (4.26 g, 28.4 mmol) in tetrahydrofuran (50 ml) was prepared, and was stirred until it was green in color and homogeneous. The solution was placed in a 500 ml Ace-Thred photochemical apparatus (Ace Glass, model 7868), and additional tetrahydrofuran (350 ml) was added to the solution. Before photolysis, a 30° C constant temperature bath was placed around the external surface of the apparatus and the temperature was allowed to equilibrate for 30 min. A nitrogen inlet was placed at the bottom of the reaction chamber, and nitrogen was bubbled through the system for a period of 5 min. Iron pentacarbonyl (3.8 ml, 29 mmol) was then added to the solution and the lamp was turned on. A 450W Hg vapor lamp, fitted with a pyrex glass sleeve filter, served as the light source. During the photolysis, the lamp was cooled by continuous circulation of water through the lamp holder. The solution was irradiated for a period of 2 h. The lamp was turned off, the solution was allowed to warm to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and the resulting solution was filtered through Celite. The solvent was removed from the filtrate on a rotary evaporator, and the residue after evaporation was dissolved in 19/1 hexane/ethyl acetate. This solution was subjected to flash chromatography on silica gel. Elution with 1/1 hexane/ethyl acetate provided a single compound which was identified as 4,4′-*N,N,N′,N′*-tetramethylazoxyaniline (4.02 g, 80%); m.p. 242–245 °C (lit. [34] m.p. 244–247 °C). ^{1}H NMR ($CDCl_3$): 8.35 (d, 2H, *J* 10.0 Hz); 8.15 (d, 2H, *J* 10.0 Hz); 6.75 (m, 4H); 3.05 (s, 12H). IR ($CDCl_3$): 1605 (s); 1525 (s); 1440 (m); 1361 (s); 1163 (w); 1087 (m) cm^{-1}. Mass spectrum (EI): 284 (*M*, 60); 268 (57); 134 (100); 120 (79); 105 (16); 77 (18). The spectral data were consistent with those previously reported for this compound [34].

Reaction of p-nitrosoiodobenzene with iron pentacarbonyl and photolysis. The general procedure was followed using *p*-nitrosoiodobenzene (0.086 g, 0.37 mmol) and iron pentacarbonyl (0.5 ml, 0.37 mmol) in tetrahydrofuran (25 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 3 h. Final purification was achieved by flash chromatography on silica gel. Elution with 19/1 hexane/ethyl acetate provided two fractions. The component in the first fraction was identified as 4,4′-diiodoazobenzene; m.p. 242–247 °C (lit. [35] m.p. 243 °C). ^{1}H NMR ($CDCl_3$): 7.85 (d, 4H, *J* 7.9 Hz); 7.65 (d, 4H, *J* 7.9 Hz). IR ($CDCl_3$): 1590 (m); 1570 (m); 1220 (m); 1210 (s); 1185 (s); 1175 (s); 1125 (s); 1050 (m); 995 (m); 810 (m) cm^{-1}. Mass spectrum (EI): 434 (*M*, 90); 279 (10); 231 (43); 203 (100); 167 (17); 149 (36); 76 (97). The spectral data were consistent with those reported previously for this compound [35]. The second fraction gave 4,4′-diiodoazoxybenzene; m.p. 205–208 °C (lit. [35] m.p. 204–205 °C). ^{1}H NMR ($CDCl_3$): 8.0 (d, 2H, *J* 8.3 Hz); 7.90 (d, 2H, *J* 8.3 Hz); 7.8 (m, 4H). IR ($CDCl_3$): 1565 (m); 1470 (s); 1450 (s); 1390 (m); 1315(m); 1210 (s); 1180 (m); 1160 (m); 1000 (s); 825 (s); 815 (s) cm^{-1}. Mass spectrum (EI): 450 (*M*, 100); 434 (20); 295 (5); 231 (18); 217 (12); 203 (67); 168 (9); 76 (31). The spectral data were consistent with those reported previously for this compound [35]. These two compounds could not be separated cleanly using column chromatography, so the yield determinations were made by GC, using biphenyl as an internal standard. The yields were as follows: 4,4′-diiodoazobenzene 36%; 4,4′-diiodoazoxybenzene 60%.

Reaction of p-nitrosobenzonitrile and iron pentacarbonyl with photolysis. The general procedure was followed using *p*-nitrosobenzonitrile (0.041 g, 0.31 mmol) and iron pentacarbonyl (0.040 ml) in tetrahydrofuran (25 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 1 h. Final purification was achieved by flash chromatography on silica gel. Elution with 2/1 hexane/ethyl acetate provided a yellow compound identified as 4,4′-dicyanoazoxybenzene (0.039 g, 85%); m.p. 225–229 °C (lit. [36] m.p. 229–230 °C). ^{1}H NMR ($CDCl_3$): 8.45 (d, 2H, *J* 8.8 Hz); 8.2 (d, 2H, *J* 8.8 Hz); 7.85 (d, 2H, *J* 8.8 Hz); 7.75 (d, 2H, *J* 8.8 Hz). IR ($CDCl_3$): 2233 (m); 1605 (w); 1490 (s); 1465 (s); 1420 (m); 1300 (m); 1135 (m); 1115 (m); 1100 (m); 1015 (m); 860 (s);

843 (m) cm^{-1}. Mass spectrum (EI): 248 (*M*, 13); 232 (6); 130 (12); 116 (20); 102 (100); 90 (14); 89 (12); 76 (16); 75 (18). The spectral data were consistent with those previously reported for this compound [36].

Reaction of benzo[c]cinnoline-N,N′-dioxide with iron pentacarbonyl and photolysis. The general procedure was followed using benzo[*c*]cinnoline-*N*,*N*′-dioxide (0.102 g, 0.481 mmol) and iron pentacarbonyl (0.050 ml, 0.38 mmol) in tetrahydrofuran (20 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 3 h. Final purification was achieved by flash chromatography on silica gel. Elution with 19/1 hexane/ethyl acetate provided a single compound identified as benzo[*c*]cinnoline-*N* oxide (0.052 g, 55%); m.p. 137–139 ° C (lit. [37] m.p. 139–140 ° C). ^1H NMR ($CDCl_3$): 8.85 (d, 1H, *J* 8.4 Hz); 8.45 (d, 1H, *J* 8.2 Hz); 8.35 (d, 1H, *J* 9.1 Hz); 7.95 (m, 2H); 7.70 (m, 3H). IR ($CDCl_3$): 1610 (w); 1585 (m); 1555 (m); 1505 (s); 1465 (s); 1395 (s); 1330 (s); 1280 (s); 1265 (s); 1240 (s); 1230 (s); 1220 (s); 1185 (s); 1155 (m); 1140 (s); 1125 (s); 1125 (m); 1035 (m); 810 (m) cm^{-1}. Mass spectrum (EI): 196 (*M*, 100); 180 (18); 166 (15); 152 (25); 140 (13); 98 (9); 76 (8). The spectral data were similar to those of an authentic sample of this compound.

Reaction of benzo[c]cinnoline-N,N′-dioxide with iron pentacarbonyl. The general procedure was followed using benzo[*c*]cinnoline-*N*,*N*′-dioxide (0.108 g, 0.509 mmol) and iron pentacarbonyl (0.050 ml, 0.38 mmol) in tetrahydrofuran (20 ml). The reaction mixture was stirred at 25 ° C for a period of 3 h. Final purification was achieved by flash chromatography on silica gel. Elution with 19/1 hexane/ethyl acetate provided two fractions. The first fraction gave benzo[*c*]cinnoline-*N*-oxide (0.032 g, 33%). The spectral data were consistent with those reported previously for this compound. The second fraction gave the starting compound benzo[*c*]cinnoline-*N*,*N*′-dioxide (0.069 g, 64%).

Reaction of 2-nitrosobiphenyl and iron pentacarbonyl with photolysis. The general procedure was followed using 2-nitrosobiphenyl (0.038 g, 0.21 mmol) and iron pentacarbonyl (0.14 ml, 1.1 mmol) in tetrahydrofuran (60 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 1 h. Final purification was achieved by flash chromatography on silica gel, using the separation method described above for the reaction of 2-nitrosobiphenyl with carbene complex **1**. In another run, the yields for the reaction were determined from GC analysis using biphenyl (0.014 g) as an internal standard. The yields and product identities were: 2,2′-azobiphenyl (15%) and 2-aminobiphenyl (22%).

Reaction of 2-nitrosobiphenyl with iron pentacarbonyl at 65 ° C. The general procedure was followed using 2-nitrosobiphenyl (0.038 g, 0.21 mmol) and iron pentacarbonyl (0.14 ml, 1.1 mmol) in tetrahydrofuran (60 ml). The solution was heated to 65 ° C for a period of 2 h. The solution was allowed to cool to 25 ° C, and biphenyl (0.014 g) was added. The yields and product identities were determined by GC analysis: 2,2′-azobiphenyl (44%); 2-aminobiphenyl (35%); carbazole (10%).

Reaction of 2-nitroso-2-methylpropane with iron pentacarbonyl. The general procedure was followed using 2-nitroso-2-methylpropane (0.095 g, 1.1 mmol) and iron pentacarbonyl (0.44 ml, 3.3 mmol) in tetrahydrofuran (15 ml). Sunlamp photolysis was used as described in the general procedure; the solution was irradiated for a period of 1 h. Naphthalene (0.026 g) was added to the solution to serve as an internal standard for GC analysis. The identity of the products was confirmed by comparison of retention times with those of authentic samples, and our mass spectral analysis. The yields, mass spectral data, and product identities were as follows. Azo-t-butane (1%): mass spectrum (EI): 71 (10); 57 (100); 41 (60). Azoxy-t-butane (4%); mass spectrum (EI): 102 (*M*, 10); 87 (15); 57 (100). t-Butylcarbodiimide (1%); mass spectrum (EI): 154 (*M*, 10); 139 (20); 83 (80); 57 (100). *N*,*N*′-Di-t-butylurea (13%); mass spectrum: 172 (*M*, 5); 157 (10); 58 (100). The mass spectral data presented for the above compounds were consistent with mass spectral data from authentic samples of the known compounds.

Reaction of nitrosobenzene with iron pentacarbonyl and acetic acid. The general procedure was followed using nitrosobenzene (0.269 g, 2.51 mmol) and iron pentacarbonyl (0.75 ml, 5.7 mmol) in tetrahydrofuran (22 ml) and acetic acid (3 ml). The reaction mixture was heated under reflux for a period of 2.5 h. After the photolysis was complete, biphenyl (0.051 g) was added to the solution to serve as an internal standard. The identities of the products were determined by co-injection with authentic samples of the known compounds. The products and yields were as follows: aniline 9%, azobenzene 15%, azoxybenzene 75%.

Reaction of azoxybenzene with iron pentacarbonyl and acetic acid. The above procedure was followed substituting azoxybenzene (0.197 g, 0.996 mmol) for nitrosobenzene. Azoxybenzene was treated with iron pentacarbonyl (0.53 ml, 3.9 mmol) in tetrahydrofuran (22 ml) and acetic acid (3 ml) as described in the above procedure. The solution was irradiated with a sunlamp for a period of 3 h. After the irradiation was finished, biphenyl (0.093 g) was added to the solution as an internal standard for GC analysis. The identities of the products were determined by co-injection with authentic samples of the known compounds. The products and yields were as follows: azobenzene 50%, azoxybenzene 49%.

Reaction of nitrosobenzene (slow addition) with iron pentacarbonyl and acetic acid. To a solution of iron pentacarbonyl (0.75 ml, 5.7 mmol) in tetrahydrofuran (22 ml) and acetic acid (3 ml) in a 50 ml round bottom flask equipped with rubber septum and condenser, under nitrogen, was added a solution of nitrosobenzene (0.119 g, 1.11 mmol) in tetrahydrofuran (10 ml) over a 30 min period. During the addition of nitrosobenzene, the reaction flask was irradiated with a sunlamp as described in the general procedure. After the addition was complete, the solution was irradiated with the sunlamp for an additional 1 h. After the photolysis was complete, biphenyl (0.054 g) was added to the solution to serve as an internal standard for GC analysis. The identities of the products were determined by co-injection with authentic samples of the known compounds. The products and yields were as follows: aniline 39%, azobenzene 9%, azoxybenzene 16%. After the mixture was analyzed by gas chromatography, the solvent was removed on a rotary evaporator. The residue after evaporation was dissolved in 1/1 hexane/ethyl acetate, and this solution was purified by flash chromatography on silica gel. Elution with 9/1 hexane/ethyl acetate afforded a mixture of azobenzene and azoxybenzene. Elution with 1/1 hexane/ethyl acetate afforded aniline [33*].

Synthesis of pentacarbonyl[methoxy(phenyl)methylene]chromium(0)(carbene complex 1). To a suspension of chromium hexacarbonyl (3.08 g, 14.0 mmol) in diethyl ether (200 ml) under nitrogen in a round bottom flask equipped with a septum at 0 °C was added by syringe a 2*M* solution of phenyllithium in cyclohexane (7.1 ml, 14 mmol) over a 10 min period. During the addition of phenyllithium, the solution turns to a dark yellow color and the chromium hexacarbonyl dissolves completely. After the addition the solution was stirred for 1 h at 25 °C under a nitrogen atmosphere. To this mixture methyl fluorosulfonate (1.1 ml, 14 mmol) was added all at once. The solution was stirred for 12 h at 25 ° C. The reaction mixture was poured into a mixture of water and diethyl ether in a separatory funnel. The ether layer was dried over sodium sulfate, and the solvent was removed on a rotary evaporator. The resulting orange solid was dissolved in hexane (3 ml) and purified by flash chromatography on silica gel, using hexane as the eluent. A single red compound (2.50 g, 57%) was obtained after removal of the solvent on a rotary evaporator; m.p. 48–50 ° C. ^{1}H NMR ($CDCl_3$): 7.22 (s, 5H); 4.60 (s, 3H). IR ($CDCl_3$): 2060 (s); 1935 (s); 1450 (w); 1230 (m). The spectral data were consistent with those reported previously for this compound [38].

Synthesis of p-nitrosobenzonitrile. The following procedure was adapted from a literature procedure [27]. A solution of 4-nitrobenzonitrile (14.8 g, 0.1 mol), ethanol (100 ml), ethylene glycol monomethyl ether (35 ml), water (8 ml), and ammonium chloride (1.5 g) was prepared in a 250 ml round-bottom flask, equipped with a condenser. The solution was heated under reflux while zinc powder (12.0 g, 0.184 mol) was added to the solution through the top of the condenser. The zinc was added in 0.2 g portions over a period of 3 h. After the addition of zinc, the reaction mixture was allowed to cool to 25 ° C. The solution was filtered, and the zinc residue was washed with hot (60 ° C) ethanol. The resulting filtrate containing 4-cyanophenylhydroxylamine was poured with stirring into a solution of ferric chloride hexahydrate (15.0 g, 0.0555 mol) in water (100 ml) at 100 ° C. The precipitate which formed in the oxidation was filtered and then dissolved in ethyl acetate (2 ml). This solution was purified by flash chromatography on silica gel using 19/1 hexane/ethyl acetate as the eluent. The resulting product was recrystallized once from a minimum amount of ethanol to yield colorless crystals of 4-nitrosobenzonitrile (4.92 g, 37%); m.p. 133–135 ° C (lit. [36] m.p. 136–137 ° C). ^{1}H NMR ($CDCl_3$): 7.95 (s, 4H). IR ($CDCl_3$): 2245 (m); 1515 (s); 1460 (m); 1405 (m); 1310 (m); 1185 (s); 1105 (s); 1095(s); 845 (s); 830 (m); 815 (m). Mass spectrum (EI): 132 (*M*, 60); 102 (100); 76 (18); 75 (28). The spectral data were consistent with those previously reported for this compound [36].

Synthesis of benzo[c]cinnoline-N,N′-dioxide. To a 500 ml round bottom flask equipped with a rubber septum, under nitrogen, was added 2,2′-dinitrobiphenyl (2.50 g, 10.2 mmol) and 80% ethanol/water solution (250 ml). The solution was stirred for 30 min at 25 ° C and a solution of potassium hydroxide (1.60 g, 28.6 mmol) in water (75 ml) was added. The solution was then warmed to 45 ° C by use of an external oil bath and tributylphosphine (4.04 g, 20.80 mmol) was added by syringe pump over a period of 18 h. The reaction was stirred at this temperature for an additional 3 h. As the reaction progressed, a white precipitate formed. The reaction mixture was filtered, and the residue after filtration was recrystallized two times from a minimum of absolute ethanol to yield a white crystalline material (0.48 g, 22%) which was identified as benzo[*c*]cinnoline-*N*,*N*′-dioxide; m.p. 249–250 ° C (dec) (lit. [39] m.p. 249–251 ° C (dec)). ^{1}H NMR ($CDCl_3$): 8.50 (m, 2H); 8.40 (m, 2H); 7.75 (m, 4H). IR ($CDCl_3$): 1570 (w); 1475 (s); 1420 (m); 1390 (s); 1335 (m); 1310 (m); 1270 (m); 1255 (m); 1235 (m); 1215 (s); 1205 (s); 1190 (s); 1180 (s); 1140 (m); 1120 (m); 1050 (m); 815 (m) cm^{-1}. Mass spectrum (EI): 212 (*M*, 5); 196 (66); 180 (68); 166 (17); 152 (100); 140 (17); 126 (24); 98 (34); 87 (22); 76 (26); 75 (30). The spectral data were consistent with those previously reported for this compound [39].

Acknowledgements

We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, and the General Research Board of the University of Maryland for support for this research. We are grateful to Prof. R.J. Newland of Glassboro State College for assistance with the operation of the GC-Mass Spectrometer. We are grateful to Ms. Deonna Emerson for synthesis of some of the starting materials.

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