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(17) ^{1}H NMR spectra of the *N*-acetyl derivatives in this series indicate that they exist as nearly 50:50 mixtures of two conformers about the N–CO bond, with interconversion being slow on the NMR time scale at ambient probe temperature, cf. ref 6.

(18) Acidification with HCl induces variable amounts of *tert*-butyl enol etherification, cf. ref 4.

(19) It is particularly important to carefully reextract the $NaHCO_3$ wash solution so as to avoid loss of the formyl enone into the aqueous phases.

(20) We thank the Eastman Chemical Co. for a generous sample of this substance.

(21) In some preparations additional resonance from CH_3CO (τ 7.91) and $(CH_3)_3C$ (τ 8.55) indicate the presence of up to ~20% of a second diastereomer.[10]

(22) The ^{1}H NMR properties of this by-product, insofar as they are discernable in the spectrum of the mixture, would be consistent with its formulation as a trans-anti-trans diastereomer of **6c**. In view of the fact that we have not encountered such a stereoisomer in any other analogous system, however, we hesitate to make such an assignment until the substance can be examined in pure form.

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(24) C. W. Shoppee, S. K. Roy, and B. S. Goodrich, *J. Chem. Soc.*, 1583 (1961).

(25) Precipitation at this point has not been observed in analogous reactions, and is probably due to salt formation at the amide function.

(26) Use of more concentrated alkali brings about partial hydrolysis of the amide.

Synthesis of 6*H*,12*H*-indazolo[2,1,*a*]-6,12-diiminoindazoles and 3-Imino-2-phenylindazolines from Azo Compounds and Isocyanides in the Presence of Octacarbonyldicobalt[1]

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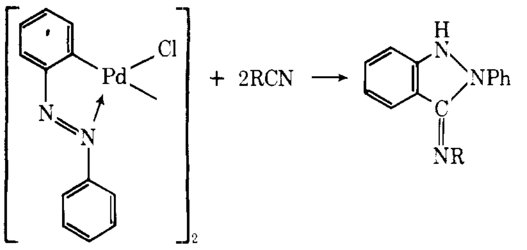
Received July 19, 1977

The reactions of azobenzenes and isocyanides in the presence of $Co_2(CO)_8$ gave 6*H*,12*H*-indazolo[2,1,*a*]-6,12-diiminoindazoles (**1**) and 3-imino-2-phenylindazolines (**2**). Orthometalation by a cobalt atom, which is considered as a first step in these reactions, occurs nucleophilically. The reaction mechanism is discussed.

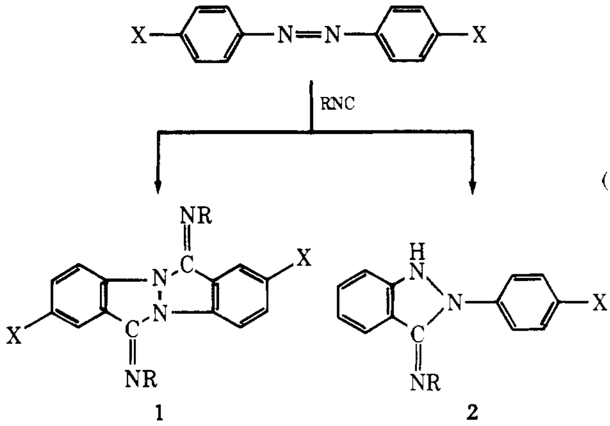
Reactions of aromatic azo compounds with carbon monoxide are catalyzed by $Co_2(CO)_8$ to produce 3-oxo-2-phenylindazolines and 2,4-dioxo-1,2,3,4-tetrahydroquinazolines.[2] Similar reactions in the presence of $Ni(CO)_4$ give 6*H*,12*H*-indazolo[2,1,*a*]-6,12-dioxoindazoles.[3] We recently showed that reaction of cyclopalladation complexes of azobenzene with isocyanides gave 3-imino-2-phenylindazolines stoichiometrically (eq 1).[6] In attempts to examine the catalytic scope of these reactions, the reactions of azobenzene derivatives with isocyanides were carried out in the presence of $Co_2(CO)_8$. We found that the aforementioned reactions produced 6*H*,12*H*-indazolo[2,1,*a*]-6,12-diiminoindazoles and 3-imino-2-phenylindazolines, depending on the substituent of RNC.



(1)

A mixture of azobenzene, 2,6-xylyl isocyanide, and $Co_2(CO)_8$ was heated in toluene at 120–125 °C. Chromatography of the mixture on alumina gave a yellow crystalline compound **1a** with the empirical formula $C_{30}H_{26}N_4$, M^+ 442 (442.54). The NMR spectrum showed one singlet due to the methyl groups at δ 2.16 ppm, suggesting a symmetrical molecular structure. The UV absorption pattern is similar to that of 6*H*,12*H*-indazolo[2,1,*a*]-6,12-dioxoindazole (**3**). The reaction of 2,6-xylyl isocyanide with a nickel azobenzene complex (**4**)[7] gave **1a** (eq 3).

A similar reaction with carbon monoxide produced **3** (eq 3). These results showed that **1a** is 6*H*,12*H*-indazolo[2,1,*a*]-6,12-[dixylyl]iminoindazole. Similar compounds were obtained when *p*-chloro- and *p*-methylazobenzene or 4-



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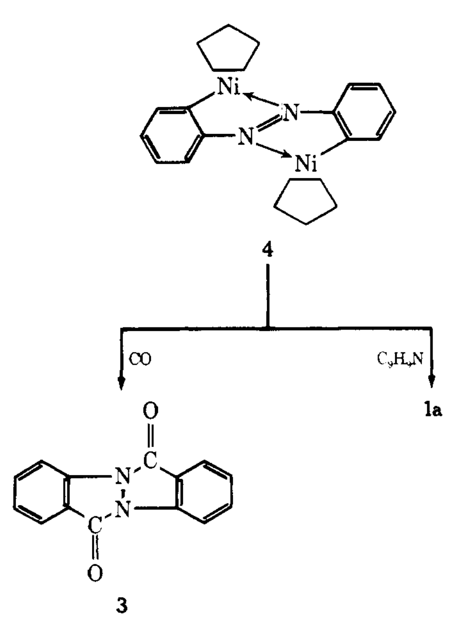


(3)

Table I. Reactions of RNC with p-$XC_6H_4N{=}NC_6H_4X$-p[a]

R	Registry no.	X	Product	Registry no.	Product (mol) $Co_2(CO)_8$ (mol)
2,6-$(CH_3)_2C_6H_3$	2769-71-3	H	**1a**	63866-01-3	2.4
2,6-$(CH_3)_2$-4-BrC_6H_2	24139-49-9	H	**1b**	63866-00-2	2.9
2,6-$(CH_3)_2C_6H_3$		CH_3	**1c**	63865-99-6	3.9
2,6-$(CH_3)_2C_6H_3$		Cl	**1d**	63865-98-5	2.0
2-$(CH_3)C_6H_4$	10468-64-1	CH_3	**1e**	63866-08-0	0.6
2-$(CH_3)C_6H_4$		CH_3	**2e**	63866-10-4	1.5
$(CH_3)_3C$	7188-38-7	H	**2a**	62247-94-3	4.2
C_6H_{11}	931-53-3	H	**2b**	62247-95-4	3.1
Ph	931-54-4	H	**2c**	63866-09-1	3.5

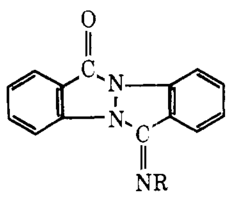
[a] Reaction temperature, 120–125 °C; time, 4 h; $Co_2(CO)_8$, ca. 0.20 g (0.58 mmol); azo compound, ca. 6.6 mmol; isocyanide, ca. 12 mmol.

bromo-2,6-dimethyphenyl isocyanide were used. However, the reactions of azobenzene with phenyl, *tert*-butyl or cyclohexyl isocyanide in the presence of $Co_2(CO)_8$ produced the corresponding 3-imino-2-phenylindazoline (**2**) without affording any compound of type **1** (eq 2). When *o*-tolyl isocyanide was used, the reaction gave a mixture of **1e** and **2e** in a 1:3 molar ratio. The results are summarized in Table I.

In an attempt to convert **2e** to **1e** the reaction of **2e** with *o*-tolyl isocyanide was carried out, but compound **2e** was recovered, suggesting that **2e** is not a precursor of **1e**.

Several attempts to examine the scope of catalysis with $Fe(CO)_5$, $Fe_2(CO)_9$, $Ni(CO)_4$, and $Mo(CO)_6$ led only to formation of metal isocyanide complexes such as $Fe(CO)_4(C_9H_9N)$, $Ni(C_9H_9N)_4$, and $Mo(CO)_4(C_9H_9N)_2$.

Treatment of **1a** with aqueous HCl in $CH_3OCH_2CH_2OH$ at reflux gave **5** and 2,6-xylylamine, but 6*H*,12*H*-indazolo[2,1,*a*]-6,12-dioxoindazole was not obtained. Similar treatment of **1d** on alcoholic KOH gave **6**.



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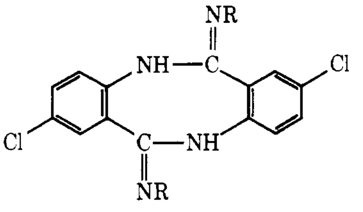

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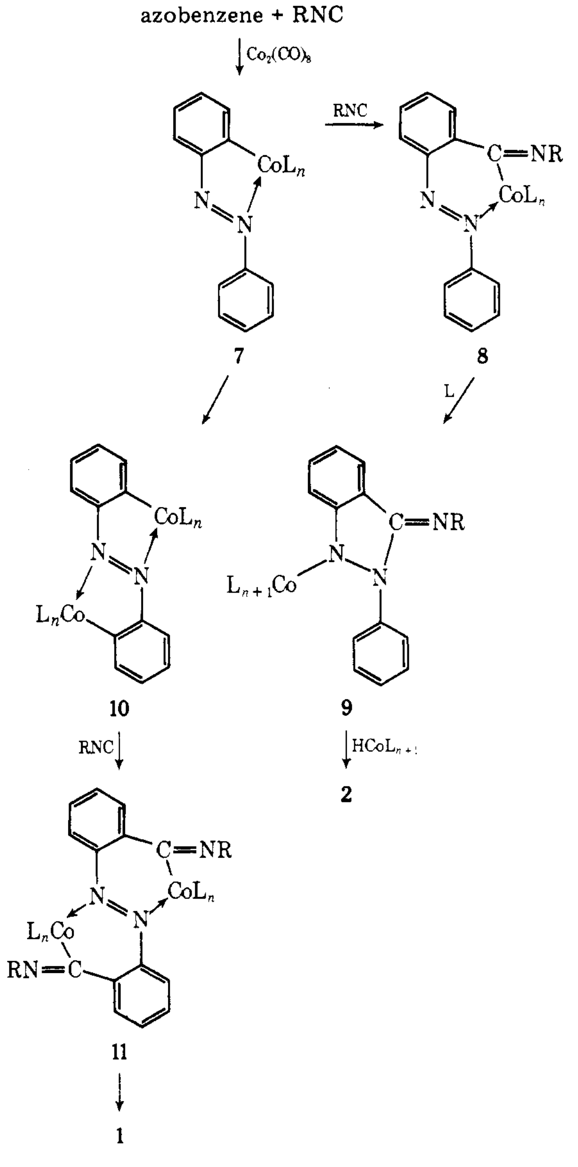
Compounds **1** and **2** are probably formed via initial orthometalation on the aromatic ring by a cobalt isocyanide complex[8] formed by the reaction of $Co_2(CO)_8$ with isocyanide, as well as the mechanism[9,10] proposed for the transition metal-catalyzed carbonylation of azobenzene, as shown in Scheme I.

An isocyanide insertion into **7**, forming **8**, and a rearrangement of a cobalt moiety to a nitrogen atom followed by cyclization of the azo function would give **9**. This species could be reduced with $HCoL_4$ to give **2**. The cobalt–isocyanide complex reformed in this reaction would again metalate the azobenzene and the catalytic cycle would be complete.

Before an isocyanide insertion into **7**, double metalation occurred to give a binuclear complex **10** in which both nitrogens are used for coordination to two metal atoms which bond to the two aromatic rings. The reaction would be completed by isocyanide insertion and cyclization of the azo function to produce **1**. A steric hindrance of bulky isocyanide would make the double metallation more favorable than an isocyanide insertion into a single metalated intermediate **7**.

Bruce and co-workers have shown that two different mechanisms (electrophilic and nucleophilic attack of metal on the aromatic ring) are operative in orthometalation of azobenzene derivatives based on a study of substituent effect.[11]

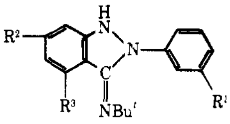
Scheme I. Formation of 3-Imino-2-phenylindazolines and 6*H*,12*H*-Indazolo[2,1,*a*]-6,12-[dixylyl]iminoindazolones



We have examined the reaction of *m*-fluoroazobenzene with *tert*-butyl isocyanide for the purpose of obtaining mechanistic information. Distribution of three isomers was determined by the proton NMR spectra. The results are summarized in Table II together with the results[11] of the metallation obtained by Bruce et al.

3-*tert*-Butylimino-2-phenyl-5-fluoroindazoline (**12c**) substituted at the ortho position to fluorine is ca. 70% of the resulting mixture. Although the process of an isocyanide in-

Table II. Isomers Formed in the Reactions of *m*-$FC_6H_4N{=}NC_6H_5$ with $Co_2(CO)_8Bu^tNC$, $CH_3Mn(CO)_5$, and $PdCl_2$



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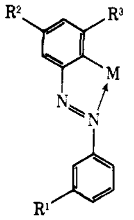

13: $Mn(CO)_4$
14: PdC_5H_6

Compd[a]	*a*	*b*	*c*	Ref
12	30		70	This paper
13	20		80	11
14	80	20		11

[a] $R^1 = F, R^2 = R^3 = H$. [b] $R^2 = F, R^1 = R^2 = H$. [c] $R^3 = F, R^1 = R^2 = H$.

sertion into a cobalt-metal σ bond was included in addition to that of metalation in the reaction in question, this result appears to be consistent with nucleophilic attack of cobalt atom on a carbon atom greatly activated by the inductive effect of fluorine, compared with that of orthometalation of *m*-fluoroazobenzene by $CH_3Mn(CO)_5$ to give **13c** as the main product.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Laboratory Devices Mel-Temp apparatus and are uncorrected. The NMR spectra were recorded on JEOL C60HL and Varian HA-100B spectrometers, using tetramethylsilane as a reference. The mass spectra were measured on a Nippondenshi Type JPS-1S mass spectrometer with a direct-inlet system. The UV spectra were recorded on Cary 14 spectrometer. Dicobalt octacarbonyl was prepared from cobalt(II) acetate.[12] Various isocyanides[13] and di-*p*-methyl- and di-*p*-chloroazobenzene[14] were prepared by procedures described in the literature. *m*-Fluoroazobenzene was prepared from nitrosobenzene and *m*-fluoroaniline in acetic anhydride. The nickel[7] and π-cyclopentadienyl palladium[11] complexes of azobenzene were prepared by procedures described in the literature.

Preparation of 6*H*,12*H*-indazolo[2,1,*a*]-6,12-diiminoindazoles. A representative reaction is described in detail. A mixture of azobenzene (1.1 g, 6.5 mmol), 2,6-xylyl isocyanide (1.5 g, 1.15 mmol), and $Co_2(CO)_8$ (0.20 g, 0.58 mmol) in toluene (15 mL) was heated at 120–125 °C for 4 h. The mixture was chromatographed on alumina. Two bands (orange and yellow) were observed. Eluting with hexane gave unreacted azobenzene and isocyanide. Eluting with hexane–benzene (1:2) gave a yellow solution. The solvent was evaporated almost to dryness under reduced pressure, and crystallization of the residue from benzene–hexane gave 6*H*,12*H*-indazolo[2,1,*a*]-6,12-[di-2,6-xylyl]iminoindazole: mp 268 °C (0.61 g, 22%); NMR ($CDCl_3$) 2.16 (s, CH_3) 6.5–8.3 (c, aromatic protons); UV (in benzene) 406 (ϵ 2.16×10^4), 288 (ϵ 9.6×10^3), 279 (ϵ 9.0×10^3), 245 (ϵ 4.2×10^4), and 288 (ϵ 3.5×10^4) nm.

Anal. Calcd for $C_{30}H_{26}N_4$: C, 81.42; H, 5.92; N, 12.66. Found: C, 81.36; H, 5.94; N, 12.63.

Similar compounds were prepared according to procedures analogous to those described above. **1b**: mp 293–294 °C; NMR ($CDCl_3$) δ 2.16 (s, CH_3) and 6.6–8.4 (*c*, aromatic protons) ppm. Anal. Calcd for $C_{30}H_{24}N_4Br_2$: C, 60.02; H, 4.03; N, 9.33. Found: C, 60.21; H, 4.05; N, 9.38. **1c**: mp 274–275 °C; NMR ($CDCl_3$) δ 2.16 (s, 2 CH_3), 2.18 (s, 4 CH_3), and 6.2–8.1 (*c*, aromatic protons) ppm. Anal. Calcd for $C_{32}H_{30}N_4$: C, 81.67; H, 6.43; N, 11.91. Found: C, 81.67; H, 6.55; N, 11.74. **1d**: mp 253–255 °C; NMR ($CDCl_3$) δ 2.13 (s, CH_3) and 6.8–8.2 (*c*, aromatic protons) ppm. Anal. Calcd for $C_{30}H_{24}N_4Cl_2$: C, 70.45; H, 4.73; N, 10.95. Found: C, 70.43; H, 4.83; N, 10.99. **1e**: mp 269 °C; NMR ($CDCl_3$) δ 2.13 (s, 2 CH_3), 2.23 (s, 2 CH_3), and 6.4–8.2 (*c*, aromatic protons) ppm. Anal. Calcd for $C_{30}H_{26}N_4$: C, 81.42; H, 5.92; N, 12.66. Found: C, 81.00; H, 5.94; N, 12.70.

Preparation of 3-Imino-2-phenylindazolines. A representative reaction is described in detail. A mixture of azobenzene (1.1 g, 6.5 mmol), *tert*-butyl isocyanide (1.7 g, 2.0 mmol), and $Co_2(CO)_8$ (0.2 g, 0.58 mmol) in toluene (15 mL) was heated at 125 °C for 4 h. Chromatography of the mixture on alumina showed two bands. They were eluted with hexane–benzene (10:1) and benzene, giving orange and pale-yellow eluates, respectively. The product from the first eluate was unreacted azobenzene and *tert*-butyl isocyanide. The product from the second one was identified as *tert*-butylamino-2-phenylindazoline (**2a**), mp 83.5–84 °C (lit.[6] mp 84 °C), by the mixture melting point with and infrared spectrum of an authentic sample of *tert*-butylimino-2-phenylindazoline. Anal. Calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 76.89; H, 7.23; N, 15.93.

2b: mp 204–205 °C (lit.[6] mp 204–205 °C). Anal. Calcd for $C_{19}H_{21}N_3$: C, 78.31; H, 7.26: N, 14.42. Found: C, 78.49; H, 7.25; N, 14.55. **2c**: mp 135–135.5 °C. Anal. Calcd for $C_{19}H_{15}N_3$: C, 79.97; H, 5.30; N, 14.73. Found: C, 79.75; H, 5.44; N, 14.82. **2e**: mp 104–105 °C (lit.[6] mp 103–104 °C). Anal. Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.47; N, 12.84. Found: C, 80.56; H, 6.44; N, 12.81.

Reaction of a Binuclear Nickel–Azobenzene Complex 4 with 2,6-Xylyl Isocyanide. A mixture of **4** (0.6 g, 1.4 mmol) and 2,6-xylyl isocyanide (0.52 g, 4.0 mmol) in toluene (15 mL) was heated at 100 °C for 10 h. The mixture was chromatographed on alumina; two bands (yellow and blue) were observed. Each was eluted with benzene and benzene–CH_2Cl_2 (1:4). Eluting with benzene gave **1a** (0.18 g, 29%). The product from the second eluate was an unreacted nickel complex (ca. 0.1 g).

Reaction of 4 with Carbon Monoxide. A mixture of **4** (0.3 g, 0.7 mmol) and carbon monoxide (60 kg/cm^2) in toluene (15 mL) in a 200-mL stainless steel autoclave was kept at 110 °C for 5 h. The mixture was chromatographed on alumina, using CH_2Cl_2 as an eluant. The yellow band was observed. Removal of the solvent gave crude **3** (0.11 g, 66.5%) as yellow crystals. Crystallization from CH_2Cl_2–hexane gave pure **3** (0.10 g), identified by an infrared spectrum of an authentic sample of 6*H*,12*H*-indazolo[2.1,*a*]-6,12-dioxoindazole.

The Reaction of Azobenzene with 2,6-Xylyl Isocyanide in the Presence of Metal Carbonyls. A mixture of azobenzene (0.9 g, 5.0 mmol), 2.6-xylyl isocyanide (1.3 g, 10 mmol), and $Ni(CO)_4$ (0.17 g, 1.0 mmol) in toluene was heated at 120 °C for 4 h. The mixture was chromatographed on alumina, using benzene as an eluant. Removal of the solvent and crystallization of the residue from benzene–hexane gave tetrakis(2,6-xylyl isocyanide)nickel (0.42 g, 72%) as yellow-orange crystals: mp 150–152 °C (dec); NMR (PhCl) δ 2.35 (s, CH_3) ppm. Anal. Calcd for $C_{36}H_{36}N_4Ni$: C, 74.11; H, 6.22; N, 9.60. Found: C, 73.99; H, 6.20; N, 9.81.

Similar reactions were carried out in the presence of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Mo(CO)_6$. The reactions gave $Fe(CO)_4(C_9H_9N)$ and $Mo(CO)_4(C_9H_9N)_2$.

$Fe(CO)_4(C_9H_9N)$: yellow crystals, mp 78–80 °C (dec). The molecular weight by mass spectroscopy was 299 (calcd 299.07). Anal. Calcd for $C_{13}H_9NO_4Fe$: C, 52.21; H, 3.03; N, 4.68. Found: C, 51.97; H, 3.15; N, 4.64.

$Mo(CO)_4(C_9H_9N)_2$: yellow crystals, mp 148–151 °C (dec). The molecular weight by mass spectroscopy was 470 (calcd 470.34). Anal. Calcd for $C_{22}H_{18}N_2O_4Mo$: C, 56.18; H, 3.86; N, 5.96. Found: C, 58.22; H, 3.67; N, 6.00.

Reaction of a Mixture of 14a and 14b with *tert*-Butyl Isocyanide. A mixture of **14** (0.3 g) and *tert*-butyl isocyanide (1.2 mL) in THF (15 mL) was heated at 120 °C for 5 h. The mixture was chromatographed on alumina, using benzene as an eluant. Benzene was removed to dryness. The NMR spectrum of the residue showed the presence of two isomers, which were identified as **12a** and **12b** in a ca. 85:15 intensity ratio: NMR ($CDCl_3$) **12a** 1.03 (s, Bu^t) ppm and **12b** 1.48 (s, Bu^t) ppm.

Reaction of *m*-Fluoroazobenzene with *tert*-Butyl Isocyanide in the Presence of $Co_2(CO)_8$. A mixture of *m*-fluoroazobenzene (0.9 g, 5.2 mmol), *tert*-butyl isocyanide (0.83 g, 10 mmol), and $Co_2(CO)_8$ (0.2 g, 0.58 mmol) in toluene (15 mL) was heated at 125 °C for 4 h. The mixture was chromatographed on alumina. Benzene eluted a mixture of two isomers (0.57 g). The NMR spectrum showed two singlets at δ 1.03 and 0.97 ppm, consisting of a relative intensity of 69:31. The former signal was identified as **12a** and the latter as **12c**. The molecular weight of the mixture by mass spectroscopy was 283 (calcd 283.35).

Registry No.—**3**, 18428-89-2; **4**, 63866-71-7; **12a**, 63866-05-7; **12b**, 63866-03-5; **12c**, 63866-02-4; azobenzene, 103-33-3; $Co_2(CO)_8$, 10210-68-1; carbon monoxide, 630-08-0; $Ni(CO)_4$, 13463-39-3; tetrakis(2,6-xylyl isocyanide)nickel, 63866-70-6; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Mo(CO)_6$, 1393906-5; $Fe(CO)_4(C_9H_9N)$, 63866-73-9; $Mo(CO)_4(C_9H_9N)_2$, 63866-72-8; *m*-fluoroazobenzene, 331-19-1; *p*-chloroazobenzene, 1602-00-2; *p*-methylazobenzene, 501-60-0.

References and Notes

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Nucleophilic Substitution on Dialkoxy Disulfides. Reactions with Mercaptans or Amines

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Received June 9, 1977

Dialkoxy disulfides (1) readily reacted with mercaptans or secondary amines to give alkoxyalkyl trisulfides (4) or alkoxyamino disulfides (5) with elimination of alcohol. These alkoxy sulfides (4 or 5) further reacted with mercaptans or secondary amines to give unsymmetrical dialkyl tetrasulfides (6), alkylamino trisulfides (7), and unsymmetrical diamino disulfide (8). However, reaction of 1 with *N,N*-dimethyl-*p*-phenylenediamine gave *p*-dimethylamino-*N*-thiosulfinylaniline (10). Reaction of 1 and benzylamine or furfurylamine afforded dibenzylideneamino tetrasulfide (11a) or difurfurylideneamino tetrasulfide (11b), whereas 1 and β-phenylethylamine or DL-α-phenylethylamine gave thioamides, PhC(=O)C(=S)NHR (13). Treatment of 1 with thiobenzamide afforded benzonitrile, sulfur, and alcohol.

Dialkoxy disulfides (1) were initially prepared by the reaction of sodium alcoholates with sulfur monochloride[1] with two structures, 1 and 2, proposed for the products. Raman spectra[2] and dipole-moment data[3] favored the structure 1, but 2 could not be rigorously excluded. In recent years, Thompson et al. reported an excellent method for the preparation of 1 by the reaction of alcohols and sulfur monochloride in the presence of triethylamine (eq 1) and proved that these compounds have the disulfide structure 1 by NMR and x-ray analysis.[4] Little attention has been paid to reactions of 1. Previous investigations were not extended beyond investigation of reactions with sodium alcoholate,[1c,5] alkyllithium,[4] and β-diketone.[4] It is seen that the products in these reactions are formed by attack of nucleophiles such as OR^-, R^-, RCO^-CHCOR on sulfur with cleavage of the sulfur–sulfur or sulfur–oxygen bond. Recently, we have also found that[6] equimolar thiocarboxylic acids readily displace an alcohol moiety and afford acylalkoxy trisulfides (3). We have now studied reactions of 1 with other nucleophiles.

ROSSOR

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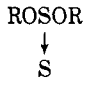
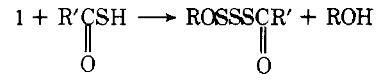


$\underset{\underset{S}{\downarrow}}{ROSOR}$

2

$$2ROH + SCl_2 + 2Et_3N \longrightarrow 1 + 2Et_3NHCl \qquad (1)$$



$$1 + R'\underset{\underset{O}{\|}}{C}SH \longrightarrow ROSSS\underset{\underset{O}{\|}}{C}R' + ROH \qquad (2)$$

3

Results and Discussion

Dialkoxy disulfides (1) react readily with equimolar amounts of mercaptan in carbon tetrachloride. The alcohol is eliminated gradually, and monosubstituted products, alkoxyalkyl trisulfides (4), are obtained in 20–50% yields along with disubstituted products, symmetrical dialkyl tetrasulfides. Elimination of alcohol was confirmed by infrared spectra and gas chromatography. Results are shown in Table I. The IR spectra of 4 showed absorptions similar to those of 1 in -SO- (660–725 cm^{1}) and $>$CO- (880–1020 cm^{-1}) stretching bands (Table III, Supplementary Material). The NMR spectra of 4 showed simple absorptions in its protons of methylene adjacent to an oxygen atom, RCH_2O- (Table III, Supplementary Material), with no apparent magnetic nonequivalence.[7]

Secondary amines were less reactive than mercaptans and their reaction with 1 required refluxing in CCl_4 for 4–8 h. Alkoxyamino disulfides (5) (Scheme I) were obtained in 19–74%

Scheme I