Syntheses and Reactions of Thiobenzophenone–Alkali Metal Complexes

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Deep-red unstable compounds were formed by the reaction of thiobenzophenone with alkali metals (Li, Na, K) in tetrahydrofuran (THF) under an atmosphere of nitrogen. It was found from the esr spectra that thiobenzophenone reacts with 1 equiv of an alkali metal to form the anion radical (thioketyl) and with 2 equiv of an alkali metal to form the dianion complex. The reactions of these complexes with carbon dioxide, acid, benzyl chloride, benzaldehyde, and benzonitrile were also carried out.

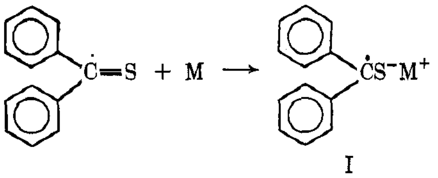
Unenolizable thioketones react with alkali metals to form colored complexes (thioketyls),[1] and, recently, Janzen, *et al.*,[2] have studied the electron spin resonance (esr) spectra of *p,p'*-dimethoxythiobenzophenone and *p,p'*-di(dimethyl)aminothiobenzophenone. Heller[3] has clarified from the esr spectra that thiobenzophenone forms the anion radical in alkali solution by irradiation.

Seman, *et al.*,[4] have studied the organic reactions of alkali metal complexes of diaryl ketone. They synthesized dialkali metal adducts of benzophenone derivatives and attempted the reaction of their complexes with many other organic compounds.

We have recently found that thiobenzophenone reacts with 1 equiv of an alkali metal to form the anion radical (thioketyl) and with 2 equiv of an alkali metal to form the dianion complex. The chemical properties of such complexes and their nucleophilic reactions to many organic compounds were examined. This paper describes the presumed nature of the alkali metal complexes of thiobenzophenone and discusses their structures and examples of the synthetic utility.

Results and Discussion

Esr Spectra.—Thiobenzophenone reacted with 1 equiv of alkali metals to form deep red thioketyls in tetrahydrofuran (THF). The esr spectrum of a THF solution of monosodium thiobenzophenone is shown in Figure 1. Its hyperfine spectrum, consisting of 70 lines, is very complex and the spectral width is about 25 G. Although it is difficult to analyze definitely, the formation of the radical anion I is suggested. The alkali metals used were lithium, sodium, and potassium and the reactivity of the alkali metal complexes increased in the order Li < Na < K. The colors of the thioketyls were all deep red.

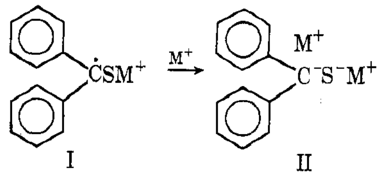


(1)

I

M = Li, Na, K

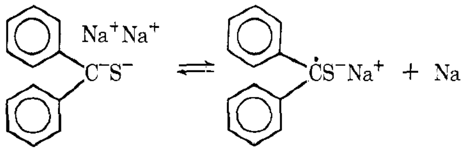
In the reaction of thiobenzophenone with more than 2 equiv of an alkali metal, a deep red dianion complex II formed.



(2)

I II

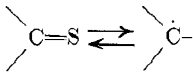
If the dianion complex has structure II, it is thought that its solution will not give an esr signal. However, the esr measurement of a THF solution of disodium thiobenzophenone gave the same hyperfine spectrum as that of thioketyl solution. From this fact, it is thought that the dianion complex II is partly in equilibrium with the anion radical I.



(3)

II I

The solution of thiobenzophenone in THF exhibited a week esr signal at 3370 G (Figure 2) also. This will be explained by the existence of radical intermediates from the reaction of thiobenzophenone with small amounts of oxygen in the air, because the thiocarbonyl group easily forms a biradical.



Visible Spectra.—A solution of thiobenzophenone in THF showed a strong absorption band at 500 mμ due to the thiocarbonyl group (Figure 3, I). Monosodium thiobenzophenone complex showed an absorption band at 530 mμ due to the excitation of an odd electron which transferred from the external orbital of a sodium atom to the lowest vacant orbital of a thiobenzophenone (Figure 3, II). The disodium thiobenzophenone complex showed an absorption band at 520 mμ. These thioketyls and dianions were all decolorized by air and moisture, and decomposed. The exchange of the visible spectrum of monosodium thiobenzophenone in air was measured and shown in Figure 4. In this figure, the 530-mμ band of the thioketyl disappears after 40 min and a new band appears at 600 mμ due to thiobenzophenone.

This is thought to show that the thioketyl decomposed slowly with oxygen and moisture in the air to form thiobenzophenone, since the surface of the solution of thioketyl was in contact with the air.

Carbonation.—The reaction of disodium thiobenzophenone with carbon dioxide was carried out by pouring a solution of the complex in THF into crushed

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(1) E. Campaigne, *Chem. Rev.*, **39**, 1 (1964).

(2) E. G. Janzen and C. M. Dubose, *J. Phys. Chem.*, **70**, 3372 (1966).

(3) H. C. Heller, *J. Amer. Chem. Soc.*, **89**, 4288 (1967).

(4) S. Seman and J. F. Eastham, *J. Org. Chem.*, **30**, 3804 (1965).

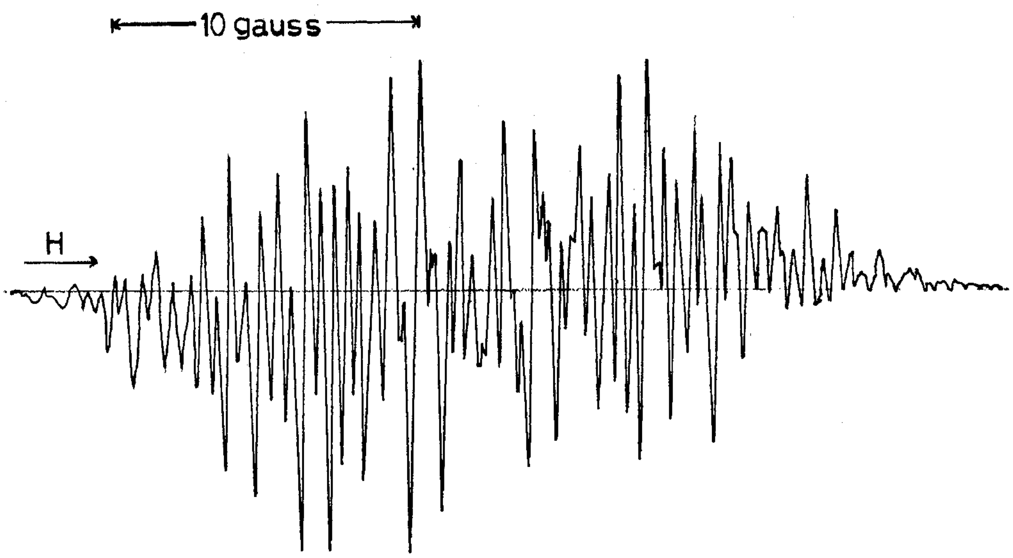


Figure 1.—Esr spectrum of monosodium thiobenzophenone in THF; c 0.19 mol/l.

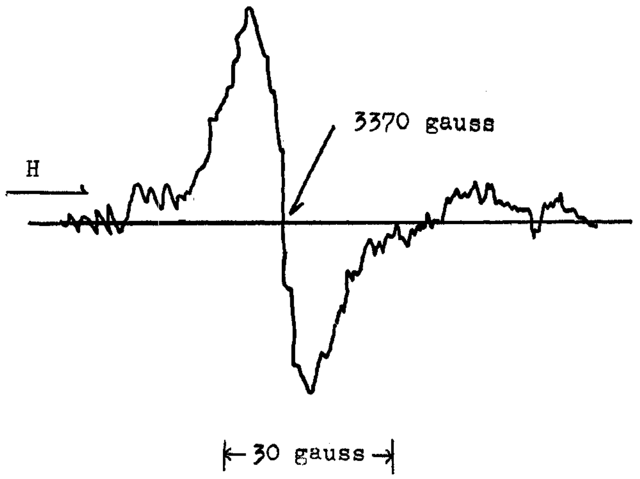
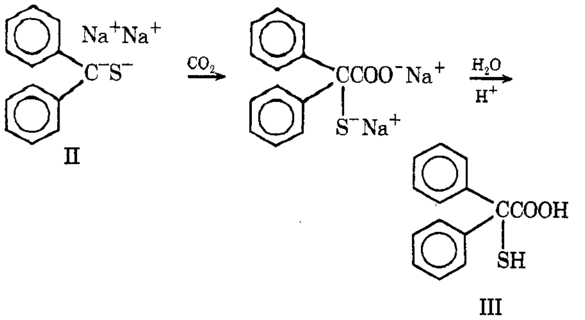


Figure 2.—Esr spectrum of thiobenzophenone in THF; c 0.19 mol/l.

Dry Ice. A white-yellow solid obtained from the acidic component was identified as thiobenzilic acid (III) by elemental analysis, melting point,[5] and infrared spectrum.

The formation of thiobenzilic acid (III) from disodium thiobenzophenone complex shows that this complex has the structure indicated by the structural formula II, which has a carbanion and a mercaptide ion, and the carbonation reaction is thought to have proceeded as shown in eq 4. Next, the carbonation



(4)

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(5) H. Becker and A. Bistrzycki, *Chem. Ber.*, **47**, 3152 (1914).

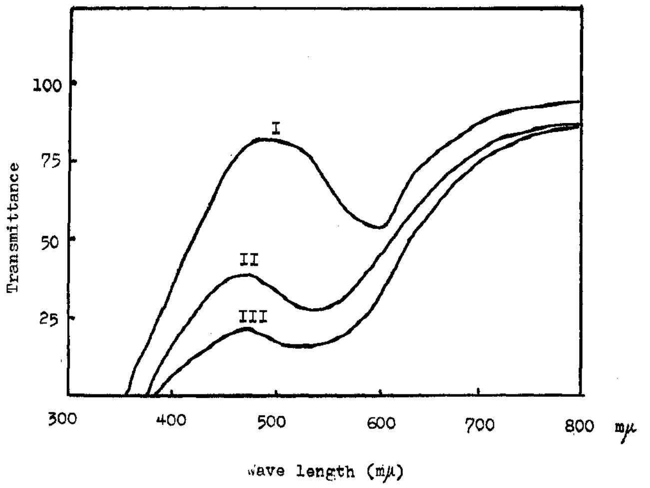


Figure 3.—The visible absorption spectra of alkali metal thiobenzophenone complexes: I, thiobenzophenone in THF; II, sodium thiobenzophenone in THF; III, disodium thiobenzophenone in THF; concentration in each case 3 × 10^{-3} mol/l.

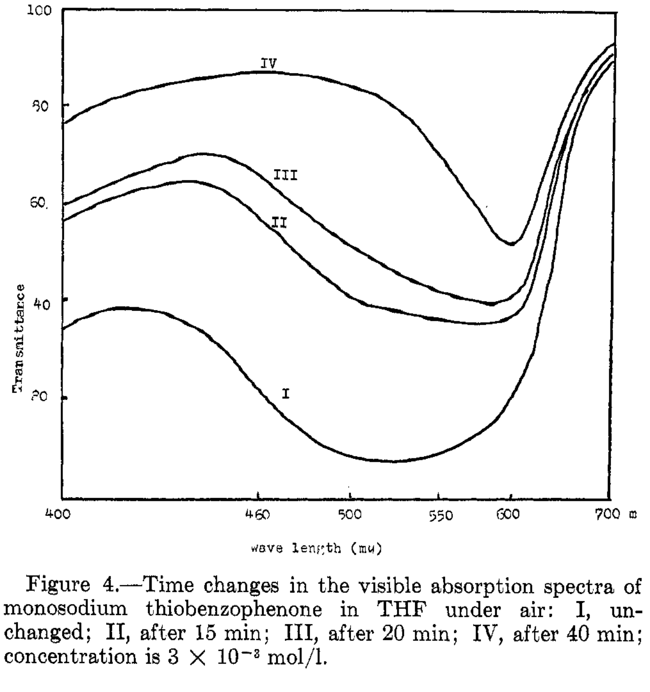
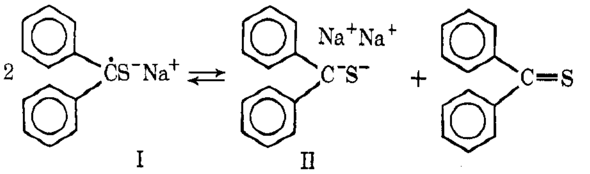


Figure 4.—Time changes in the visible absorption spectra of monosodium thiobenzophenone in THF under air: I, unchanged; II, after 15 min; III, after 20 min; IV, after 40 min; concentration is 3 × 10^{-3} mol/l.

reaction of monosodium thiobenzophenone complex gave mostly thiobenzophenone and a small amount of thiobenzilic acid (III) (4.4% yield).

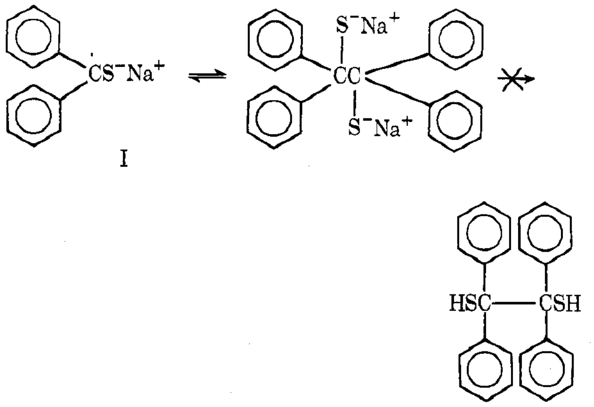
The fact that thiobenzilic acid was obtained is thought to indicate that the anion radical I partly disproportionates to the dianion II and thiobenzophenone, as shown in eq 5. Namely, it is thought that an equilibrium exists between monoanion I and dianion II, the equilibrium being far on the side of I.



(5)

I II

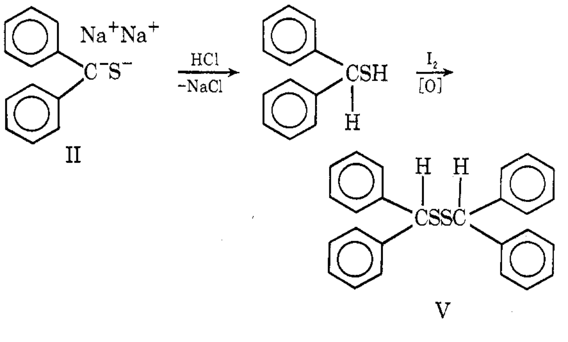
Acidic Hydrolysis.—When the THF solution of monosodium thiobenzophenone was poured into acidic ethanol, the solution became blue-violet and a large amount of sodium chloride precipitated. When the solvent was evaporated from the reaction mixture, a blue-violet solid, thought to be thiobenzophenone, was obtained. The formation of thiobenzophenone was confirmed by the fact that the reaction of this solid with 2,4-dinitrophenylhydrazine in ethanol gave thiobenzophenone 2,4-dinitrophenylhydrazone. Yet the coupling product IV of thioketyl I could not be obtained. This is thought to be due to two factors: (1) the resonance stabilization of the radical in the thioketyl with the two phenyl groups; (2) the steric hindrance of the four phenyl groups for the coupling of thioketyls.



(6)

IV

Next disodium thiobenzophenone complex was decomposed with hydrochloric acid–methanol. When the product was oxidized by air in the presence of iodine, diphenylmethyl disulfide (V) was obtained. Therefore the reaction is thought to have proceeded as in eq 7, through the formation of benzhydryl mercaptan.

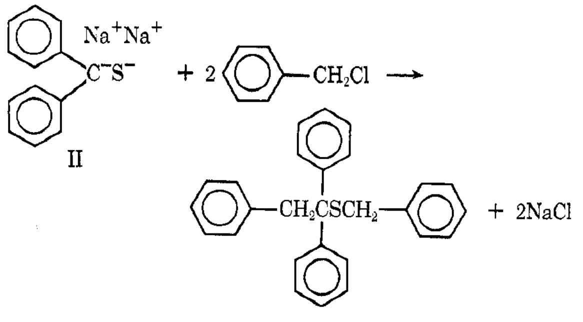


(7)

V

Reaction with Benzyl Chloride.—On the reaction of disodium thiobenzophenone complex (II) with benzyl chloride in THF under nitrogen, white, columnar crystals were obtained from the reaction mixture. It was found from infrared spectra, molecular weight, and elemental analysis that this product was a new compound, 1,1,2-triphenylethyl benzyl sulfide (VI).

This reaction may be represented by eq 8.

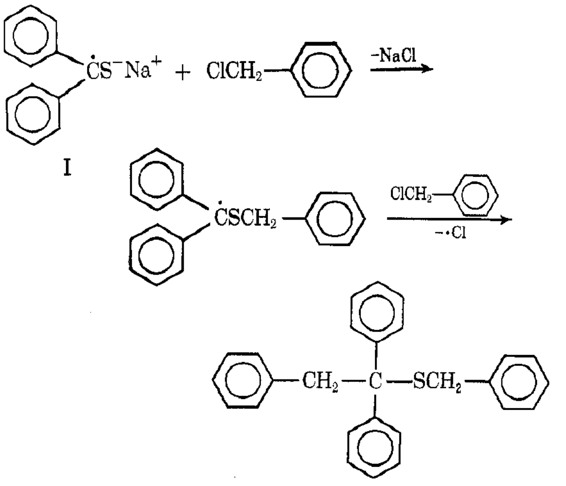


(8)

VI

As well as the dianion complex II, monosodium thiobenzophenone complex (I) reacted with benzyl chloride, and sulfide VI was obtained in 12.6% yield.

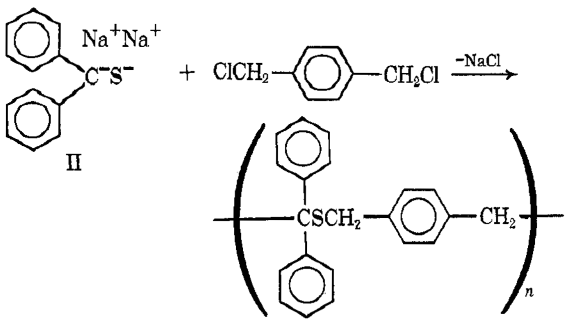
The formation of this product can be explained by the following two mechanisms. One is the mechanism in which the dianion complex, which is possibly contained in the monosodium thiobenzophenone reaction mixture, reacts with benzyl chloride as shown in eq 8. The other is ionic reaction of thioketyl I with benzyl chloride, followed by the coupling of the resulting radical with the benzyl radical (eq 9). In addition to product VI, a blue-violet oil was obtained. After a few days in the air it became brown. When it was oxidized by hydrogen peroxide, white, needlelike crystals were obtained. These crystals are thought to be a mixture of sulfoxide and sulfone, but a clear identification was not established.



(9)

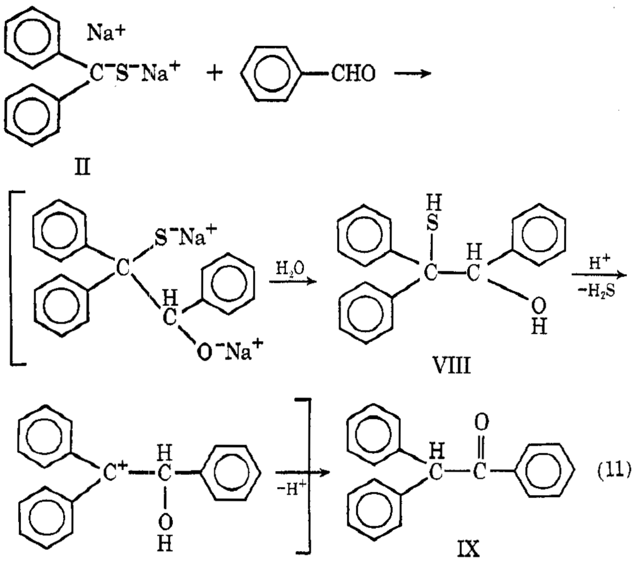
VI

Reaction with *p*-Dichloroxylene.—The reaction of disodium thiobenzophenone complex (II) with *p*-dichloroxylene gave a polymerlike product, the structure of which was thought to be VII. Its molecular weight was found to be 2170. This product was yellow and spinnable.



VII (10)

Reaction with Benzaldehyde.—On the reaction of disodium thiobenzophenone complex (II) with benzaldehyde, ω,ω′-diphenylacetophenone (IX)[6] was obtained. Therefore, this reaction is thought to have proceeded as shown in eq 11; first, compound VIII is formed and on neutralization this compound reacts with the acid to release hydrogen sulfide; and, next, by means of proton migration compound IX is formed.

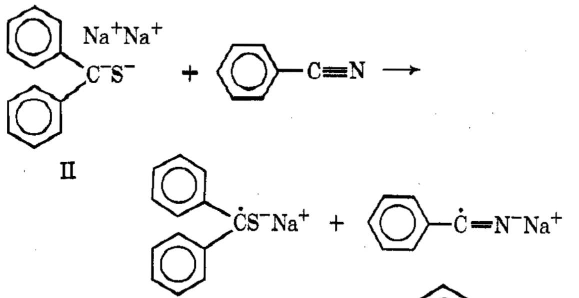


(11)

The presence of hydrogen sulfide was confirmed by the discoloration of lead acetate paper. In spite of the sufficiently careful neutralization, hydrogen sulfide was immediately produced and the product VIII was not obtained. On reaction of disodium benzophenone with benzaldehyde a compound corresponding to VIII was obtained,[4] but in the case of thiobenzophenone VIII was not obtained. Because of the weakness of the C–S bond compared to the C–O bond, the reaction indicated by eq 11 is thought to have taken place.

Next, in the case of the reaction of monosodium thiobenzophenone with benzaldehyde, a red-brown oil was obtained from the reaction mixture. This product was oxidized by hydrogen peroxide–acetic acid to white needles, which could not be clarified.

Reaction with Benzonitrile.—On reaction of disodium thiobenzophenone with benzonitrile, 2,4,6-triphenyl-1,3,5-triazine (X) and a yellow powder melting at 105–120° were obtained. The formation of the product X, known to be formed from the benzonitrile radical anion,[7] is thought likely to indicate the following reaction process: first, as shown in eq 12, a metal migrates to benzonitrile from the dianion to form two anion radicals; and, next, as shown in eq 13, benzonitrile anion radical is oxidized to form the compound X. The yellow powder was polymeric (mol wt 892) and spinnable, but the structure was not clarified.



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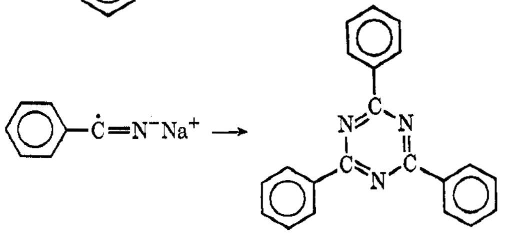


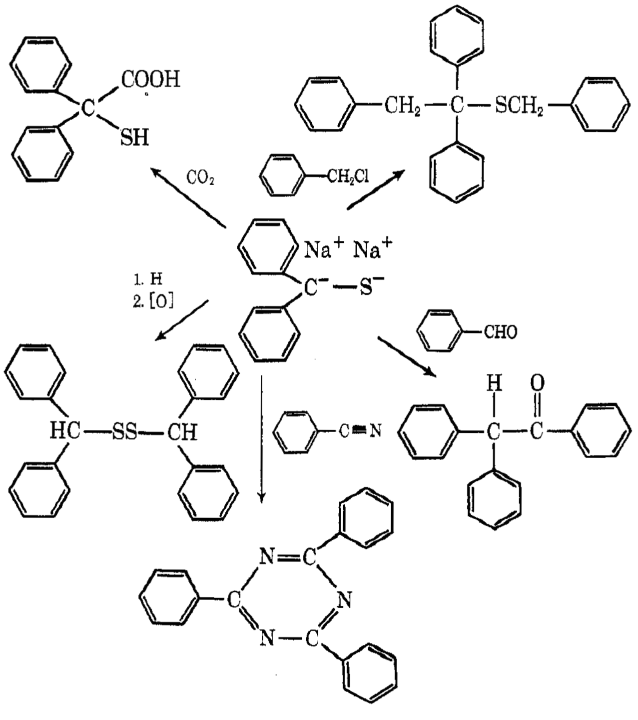
(13)

X

Next the reaction of monosodium thiobenzophenone with benzonitrile was attempted, but exchange did not occur and the starting material was recovered.

Summary.—As described above in the reactions of thiobenzophenone alkali metal complexes with organic compounds (benzyl chloride, *p*-dichloroxylene, benzaldehyde, and benzonitrile), the dianion complexes reacted easily with these compounds and results are summarized in Chart I, but the anion radical complexes hardly reacted, so that the expected compounds were not obtained.

CHART I



These results are thought to be due to the following reason: dianion complexes, having two anions localized on the carbon and sulfur of the thiocarbonyl group, are reactive, but anion radical complexes are not

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[6] A. Werner, *Chem. Ber.*, **39**, 1286 (1906).

[7] G. Greber, *Makromol. Chem.*, **69**, 174 (1963).

so reactive because they are resonance stabilized by conjugation with the phenyl group. With the anion radical complexes, anionic reactions and radical reactions thus compete with each other, so that many products are formed.

Experimental Section

Alkali metals were added to reaction mixtures in small pieces. To remove moisture THF was refluxed with potassium hydroxide and redistilled from a mixture of sodium and benzophenone. Measurements of molecular weight were performed on a Knauer vapor pressure osmometer.

Synthesis of Thiobenzophenone.—Thiobenzophenone was prepared by the method described in the literature.[8]

Synthesis of Monosodium Thiobenzophenone (I).—Thiobenzophenone (2.0 g, 0.01 mol) was stirred with sodium (0.207 g, 0.009 g-atom) in THF (100 ml) for 24 hr under nitrogen at room temperature. After 1 hr the reaction mixture turned from blue-violet to deep red in color. After 6 hr the reaction mixture was filtered under a stream of nitrogen, and all the unreacted metal particles disappeared. This thioketyl solution was placed in a sealed bottle substituted with argon gas and it was stored in a cool and dark place. For use this thioketyl solution was taken with an injector under a stream of nitrogen.

Synthesis of Disodium Thiobenzophenone (II).—Thiobenzophenone (2.0 g, 0.01 mol) was stirred vigorously with sodium (0.92 g, 0.04 g-atom) in 100 ml of THF under nitrogen at room temperature. The reaction mixture turned gradually from blue-violet to dark red in color. After 24 hr the unreacted sodium (0.46 g, 0.02 g-atom) was recovered by the filtration of the reaction mixture and the formation of the dianion complex was confirmed. The method of use and storage was the same as that of the monosodium complex.

Measurement of Esr Spectra.—The THF solution of the monosodium complex, disodium complex, and thiobenzophenone (all 0.19 mol/l.) was placed in an quartz glass tube (i.d. 3 mm) by means of an injector. The quartz glass tube was sealed with a plastic film. Measurements of these samples were carried out on a Nipondenshi JES ME-3X esr spectrometer (100 MHz).

Carbonation Reaction.—The THF solution of monosodium thiobenzophenone (100 ml, 0.36 mol/l.) was added to an excess of crushed Dry Ice with stirring. After it was left to stand overnight, the solvent was evaporated and the residue was diluted with 300 ml of water. The red aqueous solution was washed with ether. The ether layer became blue-violet and exhibited an absorption spectra at 600 mμ, which was due to the thiocarbonyl group of thiobenzophenone. The ether was evaporated and the oily residue obtained (13.1 g) was thought to be thiobenzophenone. The aqueous solution was acidified with hydrochloric acid and the white-yellow solid precipitated and was recrystallized from 50% acetic acid to give 0.39 g (4.4%) of thiobenzilic acid (III), mp 145–147° (lit.[5] mp 146–148°).

Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.84; H, 5.02.

Next 100 ml of a THF solution of disodium thiobenzophenone (0.4 mol/l.) was added to an excess of crushed Dry Ice with stirring. After it was left to stand overnight, the solvent was evaporated and the residue was diluted with 300 ml of water. The red aqueous solution was washed with ether and acidified with hydrochloric acid. The precipitated crude thiobenzilic acid, 7.38 g (82.5%, crude yield), mp 140–143°, was recrystallized from benzene to yield 4.1 g (42% yield) of thiobenzilic acid (III), mp 146–148.5° (lit.[5] m 146–148°).

Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 69.01; H, 5.05.

Acid-Decomposition Reaction.—The THF solution of monosodium thiobenzophenone (50 ml, 0.4 mol/l.) was poured into acidic ethanol (64 ml of ethanol and 16 ml of concentrated hydrochloric acid), and the solvent was evaporated. Ether was added to the residue, and the ether layer was washed with water and dried (Na_2SO_4). The ether was evaporated from the ether layer.

The residue, dissolved in 80 ml of ethanol, was treated with 2,4-dinitrophenylhydrazine (3.96 g, 0.02 mol), dissolved in 120 ml of ethanol containing a few drops of concentrated hydrochloric acid for 2 days at room temperature. From the solution hydrogen sulfide was evaporated. The solution was filtered to give 3.0 g (44.5% crude yield) of crude thiobenzophenone 2,4-dinitrophenylhydrazone, mp 216–230°.

This hydrazone was recrystallized from ethanol to give 1.2 g (16.6% yield) of a red-yellow powder: mp 230–235° (lit.[9] mp 238°, 229°); ir (KBr) 3100–3000 (NH), 1600 (benzene ring), 1500, 328 cm^{-1}.

Anal. Calcd for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89; N, 14.56. Found: C, 62.75; H, 3.72; N, 15.10.

Next 50 ml of THF solution of disodium thiobenzophenone (0.6 mol/l.) was poured into acidic methanol (150 ml of methanol and 50 ml of concentrated hydrochloric acid) and much sodium chloride precipitated. After removal of the solvent, the residue was extracted with benzene. The extracts were washed with water and dried ($CaCl_2$). Removal of the solvent left a light-yellow oil. To a solution of this oil in 50 ml of ethanol was added iodine dissolved in aqueous ethanol, until the color of iodine did not disappear. White crystals precipitated from the solution were separated and recrystallized from chloroform–ethanol (1:1) to afford 3.9 g (65.3%) of needle crystals of diphenyl methyl disulfide (V): mp 152–153° (lit.[10] mp 152°); ir (KBr) 3050, 1603, 1500, 1460, 760, 730, 710 cm^{-1}.

Anal. Calcd for $C_{26}H_{22}S_2$: C, 78.32; H, 5.58. Found: C, 78.13; H, 5.73.

Reaction with Benzyl Chloride.—To a solution of benzyl chloride (3.15 g, 0.025 mol) in 10 ml of THF was added 53 ml of a THF solution of monosodium thiobenzophenone (0.5 mol/l.). The mixture was refluxed under nitrogen for 3 hr. Removal of the solvent left a red-violet oil. It was extracted with ether, and the extracts were washed with water and dried (Na_2SO_4). Removal of solvent left a white crystal, which on recrystallization from ether gave 0.6 g (12.6%) of 1,1,2-triphenylethyl benzyl sulfide (VI), mp 126–128°. The filtrate was distilled to yield a first fraction (0.7 g), bp 148–160° (2 mm), and a second fraction (1.0 g), bp 160–165° (2 mm). Their infrared spectrum agreed with that of thiobenzophenone. These fractions changed in color from blue-violet to brown after 2 days in air. The first fraction (0.7 g) was added with stirring to a solution of 0.8 ml of 30% hydrogen peroxide and 4 ml of acetic acid at room temperature. The mixture was allowed to stand for 2 days. The white crystals were separated and recrystallized from ether to give 0.8 g of white needle crystals, mp 161–163°, mol wt 274.

Anal. Found: C, 74.44; H, 5.77.

The second fraction (1.0 g) was added with stirring to a solution of 1.2 ml of 30% hydrogen peroxide and 5.7 ml of acetic acid at room temperature. The mixture was allowed to stand for 2 days. The white crystals were separated and recrystallized from ether to give 0.1 g of white needle crystals, mp 125–129°, mol wt 228.

Anal. Found: C, 70.19; H, 5.74.

To a solution of benzyl chloride (3.52 g, 0.028 mol) in 30 ml of THF was added 30 ml of a THF solution of disodium thiobenzophenone (0.46 mol/l.). The mixture was refluxed under nitrogen for 3 hr. The mixture was cooled, poured into an excess of crushed Dry Ice to remove any unreacted dianion complex, and diluted with 100 ml of water. After removal of solvent, the residue was extracted with ether and the extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave a white solid. Recrystallization of the crude product from ether yielded 3.0 g (56.6%) of white needle crystals of 1,1,2-triphenylethyl benzyl sulfide (VI): mp 126–127°; ir (KBr) 3070, 3040, 3020, 2925–2859 (CH_2), 1600 (benzene ring), 1490, 658 cm^{-1} (CS); nmr (CCl_4) δ 3.20 [s, 2, $C_6H_5C\mathbf{H}_2[C_6H_5)_2]$, 3.57 (s, 2, $-SC\mathbf{H}_2C_6H_5$), 6.4–7.15 [m, 10, $-C(C_6H_5)_2-$], 7.2 [s, 5, $C_6\mathbf{H}_5CH_2C(C_6H_5)_2-$], and 7.23 (s, 5, $C_6\mathbf{H}_5CH_2S-$).

Anal. Calcd for $C_{27}H_{24}S$: C, 85.22; H, 6.35; mol wt, 383. Found: C, 85.36; H, 6.29; mol wt, 380.6.

Reaction with *p*-Dichloroxylene.—To a solution of *p*-dichloroxylene (5.3 g, 0.0303 mol) in 30 ml of THF was added 60 ml of THF solution of disodium thiobenzophenone (0.5 mol/l.). Immediately the dark red of the dianion complex changed to dark yellow-green. The mixture was refluxed under nitrogen for 3 hr and cooled, and the solvent was evaporated. The residue was dissolved in benzene and precipitated from methanol. The precipitate was filtered, washed with methanol and with water and methanol, and dried to give 8.2 g of yellow powder, mp 105–120°, mol wt 1160. This powder was positive for the Beilstein

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[8] B. F. Golton and E. A. Braude, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 927.

[9] M. Busch and H. Kunder, *Chem. Ber.*, **49**, 328 (1916).

[10] E. Billmann, *Justus Liebigs Ann. Chem.*, **364**, 325 (1909).

test, and it was spinnable. The reprecipitation of its benzene solution from methanol was repeated to give the yellow powder VII: mp 110–120°; mol wt 2170; ir (KBr) 3030, 3000, 2925–2840 (CH_2), 1600 (benzene ring), 1500, and 615 cm^{-1} (CS).

Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.06; H, 5.90.

Reaction with Benzaldehyde.—To a solution of benzaldehyde (1.33 g, 0.0125 mol) in 30 ml of THF was added 53 ml of THF solution of monosodium thiobenzophenone (0.5 mol/l.), and the mixture was refluxed under nitrogen. The deep red of the thioketyl was not changed and the viscosity of the mixture was increased. After 3 hr the mixture was cooled and 100 ml of water was added. After removal of the solvent, the residue was extracted with ether. The ether layer was washed with water. The water layer was acidified with hydrochloric acid to give a yellow-green precipitate. The precipitate was recrystallized from petroleum ether (bp 40–60°) to give 0.3 g of benzoic acid: mp 122–124° (sublimed at 100°); ir (KBr) 3100–3000, 2950–2500 (COOH), 1700 (C=O), 1600 cm^{-1} (benzene ring).

Removal of solvent from the ethereal layer gave a yellow oil. On distillation of this oil under nitrogen, 3 g of a blue-violet oil distilled, bp 150–165°. This oil changed from blue-violet to brown after 2 or 3 days in air. This brown oil (3 g) was stirred with a solution of 5 ml of acetic acid and 3.1 ml of 30% hydrogen peroxide at room temperature for 2 days. The white crystals were precipitated from the mixture. Recrystallization of the white precipitate from ether yielded 0.1 g of white needle crystals: mp 130–140°; mol wt 315; ir (KBr) 3100–3000, 1600 (benzene ring), 1500, 1350 (-SO_2), 1130 cm^{-1} (S=O).

To a solution of benzaldehyde (1.5 g, 0.014 mol) in 10 ml of THF was added 30 ml of THF solution of disodium thiobenzophenone (0.46 mol/l.). The mixture was refluxed under nitrogen for 3 hr. The dark red of the dianion complex gradually turned to yellow and sodium chloride was precipitated. After 3 hr the mixture was cooled, poured into crushed Dry Ice to remove any unreacted dianion complex, and diluted with 100 ml of water. After removal of the solvent, the residue was extracted with ether and the extracts were washed with water and dried (Na_2SO_4). Removal of the solvent left a white powder which on recrystallization from ether gave 1.3 g (33.4%) of white needle crystals of ω,ω'-diphenylacetophenone (IX): mp 136–137° (lit.[6] mp 137°); ir (KBr) 3070, 3050, 3010, 1680 (C=O), 1600 cm^{-1} (benzene ring).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92; mol wt, 272. Found: C, 88.21; H, 6.05; mol wt, 276.

Reaction with Benzonitrile.—To a solution of benzonitrile (2.58 g, 0.025 mol) in 30 ml of THF was added 50 ml of a THF solution of monosodium thiobenzophenone (0.5 mol/l.). The mixture was refluxed under nitrogen. After 3 hr the mixture was cooled and poured into acidic ethanol (10 ml of concentrated hydrochloric acid and 100 ml of ethanol), and it turned blue-violet in color. After removal of the solvent the residue was distilled under nitrogen to give 1.0 g (39% recovered yield) of benzontrile, bp 75–76° (9 mm), and 1.4 g (28% recovered yield) of thiobenzophenone, bp 138–140° (3 mm).

Next the reaction of a THF solution of disodium thiobenzophenone (26 ml, 0.5 mol/l.) with benzonitrile (2.58 g, 0.025 mol) was made by the same method as described above. When the dianion complex was added to benzonitrile, immediately the color of the mixture turned from deep red to red-violet. After 3 hr the mixture was poured into aqueous methanol. After removal of the solvent, the residue was extracted with ether. A pink powder (0.2 g), which was insoluble in ether, was recrystallized from chloroform to give 0.12 g of white needle crystals, 2,4,6-triphenyl-1,3,5-triazine (X), mp 234–236°. The ethereal extract was partially evaporated to induce crystallization and 0.45 g (22.1%) of 2,4,6-triphenyl-1,3,5-triazine (X) was obtained: mp 234–236° (lit.[11] mp 233–233.5°); ir (KBr) 3000–3050, 1590 (benzene ring), 1520, 1460 cm^{-1}.

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.41; H, 5.00; N, 13.62.

The ether was evaporated from the filtrate to give 1.3 g of polymeric precipitate which was spinnable. It was dissolved in benzene and precipitated from petroleum ether (bp 42–55°) to give 0.4 g of a yellow powder: mp 105–120°; ir (KBr) 3080, 3040, 1660, 1640, 1600, 1495 cm^{-1}; mol wt 892. *Anal.* Found: C, 84.25; H, 6.49.

Registry No.—I, 19495-83-1; II, 21129-36-2; VI, 34519-98-7; VII (copolymer), 9036-08-2; VII (repeating unit), 34521-12-5; benzyl chloride, 100-44-7; *p*-dichloroxylene, 623-25-6; benzaldehyde, 100-52-7; benzonitrile, 100-47-0; thiobenzophenone, 1450-31-3.

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Selectivity Differences of Some Cobalt Catalyst Systems in the Liquid Phase Oxidation of Alkyl Aromatics[1]

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A study of the products obtained in the oxidation of *p-tert*-butyltoluene and 2,2-bis(*p*-tolyl)propane at 182° and 200 psig O_2 in a mixed solvent consisting of chlorobenzene and acetic acid, and in the presence of cobaltous acetate–hydrochloric acid catalyst, has revealed some significant differences in oxidation products as compared with similar experiments using the cobalt–bromide and cobalt acetate–2-butanone catalyst systems at 182 and 138°, respectively. The use of the chloride catalyst results in carbon–carbon bond cleavage during the oxidation process and leads to significant amounts of products such as *p*-toluic acid, *p*-methylacetophenone, terephthalic acid, and *p*-acetylbenzoic acid in addition to the expected *p-tert*-butylbenzoic acid and 2,2-bis(*p*-carboxyphenyl)-propane. These results are most easily explained by a radical mechanism involving a chloride ion to chlorine atom chain.

Several important industrial processes for the liquid phase oxidation of toluene or xylenes to benzoic or phthalic acids are based on cobalt catalyst systems.[2]

The use of cobalt acetate and a ketone or aldehyde activator for the oxidation of xylenes or toluenes in acetic acid to carboxylic acids at 100° has been described by Brill.[3] Cobalt or manganese salts and various bromide promoters have been used in acetic acid solvent for the oxidation of alkyl aromatics over a range of temperatures up to 200°.[4–9] The mechanism of such

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(1) A limited preliminary account appeared in *Chem. Commun.*, 1166 (1971).

(2) The patent literature on these oxidations runs into hundreds of patents; literature references will be restricted mainly to publications dealing with mechanisms.

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