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DESULFURIZATION AND *ortho*-METALATION REACTIONS OF DIMANGANESE DECACARBONYL

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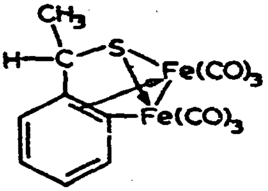
Summary

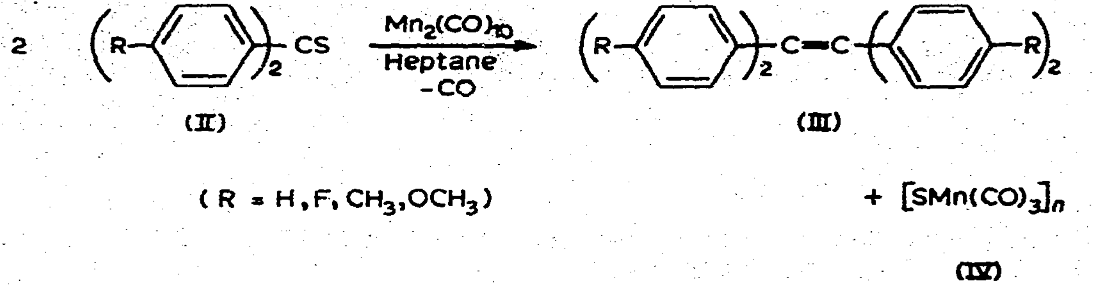
Thiobenzophenone, and 4,4'-disubstituted derivatives having moderately electron-donating (methyl, methoxy) or electron-withdrawing (fluoro) groups, react with dimanganese decacarbonyl in refluxing heptane to produce olefins (and a sulfur manganese carbonyl complex) in good yield. 4,4'-Bis(dialkylamino)-thiobenzophenones reacted with the metal carbonyl to give sulfur-donor ligand *ortho*-metalated complexes as the major product and 4,4'-bis(dialkylamino)diphenylmethanes as by-products. A mechanistic scheme is proposed for these reactions.

Thiobenzophenones react with iron [1] and ruthenium [2] carbonyls, as well as with palladium [3], platinum [3], and rhodium [4] halides, to afford sulfur—donor ligand *ortho*-metalated complexes (e.g. I) in very good yields. No reports have appeared in the literature regarding the reaction of thioketones with dimanganese decacarbonyl [$Mn_2(CO)_{10}$]. It was of considerable interest to learn whether *ortho*-metalation would occur on exposure of thiones to $Mn_2(CO)_{10}$, or whether an alternative reaction might take place.



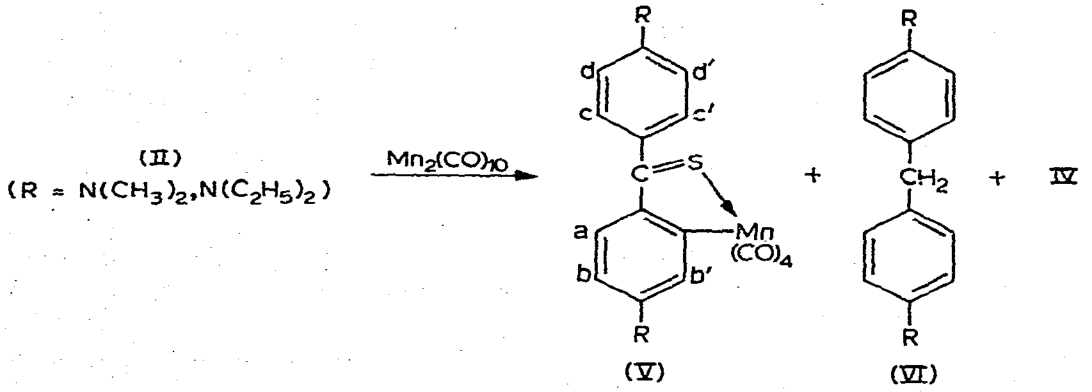
(I)

Reaction of thiobenzophenone (II, R = H) with $Mn_2(CO)_{10}$ in refluxing n-heptane affords tetraphenylethylene (III, R = H) in 69% yield. Reasonable yields of olefins were also realized by treating the metal carbonyl with thiones possessing



moderately electron-donating (II, R = CH_3, OCH_3) or electron-attracting (II, R = F) substituents (Table 1). The mole ratio of II/$Mn_2(CO)_{10}$ used was approximately 2/1. The reaction is not catalytic in the metal carbonyl.

IV, a compound displaying relatively low solubility in organic solvents, was also formed in these reactions. The IR spectrum of IV (KBr) exhibited two intense terminal metal carbonyl stretching bands at 1995 and 1915 cm^{-1}, a shoulder at 2010 cm^{-1}, and a weak band at 1978 cm^{-1}. These spectral results are similar to those reported for alkylthiotricarbonylmanganese tetramers [7—9]. Although it has not been possible, thus far, to obtain IV in analytically pure form, the IR data indicate it to be a sulfur tricarbonylmanganese complex, possibly of polymeric constitution.



Wine-red sulfur-donor ligand *ortho*-metalated complexes (V) were isolated from reaction of $Mn_2(CO)_{10}$ with thiones containing the highly activating di-

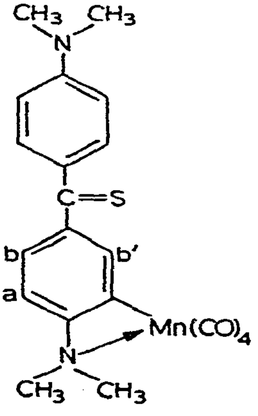
TABLE 1

YIELDS OF OLEFIN OBTAINED FROM REACTION OF II AND $Mn_2(CO)_{10}$

II,R	Yield of III (%)	M.p. (°C)	Lit. m.p. (°C)
H	69	223 —225	224 — 226[a]
F	72	208 —210	203[b]
CH_3	63	148 —150	150.0[b]
OCH_3	65	183.5—184.5	184.5—186.0

[a] Ref.5. [b] Ref.6.

methylamino and diethylamino substituents. The structure for V was assigned on the basis of analytical data and spectral results. The IR spectra for V, R = $N(CH_3)_2$ [ν(CO) (CCl_4): 2068s, 1978vs(br) and 1932vs cm^{-1}], and for V, R = $N(C_2H_5)_2$ [ν(CO) (CCl_4): 2062s, 1982vs, 1972s, 1927s cm^{-1}], in the terminal metal carbonyl stretching region, are analogous to data obtained for five-membered ring nitrogen-donor ligand *ortho*-manganated complexes derived from Schiff bases [10] and from benzo[*h*]quinoline [11]. Two singlets were observed in the proton NMR($CDCl_3$) spectrum of V [R = $N(CH_3)_2$] at δ 3.06 and 3.19 ppm, and were assigned to the dimethylamino groups of the *ortho*-metalated and uncomplexed benzene rings, by analogy with the results for substituted *ortho*-palladated and *ortho*-platinated complexes [3]. Another noteworthy feature of the NMR spectrum is the occurrence of a doublet of doublets at δ 6.45 ppm due to H_b (J_{ab} 9.0 Hz; J_{bb} 2.0 Hz). If metalation occurred *ortho* to one of the dimethylamino groups, i.e. to give the four-membered ring complex VII, then the doublet of doublets (H_b) would be expected to occur at much lower field. Furthermore, the two methyls of the complexed dimethylamino group would probably be non-equivalent. The NMR spectrum for V [R = $N(C_2H_5)_2$], shows the same characteristics as that for V [R = $N(CH_3)_2$, see Experimental].

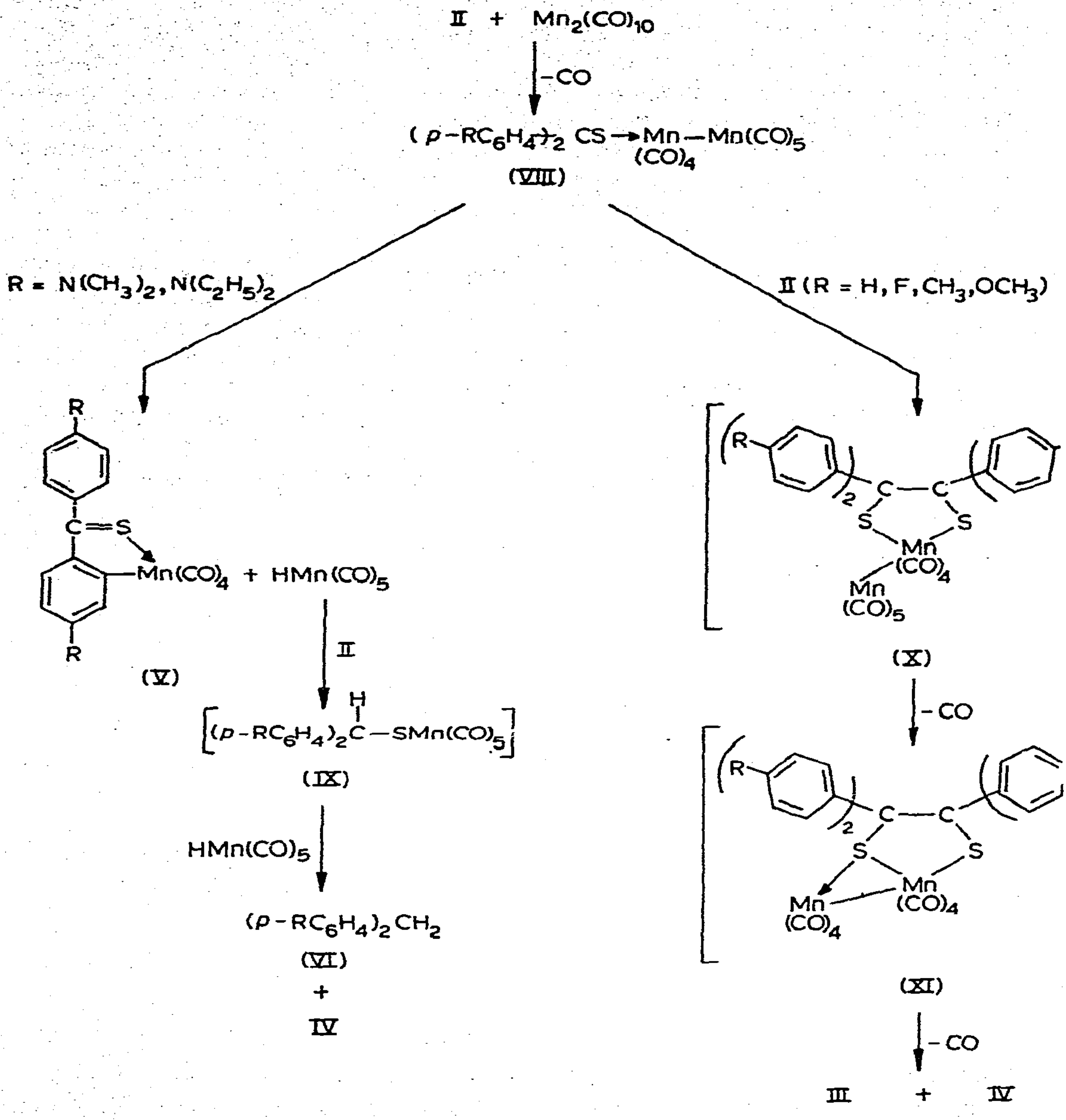


(VII)

A by-product of the reactions of $Mn_2(CO)_{10}$ and II [R = $N(CH_3)_2$, $N(C_2H_5)_2$] was the 4,4'-bis(dialkylamino)diphenylmethane [VI, R = $N(CH_3)_2$, $N(C_2H_5)_2$]. A possible pathway for formation of V and VI is presented in Scheme 1. Initial attack of the thione on the metal carbonyl would give VIII (accompanied by loss of carbon monoxide). The presence of the dialkylamino groups in the *para* positions of VIII would render the benzene ring highly susceptible to electrophilic *ortho*-metalation, thus affording V and hydridopentacarbonylmanganese. The latter can then add to the thione function of II to give VI, probably via IX.

When VIII contains R groups which are less activating than dialkylamino, then addition of thione to VIII may give X, which upon loss of carbon monoxide and S—Mn donor-ligand complexation, would afford complex XI. Collapse of the latter would generate IV and the tetraarylethylene III.

SCHEME 1



Experimental

General comments

Melting points were determined using a Fisher—Johns apparatus and are uncorrected. Infrared spectra were obtained using a Perkin—Elmer 457 spectrometer. Proton NMR spectra were determined using a Varian A60 spectrometer. An MS 902 spectrometer was used for mass spectral analyses. Dimanganese decacarbonyl was purchased from Pressure Chemical Company and used as received. All reactions were run under a dry nitrogen atmosphere.

Thiobenzophenones

4,4'-Dimethoxythiobenzophenone and 4,4'-bis(dimethylamino)thiobenzophenone were purchased from Aldrich Chemical Company. Thiobenzophenone and 4,4'-dimethylthiobenzophenone were prepared from the corresponding ketones according to the procedure of Scheeren and co-workers [12]. The latter procedure was also used to prepare 4,4'-bis(diethylamino)thiobenzophenone (43% yield, m.p. 157—158°; lit. [13] m.p. 158°) and 4,4'-difluorothiobenzophenone [52% yield; blue oil; ν(CS) (CCl_4): 1223 cm^{-1}]. 4,4'-Difluorothiobenzophenone should be stored in a freezer.

General procedure for converting thioketones to olefins

A mixture of thioketone (2.54 mmol) and $Mn_2(CO)_{10}$ (1.28 mmol) in n-heptane (40—90 ml) was refluxed with stirring for 24—28 h. The solution was cooled somewhat, filtered, and the filtrate was flash evaporated (A). The heptane-insoluble solid was treated with benzene (50—200 ml), filtered from IV, and the filtrate was flash evaporated to give the alkene III. Additional III was obtained by dissolving (A) in benzene, chromatographing on neutral alumina, and eluting with benzene or ether [any unreacted $Mn_2(CO)_{10}$ would elute off the column first]. The melting points and yields of III are listed in Table 1. Identification of III was made on the basis of m.p., IR, NMR, and mass spectra (e.g. III, R = OCH_3, gave a molecular ion peak at *m/e* 452).

Use of a catalytic amount of $Mn_2(CO)_{10}$ gave almost complete recovery of reactants.

Reaction of 4,4'-bis(dimethylamino)thiobenzophenone with $Mn_2(CO)_{10}$

A mixture of thione (0.72 g, 2.52 mmol) and $Mn_2(CO)_{10}$ (1.0 g, 2.56 mmol) in heptane (55 ml) was refluxed with stirring for 19 h. The solution was filtered and flash evaporation of the filtrate gave a mixture of $Mn_2(CO)_{10}$ and VI. The latter mixture was treated with 25 ml of hexane, filtered [IV, $Mn_2(CO)_{10}$], and the filtrate was chromatographed on neutral alumina. Elution with hexane gave unreacted $Mn_2(CO)_{10}$. Elution with ether—benzene (1/1) gave bis(dimethylamino)-diphenylmethane [0.068 g, 11%], m.p. 90—92° (lit. [4] 90°), mass spectrum (*m/e*) 254 [M^+].

The heptane-insoluble solid was treated with benzene, filtered from IV, and the filtrate was chromatographed on neutral alumina. Elution with benzene gave the *ortho*-metalated complex V [R = $N(CH_3)_2$] (0.67 g, 59%), as a wine-red air-stable solid, m.p. 182—184° (dec.). (Found: C, 56.35; H, 4,54; N, 6.11; S, 6.92. $C_{21}H_{19}MnN_2O_4S$ calcd.: C, 56.00; H, 4.25; N, 6.22; S, 7.12%.) IR(CCl_4): ν(CO) 2068s, 1978vs(br), 1932vs cm^{-1}. IR(KBr): ν(CO) 2062ms, 1980m(sh), 1968s, 1958s, 1916s, 1898(sh) cm^{-1}. Proton NMR($CDCl_3$; TMS as internal standard): δ 3.06 [s,$N(CH_3)_2$ of complexed ring], 3.19 [s,$N(CH_3)_2$ of uncomplexed ring], 6.45 (dd,H_b, J_{ab} 9.0 Hz, J_{bb} 2.0 Hz), 6.71 (d,H_{dd}, J_{cd} and $J_{c'd'}$ 9.0Hz), 7.38 (d,$H_{b'}$), 7.55 (d,$H_{cc'}$), 7.69 (d,H_a) ppm.

Reaction of 4,4'-bis(diethylamino)thiobenzophenone with $Mn_2(CO)_{10}$

A mixture of the thioketone (0.395 g, 1.16 mmol) and $Mn_2(CO)_{10}$ (0.400 g, 1.03 mmol) in n-heptane (50—55 ml) was refluxed with stirring for 24 h. Work-up as for II [R = $N(CH_3)_2$] gave VI [R = $N(C_2H_5)_2$] in 14% yield, m.p.

42–44° (lit. [15] 43.5–44.0°), and the *ortho*-metalated complex V [R = $N(C_2H_5)_2$] in 24% yield, m.p. 123–125° (dec.). (Found: C, 59.21; H, 5.39; N, 5.27; S, 6.18. Mol. wt. 492. $C_{25}H_{27}MnN_2O_4S$ calcd.: C, 59.29; H, 5.37; N, 5.53; S, 6.33%. Mol. wt. 506.5.) IR(CCl_4): ν(CO) 2062s, 1982vs, 1972s, 1927s cm^{-1}. Proton NMR($CDCl_3$; TMS as internal standard): δ 1.18 [t, $N(CH_2C\underline{H}_3)_2$ of complexed ring], 1.28 [t, $N(CH_2C\underline{H}_3)_2$ of uncomplexed ring], 3.40 [center of multiplet, methylene groups of $N(C_2H_5)_2$ of both complexed and uncomplexed rings], 6.38 (dd,H_b, J_{ab} 9.0 Hz, $J_{bb'}$ 2.5 Hz), 6.66 (d,$H_{dd'}$, J_{cd} and $J_{c'd'}$ 9.0 Hz), 7.28 (d,$H_{b'}$), 7.55 (d,$H_{cc'}$), 7.73 (d,H_a) ppm.

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References

1 H. Alper and A.S.K. Chan, J. Amer. Chem. Soc., 95 (1973) 4905.
2 H. Alper and A.S.K. Chan, J. Organometal. Chem., 61 (1973) C59.
3 H. Alper, J. Organometal. Chem., 61 (1973) C62.
4 H. Alper, unpublished results.
5 C.E. Coffey, J. Amer. Chem. Soc., 83 (1961) 1623.
6 P.J.M. Burchill and N. Thorne, J. Chem. Soc. C, (1968) 696.
7 E.W. Abel and B.C. Cross, J. Chem. Soc. A, (1966) 1141.
8 A.G. Osborne and F.G.A. Stone, J. Chem. Soc. A, (1966) 1143.
9 B.F.G. Johnson, P.J. Pollick, I.G. Williams and A. Wojcicki, Inorg. Chem., 7 (1968) 831.
10 R.L. Bennett, M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 1787.
11 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal. Chem., 60 (1973) 343.
12 J.W. Scheeren, P.H.J. Ooms and R.J.F. Nivard, Synthesis, (1973) 149.
13 D.F.J. Lynch and J.D. Reid, J. Amer. Chem. Soc., 55 (1933) 2515.
14 L. Horner and H. Nickel, Ann., 597 (1955) 20.
15 J. Arient and J. Dvorak, Chem. Listy, 48 (1954) 1581.