[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Action of Some Organometallic Compounds on Thianthrene-5-oxide

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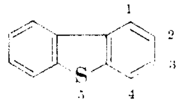
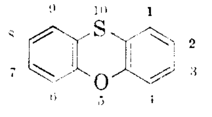
The action of some organometallic compounds on thianthrene-5-oxide was studied. The reported conversion of this sulfoxide to dibenzothiophene, by the action of *n*-butyllithium at low temperature, was found to be a very rapid reaction. Methyllithium reduced thianthrene-5-oxide to give a 60% yield of thianthrene, while ethyl- and *n*-butyl-magnesium bromide cleaved the sulfoxide to give, upon carbonation, 2-ethylsulfinyl- and 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide, respectively.

Aromatic sulfoxides have greater reactivity toward metalating agents than the corresponding sulfides and ethers. Thus, dibenzothiophene (I) did not react appreciably with *n*-butyllithium at −10°, a condition under which dibenzothiophene-5-oxide was successfully metalated to give upon carbonation, a 35.7% yield of dibenzothiophene-4-carboxylic acid.[1] Phenoxathiin (II) metalates in the 4-position,[2] but phenoxathiin-10-oxide metalates to give, upon carbonation, 1-phenoxathiincarboxylic acid.[3,4] The metalation of the sulfoxide is accompanied by reduction in these cases.

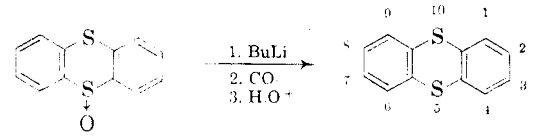


I



II

In the present work the action of some organometallic compounds on thianthrene-5-oxide (III) was investigated. An interesting reaction of III with *n*-butyllithium has been reported[5] in which the products were I, thianthrene (IV), 1-thianthrenecarboxylic acid, and 2,2′-dicarboxydiphenyl sulfide.



III IV

+ I + 1-Thianthrenecarboxylic acid + 2,2′-Dicarboxydiphenyl sulfide

TABLE I

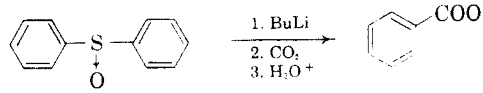
REACTION PRODUCTS OF THIANTHRENE-5-OXIDE WITH *n*-BUTYLLITHIUM

Equivalents of *n*-butyllithium	Time of reaction	T, ° C.	Yield or recovery, % I	IV	Acid	III
1.1	3 min.	−70	27.1	9.3	—	17.6
1.1	10 min.	−70	46.0	4.7	—	—
1.1[a]	7 hours	−70	50.0	...	—	—
3.0	30 min.	−70	53.2	8.0	—	—
3.0[a]	7 hours	−70	52.0	3.2	1.0[b]	—
3.0[a]	5 hours	−40	34.0	4.0	—	—
2.0[a]	7 hours	5–10	10.4	13.2	8.1[c]	—

[a] The values are taken from reference (5). [b] The acid was 2,2′-dicarboxydiphenyl sulfide. [c] The acid was 1-thianthrenecarboxylic acid.

This reaction was studied further and we found that the conversion of III to I is a very rapid reaction. The results of these experiments are given in Table I, from which it is seen that the conversion is almost complete in approximately 10 minutes. The starting material, III, could not be isolated except when the reaction time was limited to a total of three minutes at −70°.

In the reported[5] conversion of III to I, it was not established whether the carbon atoms which were holding the sulfoxide group were those which became linked directly. Our experimental studies seem to indicate that this is actually the case. The sulfoxide group is unstable to the action of *n*-butyllithium at low temperatures. Thus, Esmay[6] observed that diphenyl sulfoxide reacted with *n*-butyllithium at −70° to give fair yields of benzoic acid. We found that diphenyl sulfide, under similar conditions did



not react with *n*-butyllithium. Similarly, thianthrene which has two sulfide groups, did not react with *n*-butyllithium when the mixture was stirred at −70° for 16 hours. These facts illustrate the stability of the sulfide over the sulfoxide group under these conditions.

A reasonable mechanism for the conversion of thianthrene-5-oxide to dibenzothiophene may involve the initial formation of the intermediate species V, which may undergo an intramolecular elimination to give I. The intermediate (V) may also undergo further cleavage with more *n*-butyl-

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(1) H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, **74**, 266 (1952).

(2) H. Gilman, M. W. Van Ess, H. B. Willis, and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **62**, 2606 (1940).

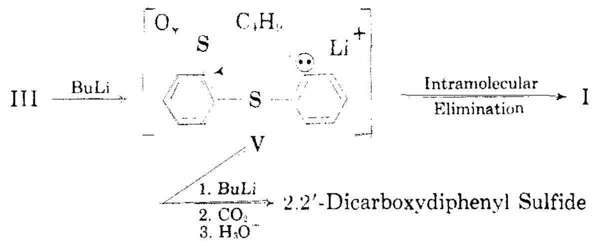
(3) D. A. Shirley and E. A. Lehto, *J. Am. Chem. Soc.*, **77**, 1841 (1955).

(4) Unpublished studies of S. Eidt.

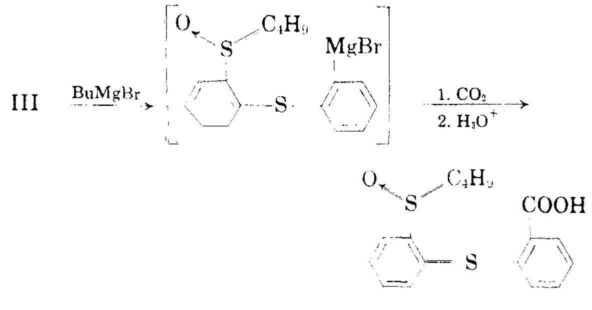
(5) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **77**, 3387 (1955).

(6) Unpublished studies of D. L. Esmay.

lithium to give a dilithio derivative, which would give 2,2′-dicarboxydiphenyl sulfide upon carbonation. Obviously the intramolecular reaction of the intermediate proceeds at a far greater rate than the other reaction.



With alkylmagnesium bromide the reaction could be arrested at the stage of the intermediate V, since, upon carbonation, the corresponding 2-alkylsulfinyl-2′-carboxydiphenyl sulfides were obtained. This is attributed to the weaker carbanion of the intermediate V when Grignard reagents are used for the cleavage of the sulfoxide III. A significant difference in the reaction of the alkylmagnesium bromides with thianthrene-5-oxide was that no reduction was observed. During metalation of a sulfoxide with n-butyllithium, the sulfoxide is partly reduced to the sulfide. If metalation takes place it is invariably accompanied by reduction. An unreduced carboxylic acid has not been obtained from the metalation of a sulfoxide with n-butyllithium and subsequent carbonation. Methylmagnesium iodide did not have any significant action on III, probably due to the insolubility of the Grignard reagent in ether at $-70°$. The results of these experiments are given in Table II.



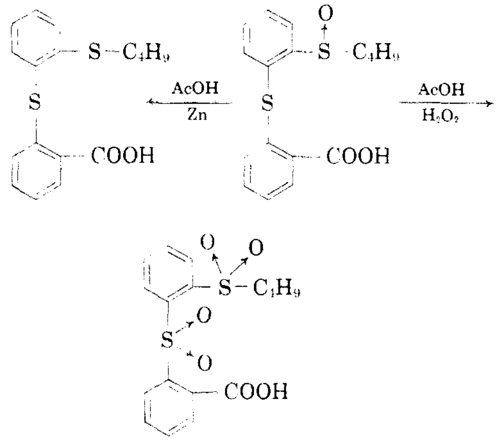
The structures of the cleavage products obtained from the action of the Grignard reagents on thianthrene-5-oxide are based on their analytical data, and their capacity of being reduced to the corresponding alkylmercapto derivatives and of being oxidized to corresponding sulfones. Attempts at synthesizing these 2-alkylsulfinyl-2′-carboxydiphenyl sulfides by an independent method were unsuccessful. The cleavage of III with Grignard reagents provides a general method for the preparation of the 2-alkylsulfinyl-2′-carboxydiphenyl sulfides.

TABLE II

REACTION PRODUCTS OF THIANTHRENE-5-OXIDE WITH ALKYLMAGNESIUM HALIDES

Alkylmagnesium halide	Equiv. of Grignard reagent	Reaction time, hrs.	T, °C.	Yield or recovery, % Acid	III
CH_3MgI	2.0	20	-70	—	63
C_2H_5MgBr	1.1	20	-70	29.0[a,b]	74
C_2H_5MgBr	3.0	20	-70	11.2[a,b]	77
n-C_4H_9MgBr	1.0	16	-70	25.4[b,c]	23
n-C_4H_9MgBr	1.0	16[d]	-70	50.0[b,c]	60
n-C_4H_9MgBr	2.0	16	-70	35.3[b,c]	54
n-C_4H_9MgBr	3.0	6	-70	10.3[b,c]	65
n-C_4H_9MgBr	1.1	48	-70	34.8[b,c]	68

[a] The acid was 2-ethylsulfinyl-2′-carboxydiphenyl sulfide. [b] The yield is based on the unrecovered thianthrene-5-oxide. [c] The acid was 2-n-butylsulfinyl-2′-carboxydiphenyl sulfide. [d] This was followed by a stirring period of 1 hour during which time the cooling bath was removed and the reaction mixture allowed to warm up to room temperature before carbonation.



With methyllithium the reaction was mainly that of the reduction of the thianthrene-5-oxide to thianthrene. Only traces of 1-thianthrenecarboxylic acid were obtained when a mixture of III with three equivalents of methyllithium was stirred at room temperature for 16 hours and subsequently carbonated. However, under these conditions, the reduction of III to thianthrene occurred to the extent of 60%, a fact which established the importance of methyllithium as an agent for reduction of a sulfoxide. The results of these experiments are given in Table III.

TABLE III

REACTION PRODUCTS OF THIANTHRENE-5-OXIDE WITH METHYLLITHIUM

Equiv. of methyllithium	Reaction time	T, °C.	Yield or recovery, % IV	Acid	III
1.1	15 min.	-70	12.5	—	21.1
1.1	16 hours	-70	21.0	—	46.0
3.0	16 hours	20–25	60.0	1[a]	—

[a] See footnote c, Table I.

EXPERIMENTAL[7]

Thianthrene-5-oxide (III) *and n-butyllithium. Run I.* To a stirred suspension of 11.6 g. (0.05 mole) of III[6] in 100 ml. of anhydrous ether at −70° was added, over a period of 10 minutes, 36 ml. (0.055 mole) of *n*-butyllithium.[8] Color Test II[9] was negative immediately after the addition of the *n*-butyllithium was complete. The pale green suspension was filtered through glass wool into a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated, water was added and the layers were separated. The ethereal layer was evaporated to dryness to give a white residue which was crystallized from methanol to yield 4.22 g. (46%) of pure dibenzothiophene (I), identified by the method of mixture melting point.

The aqueous layer was warmed to expel the dissolved ether and the white product which separated was filtered, dissolved in methanol, treated with Norit-A, and filtered. The filtrate was cooled, and the white, crystalline product was filtered and dried to yield 0.51 g. (4.7%) of thianthrene (IV), identified by the method of mixture melting point.

The aqueous filtrate from the above was cooled and acidified with 10% hydrochloric acid to give a cream-colored product which was too small to work up.

Run II. To a stirred suspension of 11.6 g. (0.05 mole) of III in 100 ml. of anhydrous ether at −70° was added, over a period of 3 minutes, 42 ml. (0.055 mole) of an ethereal solution of *n*-butyllithium which had been previously cooled to −70°. A sample of the solution was withdrawn for Color Test II, which was found to be negative, and the remaining solution was immediately carbonated as before.

The residue in the reaction flask was recrystallized from methanol to give 2.04 g. (17.6%) of III (mixture m.p.).

The remaining procedure for the working up of the reaction mixture was identical with that in run I. The ethereal layer gave 2.50 g. (27.1%) of pure I. The aqueous layer, upon warming and subsequent filtration, yielded 1.0 g. (9.3%) of pure IV. Acidification of the aqueous filtrate, after removal of the thianthrene, gave a small amount of a gummy material which did not harden upon long standing and was discarded.

Run III. This run differed from run I in that 3 equivalents of *n*-butyllithium were added to the reaction mixture over a period of 30 minutes. Color Test II was examined at 0, 15, and 25 minutes after the addition of the *n*-butyllithium solution and was found to be positive. It became negative at the end of a total reaction period of 1 hour.

The reaction mixture was carbonated and worked up as before. The ethereal layer gave 4.9 g. (53.2%) of pure I. The aqueous layer was warmed and filtered to yield 0.86 g. (8%) of pure IV. Acidification of the aqueous filtrate gave a small amount of a colorless oil, which did not harden upon standing and was discarded.

Thianthrene-5-oxide and methylmagnesium iodide. To a stirred suspension of 11.6 g. (0.05 mole) of III in 100 ml. of anhydrous ether at −70° was added, over a period of 15 minutes, 90 ml. (0.1 mole) of an ethereal solution of methylmagnesium iodide. The mixture was stirred at the low temperature for 20 hours.

The suspension was carbonated and worked up as before. The ethereal layer yielded 7.32 g. (63%) of III (mixture m.p.). No product was isolated from the aqueous layer upon acidification.

Thianthrene-5-oxide and ethylmagnesium bromide. Run I. To a stirred suspension of 23.2 g. (0.1 mole) of III in 200 ml. of anhydrous ether at −70° was added 120 ml. (0.11 mole) of an ethereal solution of ethylmagnesium bromide, and the mixture was stirred at the low temperature for a period of 20 hours. Carbonation was carried out as usual by the jet-wise addition of the suspension to a stirred slurry of Dry Ice and ether. When all the carbon dioxide had evaporated water was added and the layers were separated. The ethereal layer was evaporated to dryness. The white, crystalline residue weighed 19.4 g. and melted over the range 140–143°. Recrystallization of the crude material from methanol gave 17.2 g. of white crystals melting at 143.5–144°. An admixture of this product with an authentic specimen of III melted undepressed. The yields of the crude and pure III recovered were 88%, and 74%, respectively.

The aqueous layer was warmed to expel the dissolved ether, treated with Norit-A and filtered. The filtrate was cooled and acidified with 10% hydrochloric acid. The white product which separated was filtered, washed and dried to give 2.9 g. of an acidic material which melted with decomposition over the range of 150–154°. Recrystallization from a mixture of ethanol and petroleum ether (b.p. 60–70°) gave 2.32 g. of white crystals melting at 158–159° with decomposition.

The infrared spectrum showed absorption bands at 5.95μ, 9.84μ, and 13.76μ, indicative of the carbonyl group, the sulfoxide group and 1,2-substitution, respectively. The acid has been tentatively established as 2-ethylsulfinyl-2′-carboxydiphenyl sulfide.

Anal. Calc'd for $C_{15}H_{14}O_3S_2$: Neut. equiv., 306; S, 20.91. Found: Neut. equiv., 310, 310; S, 20.85.

The yields of the crude and pure acid, based on the unrecovered III, were 36% and 29%, respectively.

Run II. This run differed from run I only in that 3 equivalents of ethylmagnesium bromide were used for the reaction. The reaction mixture was carbonated and worked up as before. The ethereal layer gave a total of 17.83 g. (76.8%) of III (mixture m.p.). The aqueous layer gave 0.8 g. of the pure acid, melting at 158–159° with decomposition. The yield of the pure acid, based on the unrecovered III, was 11.2%.

2-Ethylmercapto-2′-carboxydiphenyl sulfide. A mixture of 0.8 g. (0.0026 mole) of the 2-ethylsulfinyl-2′-carboxydiphenyl sulfide, 15 ml. of 90% acetic acid, and 2 g. of zinc dust was refluxed for 4 hours. The supernatant, colorless solution was filtered into an excess of water, and dilute hydrochloric acid was added until the mixture was distinctly acidic (Congo Red). The product which separated was filtered, washed, and dried to yield 0.48 g. (64%) of 2-ethylmercapto-2′-carboxydiphenyl sulfide, melting at 195–196°. Further recrystallization of the white product from benzene did not raise its melting point.

Anal. Calc'd for $C_{15}H_{14}O_2S_2$: Neut. equiv., 290; S, 22.2. Found: Neut. equiv., 294, 295; S, 22.1.

Thianthrene-5-oxide and n-butylmagnesium bromide. Run I. To a stirred suspension of 23.2 g. (0.1 mole) of III in 100 ml. of anhydrous ether at −70° was added 85 ml. (0.1 mole) of an ethereal solution of *n*-butylmagnesium bromide. The resulting mixture was stirred at the low temperature for 16 hours. At the end of this period, the cooling bath was removed and stirring was continued for 15 more minutes. Powdered Dry Ice was added slowly to the mixture. When all the carbon dioxide had evaporated water was added, and the layers were separated. The residue in the reaction flask and the ethereal layer together gave 5.4 g. (23%) of III (mixture m.p.).

The aqueous layer was warmed, treated with Norit-A, filtered, and acidified with 10% hydrochloric acid. A sticky, white material which separated, solidified in a short time. The product was filtered, washed with water, and dried to give 11.3 g. of white crystals melting over the range 141–144°, with decomposition. Recrystallization from aqueous methanol gave 6.25 g. (25.4%) of the product, tentatively established as 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide, melting at 149–149.5°, with decomposition.

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(7) All melting points reported herein are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

(8) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(9) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

The infrared spectrum showed absorption bands at 5.9μ, 9.5μ, and 13.2μ, indicative of the carbonyl group, the sulfoxide group, and 1,2-substitution, respectively.

Anal. Calc'd for $C_{17}H_{18}O_3S_2$: Neut. equiv., 334; S, 19.1. Found: Neut. equiv., 336, 336; S, 18.9.

Run II. This run differed from run I in that 2 equivalents of *n*-butylmagnesium bromide were used for the reaction. At the end of 16 hours the reaction mixture was carbonated and worked up as before. Recrystallization of the residue in the reaction flask and the solid obtained from the ethereal layer gave a total of 12.55 g. (54.1%) of III (mixture m.p.).

The aqueous layer gave, after the usual treatment with Norit-A and acidification, 6.1 g. of the crude 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide. *Recrystallization from* benzene gave 5.4 g. of the pure product melting at 149–149.5°, with decomposition. The yields of the crude and pure acid, based on the unrecovered III, were 40% and 35.3%, respectively.

Run III. This run differed from run I in that 3 equivalents of *n*-butylmagnesium bromide were used for the reaction, and that the reaction period was 6 hours only. The mixture was carbonated and worked up as before. The residue in the reaction flask, and the solid obtained from the ethereal layer together gave, after recrystallization from methanol, a total of 15.03 g. (64.8%) of III (mixture m.p.). The aqueous layer yielded, after treatment with Norit-A and acidification, 1.2 g. (10.3%, based on the unrecovered III) of the pure 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide, melting at 149–149.5°.

Run IV. To a stirred suspension of 46.4 g. (0.2 mole) of III in 300 ml. of anhydrous ether at −70° was added, over a period of 15 minutes, 99 ml. (0.22 mole) of *n*-butylmagnesium bromide solution. The resulting mixture was stirred at the low temperature for a period of 48 hours. Carbonation was effected by the jet-wise addition of the cold suspension to a stirred slurry of Dry Ice and ether. The reaction mixture was subsequently worked up as before. Recrystallization of the residue in the reaction flask and the solid obtained from the ethereal layer gave a total of 31.64 g. (68.2%) of III (mixture m.p.).

The aqueous layer yielded 9.0 g. (42.4%) of the crude and 7.4 g. (34.8%) of the pure 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide, melting at 149–149.5°. The yields are based on the unrecovered III.

Run V. To a stirred suspension of 34.8 g. (0.15 mole) of III in 150 ml. of anhydrous ether at −70° was added, over a period of 15 minutes, 108 ml. (0.15 mole) of *n*-butylmagnesium bromide solution. The reaction mixture was stirred at the low temperature for 16 hours. The cooling bath was subsequently removed and the olive-green suspension was allowed to warm up during a period of 1 hour.

Powdered Dry Ice was added carefully to the reaction flask. When all the carbon dioxide had evaporated, water was added and the mixture was worked up as before. The recovered III weighed 20.8 g. (59.8%). The aqueous layer gave 11.0 g. of the crude acid melting over the range 142–148°. Recrystallization from 90% acetic acid gave 10.01 g. of the pure acid. The yields of the crude and pure 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide, based on unrecovered thianthrene-5-oxide, were 54.7% and 50%, respectively.

2-n-Butylmercapto-2′-carboxydiphenyl sulfide. To a hot solution of 10.01 g. (0.0302 mole) of 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide in 90 ml. of 90% acetic acid was added 6 g. of zinc dust, and the resulting mixture was refluxed for a period of 4 hours. The clear, colorless solution was decanted into an excess of water. The zinc lumps in the reaction flask were washed with acetic acid, and the washings were added to the above solution, which was subsequently made acidic (Congo Red) with 10% hydrochloric acid. The mixture was filtered and the residue was washed with water and dried to give 8.6 g. (91.3%) of the pure product, melting at 137–138°. If the temperature of the melting-point bath was allowed to rise very slowly the product melted at 142°.

The infrared spectrum of the product showed absorption bands at 6.05μ and 13.4μ, indicative of the carbonyl group and 1,2-substitution, respectively.

Anal. Calc'd for $C_{17}H_{18}O_2S_2$: Neut. equiv., 318; S, 20.1. Found: Neut. equiv., 321, 322; S, 20.1, 20.4.

2-n-Butylsulfonyl-2′-carboxydiphenyl sulfone. To a hot solution of 3.34 g. (0.01 mole) of 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide in 15 ml. of glacial acetic acid was added a solution of 18 g. of hydrogen peroxide (30%) in 10 ml. of glacial acetic acid. The resulting solution was refluxed for 2 hours. No crystals separated after keeping the solution in a refrigerator for 48 hours. The solution was diluted to approximately 100 ml. with water. A white, sticky product separated which hardened in a short time. The product was filtered and dried to give 3.48 g. (91%) of the pure 2-*n*-butylsulfonyl-2′-carboxydiphenyl sulfone, melting at 159.5–160.5°, with decomposition.

The infrared spectrum showed absorption bands at 5.9μ, 8.7μ, and 13.1μ, indicative of the carbonyl group, the sulfone group and 1,2-substitution, respectively. The band indicative of the sulfoxide group in the 2-*n*-butylsulfinyl-2′-carboxydiphenyl sulfide had disappeared.

Anal. Calc'd for $C_{17}H_{18}O_6S_2$: Neut. equiv., 382; S, 16.75. Found: Neut. equiv., 380, 379; S, 16.58, 16.62.

Methyllithium. Methyl bromide vapor was bubbled through a stirred suspension of 8.1 g. (1.17 g.-atoms) of lithium wire, cut into approximately 5-mm. pieces. The lithium dissolved during a period of 4 hours. After stirring for an additional period of 30 minutes the solution was transferred to a graduated separatory funnel. The yield, as determined by titration against standard hydrochloric acid, was 80%.

Thianthrene-5-oxide and methyllithium. Run I. To a stirred suspension of 23.2 g. (0.1 mole) of III in 150 ml. of anhydrous ether at −70° was added, over a period of 10 minutes, 93 ml. (0.11 mole) of the methyllithium solution. After an additional period of 5 minutes the mixture was carbonated by adding it slowly to a stirred slurry of Dry Ice and ether. When all the carbon dioxide had evaporated the mixture was filtered. The ethereal layer was concentrated and cooled. The white product which separated was filtered and dried to yield a total of 7.7 g. of crude III, melting over the range 124–127°. Two recrystallizations from methanol gave 4.9 g. (21.1%) of pure III (mixture m.p.).

The aqueous layer was warmed to expel the dissolved ether. A white product which separated was filtered and recrystallized from methanol to yield 1.50 g. (7%) of IV, identified by its mixture melting point.

The mother liquor from the recrystallization of crude III gave an additional 1.1 g. of IV. The total yield of thianthrene obtained from the reaction was 2.71 g. (12.5%).

The aqueous filtrate was cooled and acidified with 10% hydrochloric acid. No acidic material was isolated.

Run II. This run was identical with run I except that a period of 16 hours was allowed for the reaction. The mixture was carbonated and worked up as before. The yield of the recovered III was 10.6 g. (46%) and that of IV was 4.5 g. (21%). No acidic product was isolated from the aqueous layer after acidification.

Run III. To a stirred suspension of 11.6 g. (0.05 mole) of III in 100 ml. of anhydrous ether was added, over a period of 30 minutes, 180 ml. (0.15 mole) of the methyllithium solution. The addition was carried out at room temperature and the mixture was subsequently stirred for a period of 16 hours. The sulfoxide had not dissolved after two equivalents of methyllithium had been added, and a partial solution was effected only after the addition of the third equivalent had been completed. An orange-brown color developed slowly in the mixture which was carbonated and worked up as before. No thianthrene-5-oxide was recovered in this run.

The total yield of pure IV, obtained from the recrystallization of the residue in the reaction flask, the product from the evaporation of the ethereal layer, and the material which had separated upon warming the aqueous layer, was 6.5 g. (60%).

The aqueous filtrate was cooled and acidified with 10% hydrochloric acid to yield 0.19 g. of a brown powder melting over the range 205–215°. Recrystallization from glacial acetic acid gave 0.14 g. (1%) of pure 1-thianthrenecarboxylic acid. The identity of the product was established by comparison of the infrared spectrum and mixture melting point determination with an authentic specimen.[10]

Acknowledgment. The authors wish to thank the Institute for Atomic Research, Iowa State College, for making available to us the Baird double beam infrared spectrophotometer used in the determination of the spectra of the compounds reported in this paper. We are grateful to Mr. Robert McCord for the actual determination of the spectra.

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[10] H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **65**, 1461 (1943).