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Registry No.-2,2-Dimethylglutaric acid, 681-57-2; 2,2-dimethyl-1,5-pentyl di-p-toluenesulfonate, 62718-14-3; 2,2-dimethylpentane-1,5-diol, 3121-82-2; 3-thiaheptanedioic acid diethyl ester, 63449-37-6; 3-oxothiapyran, 19090-03-0.

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New Effective Desulfurization Reagents

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Hydrocarbons and amines are formed in good yields by treatment of thioketones and thioamides, respectively, with iron pentacarbonyl and potassium hydroxide [i.e., $HFe(CO)_4^{-}$]. A different, and useful, desulfurization reaction occurred by the use of dicobalt octacarbonyl, the cobalt tetracarbonyl anion, or cyclopentadienyliron dicarbonyl dimer as reagents. Mechanisms are proposed for several of these reactions.

There is considerable current interest in the desulfurization of fuel oil and flue gases. A variety of materials (e.g., butagas)¹ have been employed, with mixed success, as desulfurization reagents. We have initiated a study directed toward the development of new desulfurization reagents, the results of such an investigation being potentially applicable to the fuel oil desulfurization problem. This paper describes the use of several iron and cobalt carbonyls in the desulfurization of thiocarbonyl compounds.²

Iron pentacarbonyl reacts with 3 equiv of hydroxide ion to generate the hydridotetracarbonylferrate anion $[HFe(CO)_4^-]$. The latter can effect a variety of interesting transformations including the room temperature reduction of nitroarenes to anilines in high yields.³ We have now found the hydride to be a convenient desulfurization reagent.

Aliphatic and aromatic thicketones (1) react with 4 equiv

 $R_{2}C = CR_{2}$

of $HFe(CO)_4^-$ in hot 1,2-dimethoxyethane (8–12 h) to give the corresponding hydrocarbon, 2, in 60-81% yield. Thioamides also react with $HFe(CO)_4^-$ affording amines in lower, but reasonable, yields as compared to thioketones. Product yields and melting points or boiling points are listed in Table I.

Treatment of 4,4'-dimethoxythiobenzophenone (1, R = p-CH₃OC₆H₄) with DFe(CO)₄⁻ [from KOD and Fe(CO)₅] affords the dideuterio compound, $(p-CH_3OC_6H_4)_2CD_2$, in 74% yield. Similarly 2,2'-dideuterioadamantane was obtained in 78% yield from adamantanethione.

A different desulfurization reaction takes place when the cobalt tetracarbonyl anion is employed as the reagent. Reaction of bis(triphenylphosphine)iminium tetracarbonylcobaltate $[(Ph_3P)_2N+Co(CO)_4^{-}]^4$ with thiobenzophenones in benzene at 90-100 °C (Carius tube) affords tetraarylethylenes (3) in 45-70% yields (Table II). Significantly higher yields of 3 (71–83%) could be realized by simply refluxing a mixture of the thione and dicobalt octacarbonyl $[Co_2(CO)_8)]$ in benzene for 5 h. Desulfurization was also observed using the cyclopentadienyliron dicarbonyl dimer $[C_5H_5Fe(CO)_2]_2$, but this reagent is less effective than dicobalt octacarbonyl.

Possible pathways for the $HFe(CO)_4^-$ ion reaction are illustrated in Scheme I. Thiophilic addition of the iron hydride to the thione would give 4 which can then undergo a hydride shift to form 5. The latter is convertible to the hydrocarbon 2, either by attack of another molecule of $HFe(CO)_4^-$ or by

Table I. Products Obtained from Reactions of Organosulfur Compounds with Fe(CO)5 and KOH

Registry no.	Reactant	Product ^a	Yield, %	Mp or bp, °C	Lit. mp or bp, °C
1450-31-3	Ph_2CS	Ph_2CH_2	60	265-267	264.3 ^b
1141-08-8	$(p-CH_3C_6H_4)_2CS$	$(p-CH_3C_6H_4)_2CH_2$	61	138–140 (4 mm)	150 (10 mm) ^c
958-80-5	$(p-CH_3OC_6H_4)_2CS$	$(p-CH_3OC_6H_4)_2CH_2$	77	52-53	52-53 ^d
1226-46-6	$(p - (CH_3)_2 NC_6 H_4)_2 CS$	$(p-(CH_3)_2NC_6H_4)_2CH_2$	81	90-91	$91 - 92^{b}$
23695-65-0	Adamantanethione	Adamantane	74	266-268	268^{b}
636-04-4	PhCSNHPh	PhCH ₂ NHPh	38	36-38	37–38 ^b
637-53-6	CH ₃ CSNHPh	$CH_3C\tilde{H}_2NHPh$	51	100-103 (20 mm)	97.5–98 (18 mm) ^b

^a Infrared, nuclear magnetic resonance, and mass spectral data were in excellent accord with those for authentic samples. ^b "Handbook of Chemistry and Physics", 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969. ^c A. B. Galun, A. Kaluszyner, and E. D. Bergmann, J. Org. Chem., **27**, 1426 (1962). ^d L. H. Conover and D. S. Tarbell, J. Am. Chem. Soc., **72**, 3586 (1950).

1, R =	Metal carbonyl	Yield of 3, ª %	Mp, °C	Lit. ^{<i>b</i>} mp, °C
Ph	Α	45	222-224	224-226
	В	71		
	С	55		
p-CH ₃ - OC ₆ H ₄	Α	70	184–185	184.5–186
• -	В	75		
	С	68		
$p-CH_3C_6H_4$	Α	58	149 - 150	150.0 - 150.5
	В	83		
	С	68		

Table II. Yields of Olefins (3) Formed By Reaction of [(Ph₃P)₂N⁺Co(CO)₄⁻] (A), Co₂(CO)₈ (B), or [C₅H₅Fe(CO)₂]₂ (C) with Thiones (1)

^a Spectral properties [IR, NMR (¹H, ¹³C), MS] were in excellent accord with that for authentic samples. Yields are based on 1. ^b C. E. Coffey, J. Am. Chem. Soc., 83, 1623 (1961).

decomplexation to the carbanion 6, followed by protonation.

Thiophilic addition (to give 7) is also the probable initial step in the reaction of 1 with $(Ph_3P)_2N^+Co(CO)_4^-$ (Scheme II). Since no hydride is present in 7, a second thiophilic addition can take place to give 8. Intramolecular displacement of $-SCo(CO)_4$ from 8 would generate the thiirane (episulfide), 9. Desulfurization of the latter by $Co(CO)_4^-$ [or perhaps by the generated $-SCo(CO)_4$] results in olefin formation. Some support for the conversion of 9 to 3 comes from the observed desulfurization of trans-2,3-diphenylthiirane to trans-stilbene in 71% yield by the cobalt tetracarbonyl anion. A similar mechanism has been suggested by Beak and Worley⁵ for the reaction of thiobenzophenones with Grignard and organo-lithium reagents.

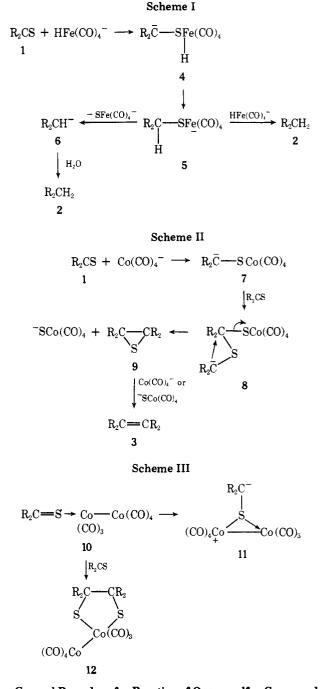
For the neutral metal carbonyl, $Co_2(CO)_8$, the initial step may involve formation of the sulfur-donor ligand complex 10 (Scheme III). The transformation of 10 to the alkene 3 may occur via the sulfur bridging zwitterionic complex 11, or via reaction with additional thione to give 12.

Experimental Section

General. Melting points were determined using a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 1R20A spectrometer. Nuclear magnetic resonance spectra were determined using a Varian T60 spectrometer, and a Varian MS902 spectrometer was employed for recording mass spectra.

The thioketones were prepared by reaction of the corresponding ketones with phosphorus pentasulfide.^{6,7} Cyclopentadienyliron dicarbonyl dimer was purchased from Pressure Chemical Co., and was used as received. Bis(triphenylphosphine)iminium tetracarbonylcobaltate was synthesized from dicobalt octacarbonyl according to the procedure of Ruff and Schlientz.⁴

Solvents were dried by standard techniques. All reactions were run under a dry nitrogen atmosphere.



General Procedure for Reaction of Organosulfur Compounds with the Hydridotetracarbonylferrate Anion. A mixture of iron pentacarbonyl (3.0 mL, 22.1 mmol), KOH (3.69 g, 66 mmol), and water (6.0 mL) was refluxed in 1,2-dimethoxyethane (90 mL) for 1.5 h to generate $HFe(CO)_4^-$. The organosulfur compound (5.0–5.6 mmol)

in 1.2-dimethoxyethane (15-35 mL) was added to this solution and the mixture was refluxed for 8-12 h. The solution was cooled and filtered, and the filtrate was concentrated in vacuo. The crude product was treated with ether (150-200 mL) and filtered, and the filtrate was washed with equal volumes of water until the aqueous layer was colorless (three or four washings). The ether extract was dried (MgSO₄), percolated through a short column of Florisil (if necessary), and concentrated to give the pure desulfurized product.

General Procedure for Reaction of Thiones with Bis(triphenylphosphine)iminium Tetracarbonylcobaltate and Cyclopentadienyliron Dicarbonyl Dimer. The thicketone (2.5 mmol) and $(Ph_3P)_2N^+Co(CO)_4^-$ or $[C_5H_5Fe(CO)_2]_2$ (1.4 mmol) in benzene (5–7 mL) was heated in a Carius tube at 90–100 °C for 4 days. During this period, a large amount of black precipitate was formed. The tube was opened, the black material was filtered, and the filtrate was concentrated to 2-3 mL. The latter was chromatographed on silica gel using petroleum ether (bp 80-100 °C). Elution with benzenepetroleum ether (1:5 to 1:1) gave the olefin 3.

General Procedure for the Reaction of Thiones with Dicobalt Octacarbonyl. A mixture of the thione (2.7 mmol) and dicobalt octacarbonyl (0.51 g, 1.5 mmol) in benzene (50 mL) was refluxed for 5

h. The solution was cooled and filtered, and evaporation of the filtrate gave 3. Crystallization of the latter from benzene-petroleum ether gave the pure crystalline olefin 3.

Acknowledgment. We are grateful to Imperial Oil Ltd. for support of this research.

Registry No.—Fe(CO)₅, 13463-40-6; $[(Ph_3P)_2N^+Co(CO)_4^-]$, 53433-12-8; $Co_2(CO)_8$, 10210-68-1; $[C_5H_5Fe(CO)_2]_2$, 12154-95-9; $HFe(CO)_4^-$, 18716-80-8.

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Chemistry of Heterocyclic Compounds. 25. Selective Metalation of the Pyridine Nucleus at the 3-Position¹

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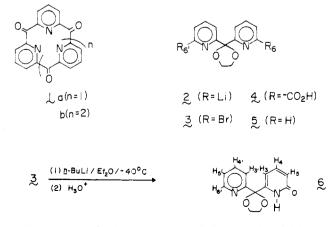
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Treatment of bis(6-bromo-2-pyridyl) ketone ketal (3) with n-butyllithium in diethyl ether at -40 °C resulted in the isolation of pyridone 6 after normal hydrolytic workup. Selective metalation of the 3 position of 3 has been demonstrated by labeling studies. The formation of pyridone 6 is proposed to occur by first 1,4-elimination-fragmentation of one pyridine nucleus, followed by cyclization upon workup.

(1)**5-8**4Lr

In one of our synthetic routes to trione $1a^{3}$ as well as the related pyridine-based xanthoporphinogen model compounds (1b), the intermediary bis(6-lithio-2-pyridyl) ketone ketal (2) was of pivotal importance. Attempted conversion of 34 to either diacid 4, according to the standard metalation-carboxylation procedure of Gilman et al.,⁵ or to 2,2-bis(2-pyridyl)-1.3-dioxolane (5) via metalation-hydrolysis, gave in both cases the undesired pyridone 6 as a major side product. We herein describe the directive metalation of the 3-position of the pyridine nucleus under normal metalation conditions⁵ and propose procedures to circumvent, as well as a rationale for, pyridone formation.



Treatment of bis(6-bromo-2-pyridyl) ketone ketal (3) with *n*-butyllithium (10% mol excess) in diethyl ether at -20 °C

for 1 h, followed by carboxylation and mild hydrolysis, gave (30%) pyridone 6 along with the starting ketal as the major nonacidic components. Structure proof of 6 was achieved by reaction of methyl 2-pyridinecarboxylate and 2-bromo-6lithiopyridine,^{5,6} affording (70%) 2-pyridyl 6-bromo-2-pyridyl ketone (7), which upon base-catalyzed ketalization⁴ gave (75%) ketal 8. Treatment of 8 with potassium tert-butoxide

in anhydrous tert-butyl alcohol7 afforded a 39% overall yield of pyridone 6. In general, hydrolyses of these pyridyl ketals occur only under rigorous conditions (6 h in refluxing concentrated hydrochloric acid or 12-18 h in warm 80% acetic acid); thus, the ketals herein described would be unaffected by the hydrolytic workup procedure.

Pyridone 6 was isolated from 3 in comparable yield when the carboxylation step was eliminated. In order to assure the complete exclusion of oxygen, rigorous degassing procedures⁸ were conducted and the reaction was conducted under an argon atmosphere; the yield of 6 remained virtually constant. However, either utilization of better anion stabilizing solvents, such as dimethoxyethane or tetrahydrofuran, or reduced reaction temperatures (-60 to -90 °C) suppressed pyridone formation, in favor of products arising from lithiated ketal. Table I summarizes the diversified reaction conditions vs. the product distribution.

In order to ascertain the position(s) of lithiation, ketal 3 was