Journal of Organometallic Chemistry, 121 (1976) 225–235

REACTION OF THIOBENZOPHENONES WITH THE MANGANESE PENTACARBONYL ANION

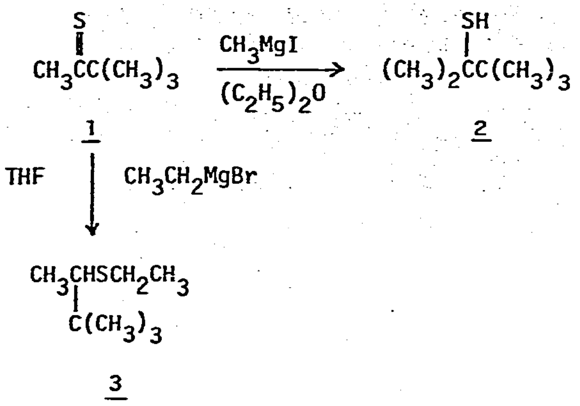
Howard Alper* and Hang-Nam Paik
Department of Chemistry
University of Ottawa
Ottawa, Ontario, Canada K1N 6N5

(Received August 30th, 1976)

ABSTRACT

The first study of the reactions of thioketones with metal carbonyl anions is described. Reaction of thiobenzophenones with the manganese pentacarbonyl anion and methyl iodide or benzyl bromide in methanol affords the complexes $[Ar_2CHSMn(CO)_4]_2$, identified on the basis of analytical and ir, as well as nmr (^1H, ^{13}C) spectral data. The reaction is proposed to occur via charge-transfer and radical intermediates.

There has been considerable recent interest in the reactions of nucleophiles, particularly Grignard reagents and organolithium compounds, with thioketones[1]. What is intriguing about this subject is that nucleophilic addition can occur at the sulfur (thiophilic) and/or carbon atom of the thiocarbonyl group (e.g., 1 → 2 or 3 as the major products)[1c], although the factors which govern the site of addition are not well understood.



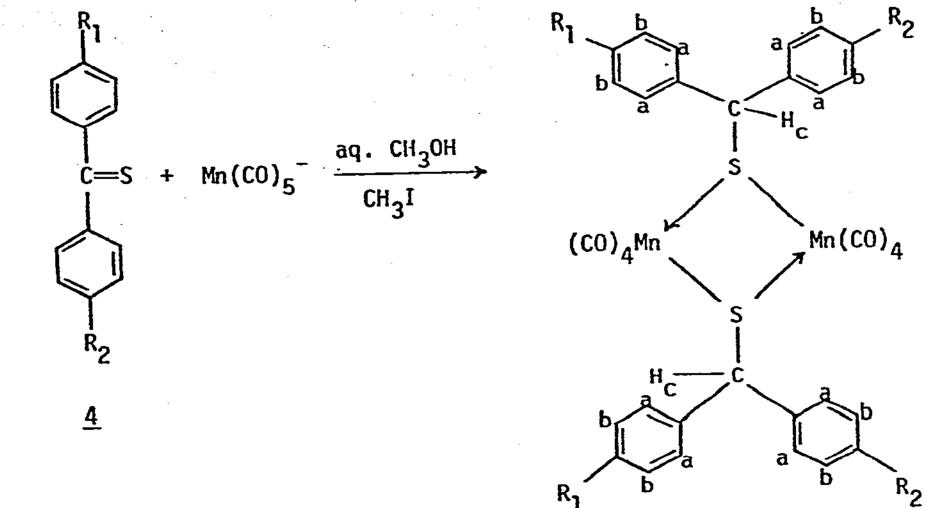
$$\begin{tikzcd} \overset{S}{\overset{\|}{CH_3CC(CH_3)_3}} \arrow[r, "CH_3MgI", "(C_2H_5)_2O"'] \arrow[d, "CH_3CH_2MgBr", "THF"'] & \overset{SH}{\overset{|}{(CH_3)_2CC(CH_3)_3}} \\ \underset{C(CH_3)_3}{\underset{|}{CH_3CHSCH_2CH_3}} & \end{tikzcd}$$

1 2 3

The reactions of transition metal carbonyl anions is another area of great interest in recent years[2]. Although many different systems have been examined, there have been no publications, to our knowledge, on the reactions of thioketones with metal carbonyl anions. An investigation of the latter reactions may eventually provide answers to the following: does addition of the metal carbonyl anion occur at the sulfur and/or carbon atom of the thione; is the position of attack a function of nucleophilic strength; what is the mechanism of the thiophilic process (several mechanisms have been proposed)[1]. This paper reports a study of the reactions of thiobenzophenones with the manganese pentacarbonyl anion [$Mn(CO)_5^-$].

RESULTS AND DISCUSSION

Treatment of thiobenzophenone [4, $R_1 = R_2 = H$] and a series of para-substituted thiobenzophenones [4, $R_1 = R_2 = CH_3$, $N(CH_3)_2$, F, OCH_3; $R_1 = OCH_3$, $R_2 = H$] with $Mn(CO)_5^{\ominus}$ and methyliodide (or benzylbromide) in aqueous methanol gave the yellow dimanganese octacarbonyl complex, 5. The yields and melting points of analytically pure materials (crude



4

5

yields were higher) are given in Table I, and pertinent infrared (ir), proton and carbon-13 nuclear magnetic resonance (nmr) spectral data are listed in Table II.

Terminal metal carbonyl stretching bands occurred in the ir at 2050 - 2065, 1990 - 1998, and 1960 - 1966 cm^{-1}, and a weak absorption appeared in the region of 1920 - 1940 cm^{-1}. Simple alkyl or perfluoroalkyl analogs of 5, obtained from disulfides[3] or sulfenyl halides[4], display a similar ir carbonyl absorption pattern.

The methine proton of 5 (H_c) gave a singlet signal in the proton nmr at δ 4.98 - 5.12 ($CDCl_3$), in good agreement with data for related diarylmethyl sulfides [e.g., $Ph_2CHSC_4H_9$].[5] The benzylic carbon exhibited an absorption at δ 57.1 - 61.4 in the ^{13}C nmr spectrum,[6] while those carbons to which the benzylic carbon was attached gave a signal at δ 142.8.

The complexes decomposed on attempted electron impact mass spectrometry. However, molecular weight measurements obtained for several of the complexes agree well with calculated values.

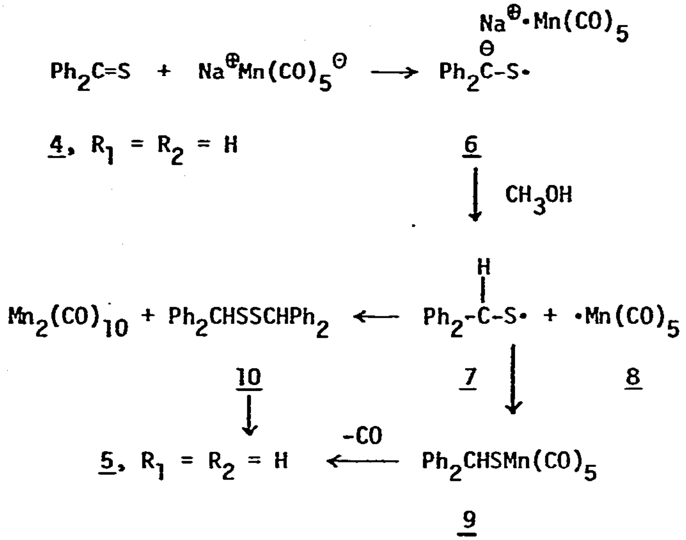
Table I. Yields, Melting Points, and Analytical Data for 5.

			Analysis found (calc'd.)			
5, R_1=R_2=	Yield %	Mp, °C(dec)	C	H	S	Mn
CH_3,CH_3[a]	32	140	57.53(57.87)	3.93(3.83)	7.62(8.13)	13.41(13.93)
OCH_3, H	21	117	53.97(54.55)	3.50(3.31)	7.96(8.09)	13.82(13.86)
OCH_3, OCH_3	29	129	53.40(53.52)	3.61(3.55)	7.78(7.52)	13.30(12.89)
H, H[b]	11	110-115	55.42(55.74)	3.08(3.03)		
F, F	14	127	50.50(50.76)	2.45(2.26)		12.98(13.50)
$N(CH_3)_2$, $N(CH_3)_2$[c]						

[a] Molecular weight (osmometry) calculated: 788. Found, 770. [b] Molecular weight (osmometry) calculated: 732. Found, 699. [c] Isolated in trace quantities. Low yield is due to heterogeneous reaction mixture.

The results for the thiobenzophenone -$Mn(CO)_5^{\ominus}$ reaction can best be rationalized by the pathway outlined in Scheme 1 (illustrated for thiobenzophenone: 4, $R_1 = R_2 = H$). The proposed initial step is formation of a charge-transfer intermediate, 6. The latter can then abstract hydrogen from solvent to give the thiyl and manganese pentacarbonyl radicals, 7 and 8, respectively. These radicals can couple with each

Scheme 1



other to give 9, or undergo self-coupling affording dimanganese decacarbonyl and the disulfide, 10. Subsequent reaction of 10 and $Mn_2(CO)_{10}$ would afford 5, $R_1 = R_2 = H$. The dimanganese octacarbonyl complex can also arise by loss of carbon monoxide from the manganese pentacarbonyl complex 9.

The hydrogen abstraction step should be facile, as witnessed by the absence of alkylated products when the reaction is effected in the presence of methyl iodide or benzyl bromide. The proposed

Table II. Ir and Nmr (^{1}H, ^{13}C) Spectral Data for 5

5, R_1=R_2=	ir,ν_{CO}, cm^{-1}(solvent)^a	^{1}H nmr, δ, ppm^b	^{13}C nmr, δ, ppm^c
CH_3, CH_3	2059m, 1993s, 1963s, 1920vw(H)	2.20(s,12H,CH_3),4.98(s,2H,H_c), 7.00(d,8H,H_b,J_{ab}=8Hz), 7.39(d,8H,H_a)	-
OCH_3,H	2060m, 1992vs, 1963s, 1930vw(C)	3.75(s,6H,R_1=OCH_3), 5.10(s,2H, Hc), 6.80-7.80(m,18H,H_a,H_b,R_2)	55.2(OCH_3), 57.1(C-H_c), 114.2(C-Hb ortho to methoxy bearing carbon), 127.6, 127.8, 128.8, 134.8(C-H_a, other C-H_b, C-R_2(142.8),aromatic carbons bearing benzylic group), 159.4(C-OCH_3)
OCH_3, OCH_3	2060m, 1995s, 1964s, 1932vw(H)	3.70(s,12H,R_1=R_2=OCH_3), 5.12 (s,2H,H_c), 6.99(d,8H,H_b,J_{ab}= 8Hz), 7.50(d,8H,H_a)	

F,F	2060m, 1993vs, 1965s, 1925w(C)		
H, H	2055m, 1990s, 1963s, 1930w (Cy)	5.00(s,2H,H_c), 7.20-7.80(m,20H,H_a,R_1,R_2)	61.4(C-H_c), 127.9, 128.2, 129.1(C-H_a,C-H_b,C-R_1, C-R_2) 142.8(aromatic carbons bearing the benzylic group)
$N(CH_3)_2$, $N(CH_3)_2$	2062m, 1998s, 1966s, 1940w (H)		

---

[a] Solvent: H-hexane, C=carbon tetrachloride, Cy = cyclohexane; vw = very weak, w = weak, m = medium, s = strong, vs = very strong. [b] $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard: s = singlet, d = doublet, m = multiplet. [c] $CDCl_3$ with TMS as internal standard.

conversion of 9 to 5 is supported by the recent observation that the related mercaptomanganese pentacarbonyl complex, $(CO)_5MnSH$, is readily converted to $[(CO)_4MnSH]_2$.[7] We have also observed that treatment of dibenzyl disulfide, $PhCH_2SSCH_2Ph$, with either $Mn(CO)_5^{\ominus}$ or $Mn_2(CO)_{10}$, results in the formation of $[PhCH_2SMn(CO)_4]_2$ (see experimental), thus supporting the 10 → 5 step in Scheme 1.

This mechanism is similar to that proposed by Ohno and coworkers[1b] for the reaction of thioketones with butyllithium, phenyllithium and sodium ethoxide in ethanol.

An investigation of the reaction of thiones with other metal carbonyl anions is currently in progress.

EXPERIMENTAL SECTION

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Drs. F. and E. Pascher, Bonn, West Germany and by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were obtained on a Beckman IR20A spectrometer, equipped with an internal calibration. Proton magnetic resonance spectra were determined on Varian T-60 and/or HA-100 spectrometers (TMS as internal standard). Carbon magnetic resonance spectra were recorded at 25.2 MHz under conditions of complete proton noise decoupling in the Fourier transform mode, using a Varian XL-100-12 nmr spectrometer equipped with the Nicolet Technology Inc. data system. Mass spectra were determined using a Varian MS 902 spectrometer.

Several of the thiobenzophenones [4, $R_1 = R_2 = OCH_3$, $N(CH_3)_2$] were purchased from Aldrich Chemical Co., and were used as received. The remaining thiobenzophenones [4, $R_1 = R_2 = CH_3$, H, F; $R_1 = OCH_3$,

R_2 = H], were synthesized according to literature methods[8-10]. Dimanganese decacarbonyl was purchased from Pressure Chemical Co., and from Alfa Inorganics, and used as received. Solvents were dried and purified by standard techniques. All reactions were run and worked up under a dry nitrogen atmosphere.

General Procedure for Reaction of $NaMn(CO)_5$ with Thiobenzophenones

The manganese pentacarbonyl anion was generated from dimanganese decacarbonyl and sodium hydroxide as described in the literature[11]. After filtration to remove manganese carbonate, the solution containing $Mn(CO)_5^{\ominus}$ was treated with the thiobenzophenone (4, 2.0 mmol) for 5 hr at room temperature, at which time methyl iodide or benzyl bromide (2.0 mmol) was added, and then the resulting mixture was allowed to stand overnight at room temperature. Filtration gave the yellow dimanganese octacarbonyl complex, 5, which was recrystallized from chloroform-hexane (a small amount of an unidentified oil was obtained on flash evaporation of the filtrate). The yields of analytically pure 5, based on 4, are listed in Table I.

Reaction of Dibenzyl Disulfide with $NaMn(CO)_5$ and $Mn_2(CO)_{10}$

(a) $NaMn(CO)_5$

Dibenzyl disulfide [0.33 g, 1.34 mmol - Eastman Organic Chemicals] was added to a solution of the manganese pentacarbonyl anion (1.30 mmol), generated as noted above, and then treated with methyl iodide as above. The resulting homogeneous solution was flash evaporated and chromatographed on silica gel with hexane. Elution with 9 : 1 hexane-benzene gave $[PhCH_2SMn(CO)_4]_2$. Recrystallization from hexane afforded the pure yellow complex in 20% yield: mp 106 - 110° dec; ir (cyclohexane) ν_{CO} 2060 m, 1993 vs, 1970 sh, 1960 vs, 1923 vw cm^{-1}; nmr ($CDCl_3$), δ 3.72 (s, 4H, CH_2), 7.37 (s, 10H, C_6H_5). Anal. Calcd. for $C_{22}H_{14}Mn_2O_8S_2$: C, 45.53; H, 2.43; S, 11.05. Found: C, 45.74; H, 2.45; S, 10.76.

(b) $Mn_2(CO)_{10}$

A mixture of dibenzyl disulfide [0.250 g, 1.02 mmol] and $Mn_2(CO)_{10}$ [0.195 g, 0.50 mmol] in degassed cyclohexane (5 ml.) was heated at 110 - 115° in a Carius tube for 20 hr. The Carius tube was then opened, and the resulting yellow solution was cooled to 0° to give a yellow compound. The latter was filtered and recrystallized from petroleum ether (bp 80 - 100°) to give pure complex in 16% yield, identical in all respects with the product obtained from dibenzyl disulfide and $NaMn(CO)_5$.

ACKNOWLEDGEMENTS

We are grateful to Imperial Oil Limited, and to the National Research Council of Canada, for support of this research. Mr. R. Capoor and Mr. B. Dawson are thanked for recording spectra on the HA-100 and XL-100-12 nmr spectrometers, respectively.

REFERENCES

1. (a) P. Beak, J. Yamamoto and C.J. Upton, J. Org. Chem., 40, 3052 (1975); (b) A. Ohno, K. Nakamura, M. Uohama, S. Oka, T. Yamabe, and S. Nagata, Bull. Chem. Soc. Japan, 48, 3718 (1975); D. Paquer, Bull. Soc., Chim. France, 1439 (1975) and references cited within these papers.
2. An excellent, recent review has appeared on the subject: J.E. Ellis, J. Organometal. Chem., 86, 1 (1975).

3. P.M. Treichel, J.H. Morris and F.G.A. Stone, J. Chem. Soc., 720 (1963).

4. J. Grobe and F. Kober, J. Organometal. Chem., 24, 191 (1970).

5. P. Beak and J.W. Worley, J. Amer. Chem. Soc., 94, 597 (1972).

6. J.B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

7. V. Kullmer and H. Vahrenkamp, Chem. Ber., 109, 1560 (1976).

8. H. Alper and A.S.K. Chan, J. Amer. Chem. Soc., 95, 4905 (1973).

9. J.W. Scheeren, P.H.J. Ooms and R.J.F. Nivard, Synthesis, 149 (1973).

10. H. Alper, J. Organometal. Chem., 73, 359 (1964).

11. R.B. King, Organometal. Syn., 1, 147 (1965).