TABLE II

THALLOUS SALTS OF OTHER SULFONIC ACIDS

No.	Thallous salt	M.p., °C.	Rel. solubility	Formula	Tl analyses, % Found	Calcd.
1	4-Methyl-1,3-benzenedisulfonate[b,c]	272–276[c] 295–297	Fairly insol.	$C_7H_6O_6S_2Tl_2$	60.5[c]	62.0
2	Benzidine-3,3′-disulfonate[a]	Chars above 350	Moderate	$C_{12}H_{10}O_6N_2S_2Tl_2$	54.8	54.4
3	D,L-Camphor-β-sulfonate[a,d]	259–260	Extremely sol.	$C_{10}H_{15}O_4STl$	46.7	46.9
4	D-Camphor-β-sulfonate (Reychler's)[a,d]	259–260	Extremely sol.	$C_{10}H_{15}O_4STl$	46.9	46.9
5	4-Amino-1-naphthalenesulfonate[a]	240–241	Quite insol.	$C_{10}H_8O_3NSTl$	47.9	47.9
6	8-Hydroxy-5,7-dinitro-2-naphthalenesulfonate[a] (dithallous salt)	Dec. *ca.* 376 explosively	Quite insol.	$C_{10}H_4O_8N_2STl_2$	56.95	56.7
7	1-Anthraquinonesulfonate[e]	475–480 dec	Moderate	$C_{14}H_7O_5STl$		
8	2-Anthraquinonesulfonate[b]	384–386	Quite insol.	$C_{14}H_7O_5STl$	41.9[g]	41.6
9	5-Nitro-1-anthraquinonesulfonate[a]	348–350	Fairly insol.	$C_{14}H_6O_7NSTl$	38.45	38.1
10	8-Nitro-1-anthraquinonesulfonate[a]	339–341	Fairly insol.	$C_{14}H_6O_7NSTl$	37.7	38.1
11	8-Hydroxy-5-quinolinesulfonate[a] (monothallous salt)	292–295	Quite insol.	$C_9H_6O_4NSTl$	47.3[g]	47.7
12	8-Hydroxy-5-quinolinesulfonate[a] (dithallous salt)	Darkens 400 Dec. 425	Quite insol.	$C_9H_5O_4NSTl_2$	64.8[g]	64.7
13	8-Hydroxy-7-iodo-5-quinolinesulfonate[a,f]	Dec. *ca.* 300	Quite insol.	$C_9H_4O_4NISTl_2$	56.0[f,g]	53.9

[a] Prepared from the free sulfonic acid. [b] Prepared from the sodium salt of the acid. [c] Part of the product always melted at 272–276° and the main part of it at 295–297° even after several recrystallizations. The analyses were consistently 1.5% low for the dithallous salt. Perhaps the original sulfonate contained a small amount of impurity not separable by the processes of preparation. [d] These thallous salts are exceedingly soluble in water, but they are very readily prepared by evaporating the solution to dryness under reduced pressure and recrystallizing from absolute ethanol. The melting point for thallous D-camphorsulfonate here recorded is somewhat lower than previously reported.[1a] The melting points for both the camphorsulfonates were determined on several different samples of these salts, and they were found to be unchanged after repeated crystallizations from absolute ethanol. The fact that both the D- and the D,L- salts have the same melting point and that a mixed-melting point of the two is undepressed indicates that the D- and L- salts form a continuous series of solid solutions in any proportion. To guarantee the identity of these salts they were examined polarimetrically. For thallous D-camphorsulfonate $[\alpha]^{25}\text{D}$ +11.8 ± 0.2°, in 5–8% aqueous solution. This value corresponds closely on the basis of equivalent D-camphorsulfonate ion concentration with the values reported for free D-camphorsulfonic acid in aqueous solution of +21.5° (Reychler, *Bull. soc. chim. France,* [3] **27**, 982 (1902)) and of +22.60° (Rewald, *Ber.*, **42**, 3137 (1909)). Our sample of thallous D,L-camphorsulfonate was found to be entirely optically inactive and, hence, uncontaminated with optically active salt. [e] It was very difficult to secure a crystalline thallous salt (fine, yellow needles) from the highly insoluble crude potassium sulfonate (Eastman Kodak Co.). This is a case of the initial salt being nearly as insoluble as the thallous salt product making isolation of the desired product very difficult. A satisfactory analysis was never obtained, although the product appeared to be pure. [f] No crystalline material could be isolated using one equivalent of thallous hydroxide. The crystalline dithallous salt decomposed so that no melting point check on purity was available. It was very difficult to analyze the product, but the analysis shown was checked. [g] These analyses required preliminary destruction of the organic matter by heating with fuming nitric acid at 300° in a sealed tube.

Melting Points.—The melting points of all compounds melting below 345° were determined on an electrically heated block similar to the Fisher–Johns melting point apparatus. All such melting points were uncorrected. The melting points of those compounds melting above 345° were determined in a Berl–Kullmann block[2] using a Weston dial type thermometer calibrated with a thermocouple.

Analyses.—Suitable modifications of the method of Meyer and Bertheim[4] were used for determining thallium content.

(4) Meyer and Bertheim, *Ber.*, **37**, 2051 (1904).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA, AND
BRIGHAM YOUNG UNIVERSITY
PROVO, UTAH

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The Reaction of Dibenzothiophene-5-oxide with *n*-Butyllithium

BY HENRY GILMAN AND DONALD L. ESMAY

The treatment of sulfoxides with organometallic compounds has resulted in reduction,[1] cleavage,[1a,2] cyclization,[1b,3] rearrangement,[3b,4] lateral metalation,[3b] sulfonium salt formation,[5] or complex formation.[3b,6] No nuclear metalation of aryl or heterocyclic sulfoxides has been reported, although metalation of the nucleus has been shown to occur with sulfides such as ethyl phenyl sulfide,[7] diphenylsulfide,[8] thiophene[9] and dibenzothiophene.[8,10]

We are reporting the reaction of dibenzothiophene-5-oxide with *n*-butyllithium[11] in diethyl ether to give upon carbonation 4-dibenzothiophenecarboxylic acid as the major product. The identity of the acid product was established by the method of mixed melting points and by comparison of spectra obtained by infrared absorption measurements.

An initial experiment at the temperature of refluxing ether gave a very small yield of 4-dibenzo-

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(1) (a) K. Fuchs and P. Gross, *Ber.*, **63**, 1009 (1930); (b) C. Courtot, M. Chaix and L. Nicholas, *Compt. rend.*, **194**, 1660 (1932); (c) H. Hepworth and H. W. Clapham, *J. Chem. Soc.*, **119**, 1188 (1921); (d) C. Courtot and C. Pomonis, *Compt. rend.*, **182**, 893 (1926).

(2) (a) E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932); (b) E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1320 (1935).

(3) (a) A. Schönberg, *Ber.*, **56**, 2275 (1923); (b) K. Fuchs and F. Breuer, *Monatsh.*, **53**, 438 (1929); (c) C. Courtot, M. Chaix and J. Kelner, *Compt. rend.*, **194**, 1837 (1932).

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(7) H. Gilman and F. J. Webb, THIS JOURNAL, **62**, 987 (1940); *ibid.*, **71**, 4062 (1949).

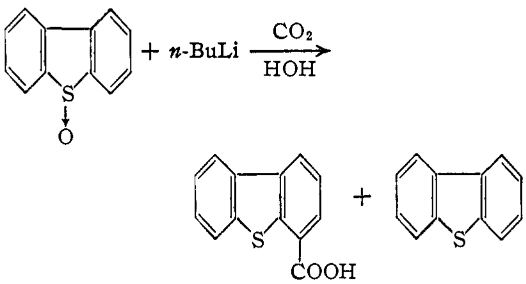
(8) H. Gilman and R. L. Bebb, *ibid.*, **61**, 109 (1939).

(9) H. Gilman and D. A. Shirley, *ibid.*, **71**, 1870 (1949).

(10) (a) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *ibid.*, **3**, 120 (1938).

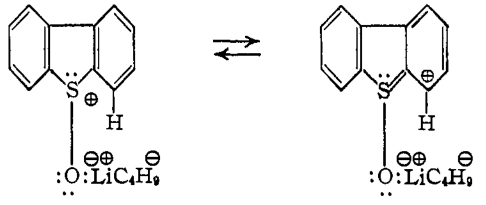
(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

thiophenecarboxylic acid, about an equal yield of dibenzothiophene, a considerable amount of an acidic gum, and a large recovery of dibenzothiophene-5-oxide (equation 1). Since reaction at a low temperature has been shown to be the method of choice for the metalation of certain reactive heterocycles,[12] it was considered of interest to determine the effect of lowering the reaction temperature in the present case. Metalation at −10° increased the yield of crude 4-dibenzothiophenecarboxylic acid to 55.4% (35.7% pure), while the yield of dibenzothiophene remained about the same (10.8%) and no starting material was recovered. It was found necessary to add 1.8 equivalents of *n*-butyllithium before a Color Test II[13] was positive and to add 3.2 equivalents before the test was positive after prolonged stirring. Color Test I[14] was positive throughout the entire reaction period. It is interesting to note that the yield of 4-dibenzothiophenecarboxylic acid compares favorably with that obtained when dibenzothiophene itself is metalated with *n*-butyllithium in diethyl ether.[8,10a,15]



(1)

Regardless of the mechanism assumed, the overall reaction involves both reduction of the sulfoxide group and metalation ortho to the carbon–sulfur linkage. Nuclear metalation ortho to a hetero atom is well-known[16]; however, in view of the established meta-directing influence of the sulfoxide group in dibenzothiophene-5-oxide,[17] ortho-substitution in the present case was somewhat unexpected. The isolation of dibenzothiophene in substantial yields would seem to indicate an initial reduction of the dibenzothiophene-5-oxide to dibenzothiophene with subsequent metalation of the reduced compound to yield 4-dibenzothienyllithium. However, two attempts to metalate dibenzothiophene under analogous low-temperature conditions were unsuccessful as evidenced by the quantitative recovery of starting material after carbonation. In addition, only a trace of acidic material was isolated when the same reaction was carried out with dibenzothiophene in the presence of a catalytic amount of dibenzothiophene-5-oxide. The demonstration that the addition of organometallic compounds to nitriles[18] and ketones[19] proceeds through the initial formation of a complex suggests the possibility that a similar complexation occurs in the present instance between the metal end of the *n*-butyllithium dipole and the unshared electrons of the oxygen atom (equation 2). The electron shift induced by such a complex formation would then facilitate the removal of a proton by the carbanion end of the attacking molecule with subsequent (or concerted) rearrangement of the lithium cation to give the observed ortho metalation.[20] An initial, simultaneous complexing between the remaining unshared electrons of the oxygen atom and at least one additional molecule of *n*-butyllithium would explain the fact that Color Test II did not remain positive until three equivalents of *n*-butyllithium had been added and the fact that complete solution did not occur until two equivalents were present. Decomposition of this complex on termination of the reaction would then lead to the observed reduction and metalation. Furthermore, decomposition of the complex without metalation would yield dibenzothiophene. Although *n*-butanol would be the most probable reduction by-product,[21] none has been isolated as yet.



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Experimental

Metalation of Dibenzothiophene-5-oxide. Run I.—To a stirred suspension of 14.0 g. (0.07 mole) of dibenzothiophene-5-oxide[17] in 100 ml. of dry ether was added 64.4 ml. of a 1.308 *M* ether solution of *n*-butyllithium[11] (0.084 mole; 20% in excess of 1.0 equivalent) at such a rate that a spontaneous, gentle reflux was maintained. Twenty minutes was required for the addition of the *n*-butyllithium, during which time the initial light orange color gradually deepened to a dark orange. The mixture, which contained undissolved dibenzothiophene-5-oxide, was refluxed for six hours and carbonated by pouring jetwise into a slush of ether and Dry Ice.[12] Color Test I[14] was positive throughout, but Color Test II,[13] initially positive, gradually became weaker until the final test was negative. After hydrolysis with water, considerable insoluble material was filtered off and the ether and alkaline layers were separated. Acidification of the aqueous layer yielded 1.4 g. (8.7%) of nearly white acid melting at 240–245°. Recrystallization from dilute methanol raised the melting point to 254–255°. A mixed melting point with authentic 4-dibenzothiophenecarboxylic acid[10a] showed no depression. The neutral, ether-insoluble material weighed 5.4 g. (35.7% recovery), melted at 185–187°, and was established as being dibenzothiophene-5-oxide by a mixed melting point with an authentic specimen. The ether layer was dried over sodium sulfate and the solvent was removed by distillation. The gummy residue was crystallized from dilute ethanol to yield 1.0 g. (7.7%) of

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[12] H. Gilman and J. A. Beel, This Journal, **71**, 2328 (1949); *ibid.*, **73**, 774 (1951).

[13] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

[14] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[15] H. Gilman and C. G. Stuckwisch, *ibid.*, **67**, 877 (1945).

[16] H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 536.

[17] R. K. Brown, R. G. Christiansen and R. B. Sandin, This Journal, **70**, 1748 (1948).

[18] C. G. Swain, *ibid.*, **69**, 2306 (1947).

[19] C. G. Swain and L. Kent, *ibid.*, **72**, 598 (1950).

[20] For a complete discussion of a similar mechanism proposed to explain the high reactivity toward metalation or halogen–metal interconversion of a nuclear position ortho to oxygen, see S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **16**, 8 (1951).

[21] (a) V. Grignard and L. Zorn, *Compt. rend.*, **150**, 1177 (1910); (b) H. Gilman and R. E. Fothergill, This Journal, **51**, 3501 (1929).

nearly pure dibenzothiophene in three fractions melting within the range of 97–99°. Identity was established by the method of mixed melting points.

Run II.—A stirred suspension of 5.0 g. (0.025 mole) of dibenzothiophene-5-oxide in 250 ml. of dry ether was cooled in an acetone–Dry Ice-bath to $-10 \pm 5°$ (internal) while a total of 57.9 ml. of a 1.378 *M* ether solution of *n*-butyllithium (3.2 equivalents) was added over a period of 5.5 hours. The addition of the *n*-butyllithium was interrupted at predetermined intervals in order to follow the course of the reaction with color tests. A Color Test II was not positive until after 1.8 equivalents of *n*-butyllithium had been added. The mixture did not give a positive Color Test II after prolonged stirring until 3.2 equivalents of *n*-butyllithium were present. Color Test I was positive throughout. There was definite evidence of undissolved starting material until 2.0 equivalents of *n*-butyllithium had been added, at which point a finely divided precipitate began to form and the undissolved platelets of dibenzothiophene-5-oxide disappeared. Carbonation and hydrolysis were effected as in Run I. The ether and aqueous layers were easily separated as no insoluble material was present. Acidification of the aqueous layer yielded 3.1 g. (55.4%) of 4-dibenzothiophenecarboxylic acid; m.p. 232–246°. Recrystallization from dilute methanol yielded 2.0 g. of pure acid (35.7%) which melted at 256–256.5°. Infrared absorption measurements of this acid showed its spectrum to be identical with that of an authentic sample of 4-dibenzothiophenecarboxylic acid.[10a] From the ether layer there was isolated 0.5 g. (10.8%) of dibenzothiophene.

Run III.—The procedure for this run was exactly the same as that followed in Run II except that only 1.0 equivalent of *n*-butyllithium was added and that the mixture was stirred for seven hours. By working up the carbonated mixture as described in Run II there was obtained 0.2 g. (3.5%) of 4-dibenzothiophenecarboxylic acid, 2.8 g. (56.0%) of recovered dibenzothiophene-5-oxide and 0.2 g. (4.4%) of dibenzothiophene.

Metalation of Dibenzothiophene.—A solution of 4.6 g. (0.025 mole) of dibenzothiophene was treated at −10° with 1.4 equivalents of *n*-butyllithium in exactly the same manner as reported in Run II above. On working up the carbonated reaction mixture, no acidic material was found in the aqueous layer and the ether layer yielded 4.0 g. (89.4% recovery) of dibenzothiophene. Identical results were obtained in a check run with 89.3% of the starting material being recovered. When dibenzothiophene is treated with *n*-butyllithium for 24 hours at the temperature of refluxing ether, yields of 4-benzothiophenecarboxylic acid of 50–60% are obtained after carbonation.[8,10a,15]

A third run was made in which 0.5 g. (0.0025 mole) of dibenzothiophene-5-oxide was added to the initial solution of 4.6 g. (0.025 mole) of dibenzothiophene. Only a trace of acidic material was isolated and 91.3% of the starting dibenzothiophene was recovered.

The low-temperature metalation of sulfones, other sulfoxides and related types is being examined in order to determine the mechanism and scope of the reaction.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

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Mechanism of Aquation of Carbonatopentaamminocobaltic Ion in Acid Solution

BY JOHN P. HUNT, AARON C. RUTENBERG AND HENRY TAUBE

The transformation of $[\mathrm{Co(NH_3)_5Co_3^+}]$ to $[\mathrm{Co(NH_3)_5H_2O^{+++}}]$ takes place rapidly in water, and even more rapidly when the solution is acidified.[1] The net change in acid solution is described by the equation

$$\mathrm{Co(NH_3)_5CO_3^+ + 2H^+ = Co(NH_3)_5H_2O^{+++} + H_2CO_3}$$

Interest in this reaction developed out of research which is in progress on the mechanisms of substitution in hexacoördinated complex ions. We have performed some tracer experiments to learn whether the metal ion–oxygen bond or the carbon–oxygen bond breaks in the removal of carbonate from the complex ion. In the former event but not in the latter, the oxygen found in the resulting aquo ion will be derived from the solvent. The results obtained show that at least 99% of the change proceeds leaving the Co(III)–O bond intact. The mechanism is therefore of the type observed in the hydrolysis of certain esters.[2]

Kinetic experiments[1] have shown that the rate of aquation in acid is proportional to the concentration of the bicarbonato ion, $[\mathrm{Co(NH_3)_5CO_3H^{++}}]$. This ion is analogous in structure to H_2CO_3, but has H^+ in the acid replaced by $\mathrm{Co(NH_3)_5^{+++}}$. The tracer result shows that the mechanism of the aquation in acid is analogous to the change: $\mathrm{H_2CO_3 = H_2O + CO_2}$, and a comparison of the specific rates of the two reactions is therefore of interest. From the work of Lamb and Mysels,[1] the specific rate of decomposition of $\mathrm{Co(NH_3)_5CO_3H^{++}}$ at 0° is calculated as 0.19 min.$^{-1}$. Combining the value 0.0012 quoted by Faurholt[3] for the quotient $(\mathrm{H_2CO_3})/(\mathrm{CO_2})$ at equilibrium, with the specific rate measured by Mills and Urey[4] for the formation of H_2CO_3, the specific rate of decomposition of H_2CO_3 is calculated as 105 min.$^{-1}$. The higher value for H_2CO_3 as compared to $\mathrm{Co(NH_3)_5CO_3H^{++}}$ is not unexpected in view of the greater acidity of H^+ as compared to $\mathrm{Co(NH_3)_5H_2O^{+++}}$. ($\mathrm{Co(NH_3)_5H_2O^{+++}}$ is a weak acid[5]—$K_{\mathrm{diss.}} = 6 \times 10^{-7}$ at 15° and $\mu = 0.1$.)

The tracer result we have obtained demonstrates rather strikingly the inertia to substitution of the Co(III)–O bond in the complex ion. A mechanism similar in type to that established will come into question in other reactions involving replacement of a complex ligand from the central ion, for example in the aquation of acetatopentamminocobaltic ion. A system in which this type of mechanism probably operates is in the reaction of $\mathrm{Cr(H_2O)_6^{+++}}$ with polymolybdates. Hall and Eyring[6] have shown the hexamolybdatochromic ion is formed rapidly. Substitutions on Cr(III) are in general slow, on Mo(VI) rapid. In the reaction therefore the Cr–O bond is probably preserved and the Mo–O bonds broken and re-established.

Experimental

The salt $[\mathrm{Co(NH_3)_5CO_3}]\mathrm{NO_3 \cdot H_2O}$ was prepared[7] following the method described by Lamb and Mysels.[1] A solution of the salt in water was found to give no precipitate of $CaCO_3$ initially when Ca^{++} was added but after a period of time a precipitate began to appear.

Two tracer experiments were performed. In one, 2 g. of salt was dissolved in 75 ml. of enriched water (mole fraction $O^{18} = N \simeq 8 \times 10^{-3}$) at room temperature. After a period of ten minutes the salt had dissolved, the solution was then cooled to 0° and *ca.* 1.5 ml. of concd. HCl was added. A few minutes later, the ion $\mathrm{Co(NH_3)_5H_2O^{+++}}$ was precipitated as the salt $\mathrm{Co(NH_3)_5H_2OCl_3 \cdot HgCl_2}$. This compound was filtered off, dried and heated to yield water. The iso-

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(6) H. T. Hall and H. Eyring, THIS JOURNAL, **72**, 782 (1950).

(7) We are indebted to Mr. John Below for preparing the compound.