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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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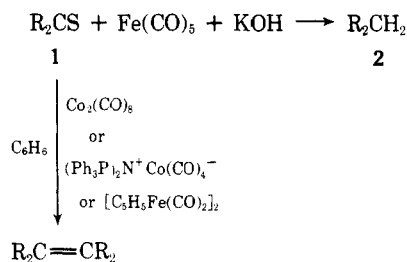
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Hydrocarbons and amines are formed in good yields by treatment of thioketones and thioamides, respectively, with iron pentacarbonyl and potassium hydroxide [i.e., $\text{HFe}(\text{CO})_4^-$]. A different, and useful, desulfurization reaction occurred 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 [$\text{HFe}(\text{CO})_4^-$]. 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 thioketones (**1**) react with 4 equiv



of $\text{HFe}(\text{CO})_4^-$ in hot 1,2-dimethoxyethane (8–12 h) to give the corresponding hydrocarbon, **2**, in 60–81% yield. Thioamides also react with $\text{HFe}(\text{CO})_4^-$ 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*- $\text{CH}_3\text{OC}_6\text{H}_4$) with $\text{DFe}(\text{CO})_4^-$ [from KOD and $\text{Fe}(\text{CO})_5$] affords the dideuterio compound, (*p*- $\text{CH}_3\text{OC}_6\text{H}_4$)₂CD₂, 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]⁻ 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 [Co₂(CO)₈] in benzene for 5 h. Desulfurization was also observed using the cyclopentadienyliron dicarbonyl dimer [C₅H₅Fe(CO)₂]₂, but this reagent is less effective than dicobalt octacarbonyl.

Possible pathways for the $\text{HFe}(\text{CO})_4^-$ 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 $\text{HFe}(\text{CO})_4^-$ or by

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 (MgSO_4), 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(tri-phenylphosphine)iminium Tetracarbonylcobaltate and Cyclopentadienyliron Dicarbonyl Dimer. The thioketone (2.5 mmol) and $(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-$ or $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (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 benzene-petroleum 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.

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Registry No.— $\text{Fe}(\text{CO})_5$, 13463-40-6; $[(\text{Ph}_3\text{P})_2\text{N}^+\text{Co}(\text{CO})_4^-]$, 53433-12-8; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, 12154-95-9; $\text{HfFe}(\text{CO})_4^-$, 18716-80-8.

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

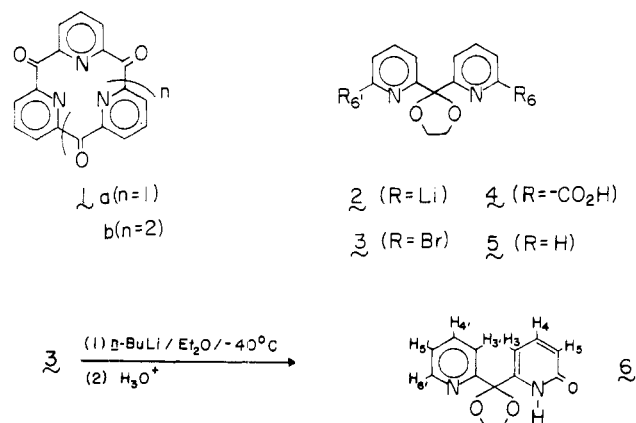
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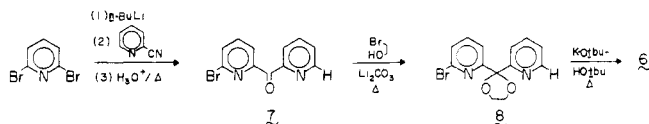
Treatment of bis(6-bromo-2-pyridyl) ketone ketal (3) with *n*-butyllithium in diethyl ether at –40 °C resulted in the isolation of pyridone 6 after normal hydrolytic workup. Selective metalation of the 3 position of 3 has been demonstrated by labeling studies. The formation of pyridone 6 is proposed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

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-6-lithiopyridine,^{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