[Contribution from the Department of Chemistry, Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Cyclic Sulfones.[1] Preparation of 2,5-Di-(halophenyl)-3,4-dihydroxythiophene-1-dioxides

By C. G. Overberger, Ramon A. Gadea,[2] Jane Ann Smith[2] and Irving C. Kogon

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The reaction for the preparation of 2,5-diarylthiophene-1-dioxides by the condensation of ethyl oxalate with aryl methyl sulfones has been extended. Four new 2,5-di-(halophenyl)-3,4-dihydroxythiophene-1-dioxides are reported and characterized by formation of their dibenzoates and quinoxalines. Some unsuccessful attempts to effect related condensation reactions are discussed. The preparation of *n*-octyl thiodiacetate, *n*-octyl sulfonyldiacetate and a new procedure for the preparation of ethyl sulfonyldiacetate are described.

In an earlier paper, the condensation of ethyl oxalate with aryl methyl sulfones was reported.[3] The scope of the reaction has been extended to obtain halo derivatives of this type of thiophene dioxide for pharmaceutical testing and to make available additional examples of this heterocyclic ring system for a current study of its chemical reactivity.

This paper will describe the condensations of ethyl oxalate with *o*-chlorobenzyl sulfone, 2,4-dichlorobenzyl sulfone, 2,4,5-trichlorobenzyl sulfone and *p*-bromobenzyl sulfone. A study of molecular models indicates that the presence of an ortho chloro group in the phenyl ring of the sulfones is partially responsible for the reduced yields in the condensation reaction, when compared with the benzyl or *p*-chlorobenzyl sulfone due to steric hindrance in the addition of the carbanion from the sulfone to the carbonyl group of the ethyl oxalate.

Keto–enol tautomerism of the 2,5-diaryl-3,4-dihydroxythiophene-1-dioxides was demonstrated by a positive characteristic ferric chloride test, the solubility in dilute sodium carbonate, the formation of a dibenzoate and the formation of a quinoxaline.

The aryl sulfides, sulfoxides and sulfones were prepared by conventional procedures, although specific experimental conditions were important for high yields of product.

Attempts to condense benzil with ethyl sulfonyl diacetate or the octyl ester with both acidic and basic catalysts were unsuccessful. A new procedure for the preparation of ethyl sulfonyl diacetate by oxidation of ethyl thiodiacetate with potassium permanganate in acetic acid is described. Previous workers have oxidized the thiodiacetic acid to obtain the sulfonyl diacetic acid[4] followed by esterification to give the diester.[5] Attempts to condense ethyl diethylmalonate and ethyl malonate with both benzyl sulfone and ethyl sulfonyldiacetate with a number of basic catalysts were unsuccessful in that six-membered rings could not be isolated. The preparations of *n*-octyl thiodiacetate and *n*-octyl sulfonyldiacetate are also described.

Results obtained from the pharmaceutical screening of this and related types of thiophene dioxides will be reported elsewhere.

Experimental[6]

2,4-Dichlorobenzyl Sulfide, Sulfoxide and Sulfone.[7]—2,4-Dichlorobenzyl sulfide was prepared from purified 2,4-dichlorobenzyl chloride (Heyden Chemical Company) according to the general procedure of Shriner, Struck and Jorison[8] and that of reference 3a (95.6%), m.p. 36–37°. Purification was obtained by recrystallization from ethanol.

Anal.[9] Calcd. for $C_{14}H_{10}Cl_4S$: C, 47.7^5; H, 2.86. Found: C, 47.81; H, 2.80.

When 35.2 g. (0.1 mole) of 2,4-dichlorobenzyl sulfide was treated with 28 g. (0.247 mole) of 30% hydrogen peroxide in glacial acetic acid at room temperature, 40.2 g. of an impure white amorphous precipitate resulted, m.p. 146–152°. Recrystallization from ethanol gave 32.1 g. (87.2%) of 2,4-dichlorobenzyl sulfoxide, m.p. 155–155.4°.

Anal. Calcd. for $C_{14}H_{10}Cl_4OS$: C, 45.68; H, 2.74. Found: C, 45.57; H, 2.97.

2,4-Dichlorobenzyl sulfone was prepared according to the procedure reported previously.[3a] From 35.2 g. (0.1 mole) of 2,4-dichlorobenzyl sulfide in 170 ml. of glacial acetic acid and 56.6 g. (0.5 mole) of 30% hydrogen peroxide, there was obtained 39.3 g. of 2,4-dichlorobenzyl sulfone, m.p. 189–192.0°. Recrystallization from dioxane gave 34.8 g. (90.6%), m.p. 196–197°.

Anal. Calcd. for $C_{14}H_{10}Cl_4O_2S$: C, 43.77; H, 2.62. Found: C, 43.66; H, 2.52.

Condensation of 2,4-Dichlorobenzyl Sulfone with Ethyl Oxalate.—The procedure was similar to that described in reference 3a except that a number of experimental modifications were employed in isolating the product. From 19.2 g. (0.05 mole) of 2,4-dichlorobenzyl sulfone, 54 g. (0.37 mole) of ethyl oxalate and 2.5 g. (0.11 g. atom) of sodium dissolved in 50 ml. of anhydrous alcohol, there was obtained, after drying, 13.5 g. (61.6%) of crude product, m.p. 225–235°. The reaction mixture was initially heated to 82.5° and a clear solution was obtained. After a reflux of 20 hours, the color turned to a light brown. The reaction mixture was allowed to stand at room temperature for one week and the volatile material removed under vacuum. The solid residue was added to cold water and the suspension extracted with ether. The ether layer was then washed with a dilute salt solution. On standing, 2 g. of 2,4-dichlorobenzyl sulfone separated and was removed by filtration, m.p. 198–200°. The ether layer was then extracted several times with cold dilute sodium carbonate solution. The alkaline extracts were acidified with concentrated hydrochloric acid to give an oily precipitate which crystallized on standing.

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(1) This is the fifth in a series of papers concerned with cyclic sulfones. For the previous paper, see C. G. Overberger and J. Hoyt, This Journal, **73**, 3957 (1951).

(2) This paper comprises parts of theses presented by Ramon A. Gadea and Jane A. Smith in partial fulfillment of the requirements for the Master of Science Degree in the graduate school of the Polytechnic Institute of Brooklyn.

(3) (a) C. G. Overberger, S. P. Ligthelm and E. A. Swire, This Journal, **72**, 2856 (1950); (b) see also R. H. Eastman and R. M. Wagner, *ibid.*, **71**, 4089 (1949).

(4) J. M. Loven, *Ber.*, **17**, 2817 (1884).

(5) (a) H. J. Backer and W. Stevens, *Rec. trav. chim.*, **59**, 423 (1940); (b) J. P. Alden and B. Huston, This Journal, **56**, 413 (1934).

(6) All melting points are corrected unless otherwise stated.

(7) The sulfide, sulfoxide and sulfone were prepared by Mr. Edwin A. Swire.

(8) R. L. Shriner, H. C. Struck and W. J. Jorison, This Journal, **52**, 2060 (1930).

(9) Analyses by R. E. Schachat, H. Biletch and Pao-tung Huang, Polytechnic Institute of Brooklyn; Drs. Weiler and Strauss, Oxford, England; Mr. H. S. Clark, Urbana, Illinois; Dr. K. Ritter, Zurich, Switzerland.

The solid was removed by filtration and washed with cold dilute hydrochloric acid. After a drying period, the crude material was redissolved in cold dilute sodium carbonate solution, any insoluble material was removed by filtration and the product reprecipitated with concentrated hydrochloric acid. The product was recrystallized successively from a 1:1 solution of toluene and chlorobenzene and then chlorobenzene (42.5%); m.p. 239–240°. An analytical sample recrystallized from chlorobenzene melted at 239–240°.

Anal. Calcd. for $C_{16}H_8Cl_4O_4S$: C, 43.86; H, 1.84. Found: C, 43.98; H, 1.90.

The white product was very soluble in alcohol, hot toluene, monochlorobenzene, ethyl ether, and was insoluble in water. With dilute solutions of sodium carbonate and sodium hydroxide, yellow solutions result which decompose on standing. A characteristic green to green-red color is obtained with ferric chloride solution.

The quinoxaline was prepared from 0.2 g. (0.00046 mole) of 2,5-di-(2,4-dichlorophenyl)-3,4-dihydroxythiophene-1-dioxide and 0.2 g. (0.0018 mole) of recrystallized *o*-phenylenediamine dissolved in 10 ml. of toluene and 2 ml. of glacial acetic acid. The mixture was refluxed 4 hours and allowed to stand for 18 hours while a solid slowly separated. The light green needles were removed by filtration, washed with alcohol and dried; 0.2 g. (86%), darkening at 216°, m.p. with decomposition 243°, rate of heating from 200°, 2°/min. The solid was warmed in glacial acetic acid, again removed by filtration and washed with alcohol. The product gave a red-purple color in concentrated sulfuric acid.[3a] On heating, the solid started to darken at 216° and melted with decomposition at 239° when heated at the rate indicated previously.

Anal. Calcd. for $C_{22}H_{12}Cl_4N_2O_2S$: C, 51.78; H, 2.37. Found: C, 52.02; H, 2.46.

The dibenzoate was prepared from 1 g. (0.0023 mole) of 2,5-di-(2,4-dichlorophenyl)-3,4-dihydroxythiophene-1-dioxide and 11.0 g. (0.078 mole) of benzoyl chloride in dry pyridine to give 1.3 g., m.p. 220–232°, of crude dibenzoate. The product was first recrystallized with "Darco" from toluene, then from a toluene–alcohol solution, 0.7 g. (47.7%), m.p. 231–233°, and finally from chlorobenzene, m.p. 233–234°.

Anal. Calcd. for $C_{30}H_{16}Cl_4O_6S$: C, 55.75; H, 2.50. Found: C, 55.98; H, 2.85.

2,4,5-Trichlorobenzyl Sulfide, Sulfoxide and Sulfone.—2,4,5-Trichlorobenzyl sulfide was prepared as described previously.[3a] From 45.8 g. (0.2 mole) of purified 2,4,5-trichlorobenzyl chloride (Heyden Chemical Company) in 50 ml. of absolute alcohol and 13.0 g. (0.1 mole) of hydrated sodium sulfide chips in 55 ml. of water, there was obtained, on refluxing the solution for 15 minutes and allowing it to stand overnight at room temperature, 40.9 g. of crude product. The crude product was successively crystallized from alcohol and a solution of alcohol and benzene (2:1) and the solid washed with cold benzene; 35.5 g. (84.4%), m.p. 96.5–98.0°. An analytical sample was recrystallized from D.C. naphtha (b.p. 103–144°), m.p. 98.5–99°.

Anal. Calcd. for $C_{14}H_8Cl_6S$: C, 39.94; H, 1.91. Found: C, 40.16; H, 1.93.

The solid precipitate obtained by allowing 4.2 g. (0.01 mole) of 2,4,5-trichlorobenzyl sulfide to react with 1 ml. (0.01 mole) of 30% hydrogen peroxide in 20 ml. of glacial acetic acid for 12 days at room temperature was removed by filtration. The sulfoxide was purified by leaching with boiling glacial acetic acid, then with alcohol and water, 4.15 g. (96%), m.p. 199–200°.

Anal. Calcd. for $C_{14}H_8Cl_6OS$: C, 38.48; H, 1.84. Found: C, 38.27; H, 2.04.

From 8.4 g. (0.02 mole) of 2,4,5-trichlorobenzyl sulfide and 10 ml. (0.1 mole) of 30% hydrogen peroxide in 55 ml. of glacial acetic acid, there was obtained on refluxing for 13 hours, 8.8 g. (97.3%) of 2,4,5-trichlorobenzyl sulfone, m.p. 259–259.5°. An analytical sample was prepared by washing the solid with boiling glacial acetic acid and cold 95% ethanol, m.p. 259–259.5°.

Anal. Calcd. for $C_{14}H_8Cl_6O_2S$: C, 37.12; H, 1.78. Found: C, 37.45; H, 1.90.

The product can be recrystallized from large quantities of dioxane, m.p. 259–260°.

Condensation of 2,4,5-Trichlorobenzyl Sulfone with Ethyl Oxalate.—The procedure was similar to that previously described.[3a] From 13.6 g. (0.03 mole) of 2,4,5-trichlorobenzyl sulfone, 26.29 g. (0.18 mole) of ethyl oxalate and 1.5 g. (0.065 g. atom) of sodium in 50 ml. of absolute ethanol, there was obtained 1.6 g. (11.6%), m.p. 290–292°. The time of reflux was 22 hours. Eight grams of starting material was recovered. Recrystallization of the product from absolute ethanol gave 1.5 g. of white crystals, m.p. 291–292°.

Anal. Calcd. for $C_{16}H_8Cl_6O_4S$: C, 37.90; H, 1.19. Found: C, 38.15; H, 1.46.

The quinoxaline was prepared from 0.55 g. (0.0012 mole) of 2,5-di-(2,4,5-trichlorophenyl)-3,4-dihydroxythiophene-1-dioxide and 0.13 g. (0.0011 mole) of *o*-phenylenediamine in an alcohol–toluene solution (8:1) at room temperature to give 0.21 g. of a greenish-tan precipitate, purified by leaching in hot acetic acid, m.p. 247° with decomposition (16%). The product gave the characteristic red-purple coloration in concentrated sulfuric acid.[3a]

Anal. Calcd. for $C_{22}H_{10}Cl_6N_2O_2S$: C, 45.62; H, 1.74; N, 4.84. Found: C, 45.37; H, 1.95; N, 4.66.

The dibenzoate was prepared according to the previously described procedure for the dibenzoate of the 2,4-dichloro derivative, m.p. 275–276°. The product was purified by recrystallization from chlorobenzene with Darco, leaching with hot ethyl acetate and successive recrystallizations from chlorobenzene.

Anal. Calcd. for $C_{30}H_{14}Cl_6O_6S$: C, 50.4; H, 1.97. Found: C, 50.5; H, 1.89.

***o*-Chlorobenzyl Sulfide, Sulfoxide and Sulfone.**—The previously described general procedure was employed to prepare the sulfide. The reaction mixture was refluxed for two hours. The crude *o*-chlorobenzyl sulfide was recrystallized from D.C. naphtha (b.p. 103–144°) to give an 88.3% yield, m.p. 51.5–52.0° (52°, no yield stated).[10]

Anal. Calcd. for $C_{14}H_{12}Cl_2S$: C, 59.37; H, 4.27. Found: C, 59.15; H, 4.38.

o-Chlorobenzyl sulfide, 2.85 g. (0.01 mole) was dissolved in 10 ml. of glacial acetic acid. The reaction mixture was maintained at 20–25° by cooling and 0.9 ml. (0.009 mole) of 30% hydrogen peroxide was added in 0.01-ml. portions over a two-hour period. The reaction mixture was allowed to stand at room temperature an additional day. A small quantity of fine needle crystals separated which were recrystallized from glacial acetic acid, m.p. 190–190.5°. This proved to be the sulfone. The filtrate was diluted with a large volume of water and the precipitated sulfoxide removed by filtration, 2.7 g. (90.4%), m.p. 127–128°. The sulfoxide was purified by successive recrystallizations from absolute ethanol, m.p. 125–126°.

Anal. Calcd. for $C_{14}H_{12}Cl_2OS$: C, 56.19; H, 4.04. Found: C, 56.15; H, 4.11.

From 5.7 g. (0.02 mole) of *o*-chlorobenzyl sulfide dissolved in 35 ml. of glacial acetic acid and 0.10 mole of 30% hydrogen peroxide on refluxing for 3 hours, there was obtained on cooling 5.9 g. of crude product. The product was washed in cold alcohol and glacial acetic acid, then leached with hot glacial acetic acid, the solid removed by filtration and dried at 60°, 5.9 g. (93.0%), m.p. 188.5–189°. The product can be recrystallized from absolute ethanol, m.p. 188.5–189°.

Anal. Calcd. for $C_{14}H_{12}Cl_2O_2S$: C, 53.34; H, 3.84. Found: C, 53.17; H, 3.83.

Condensation of *o*-Chlorobenzyl Sulfone with Ethyl Oxalate.—The procedure was similar to that previously described.[3a] From 4.9 g. (0.02 mole) of *o*-chlorobenzyl sulfone, 4.3 g. (0.03 mole) of ethyl oxalate and 0.92 g. (0.04 g. atom) of sodium in 30 ml. of absolute ethanol, there was obtained 2 g. (27.1%), m.p. 157.5–159.5°. One and one-half grams of starting material was recovered, m.p. 185–186°. Purification was effected by recrystallization from toluene; 1.98 g., m.p. 158–159.5°.

Anal. Calcd. for $C_{16}H_{10}Cl_2O_4S$: C, 52.1; H, 2.73. Found: C, 51.8; H, 2.44.

The product is soluble in alcohol, ethyl ether, hot toluene and hot chlorobenzene and practically insoluble in water. It gave a characteristic green color with ferric chloride solution.

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[10] G. Speroni and G. Manelli, *Gazz. chim. ital.*, **70**, 472 (1940).

The quinoxaline derivative was prepared in an ether–alcohol solution by allowing the reactants to stand overnight. The mixed precipitate of orange and light yellow material was removed by filtration, 0.45 g. The crude product was heated in alcohol and the light yellow product removed by decantation from the heavier orange particles. The orange crystals gave the characteristic red color with concentrated sulfuric acid.[3a] On heating, it darkened at 227°and melted at 236° with decomposition, rate of heating 2°/min. over 200°.

Anal. Calcd. for $C_{22}H_{19}Cl_2N_2O_2S$: N, 6.35. Found: N, 6.23.

The dibenzoate was prepared according to a method described by Hickinbottom,[11] using sodium carbonate; m.p. 214–215°, recrystallized from a solution of alcohol and toluene (1:2).

Anal. Calcd. for $C_{30}H_{18}Cl_2O_6S$: C, 62.40; H, 3.19. Found: C, 62.15; H, 3.37.

***p*-Bromobenzyl Sulfide and Sulfone**.—The methods were similar to previous procedures. In the preparation of the sulfide, after solution of the *p*-bromobenzyl bromide in ethanol, the sodium sulfide aqueous solution was added dropwise and then refluxed for three hours (77%), m.p. 54–56°. Recrystallization from 95% ethanol gave a m.p. 59–60° (58–59°, no yield reported).[12]

Since ref. 12 may have erroneously reported the sulfone, some detail for its preparation seems advisable. In 150 ml. of glacial acetic acid was dissolved 37.2 g. (0.1 mole) of *p*-bromobenzyl sulfide. The solution was heated to 70° and 56.6 g. (0.5 mole) of 30% hydrogen peroxide was added slowly, keeping the temperature at 70–75°. White solid began to separate before the addition was complete. The reaction mixture was refluxed for 2.5 hours and allowed to stand overnight. The solid was removed by filtration and washed with alcohol and water, 37.0 g. (92%), white powder, m.p. 252–254°. Recrystallization from dioxane three times gave a m.p. 261–262°.

Anal. Calcd. for $C_{14}H_{12}Br_2O_2S$: C, 41.62; H, 2.99. Found: C, 41.59; H, 2.87.

Jackson and Hartshorn[12] reported a melting point of 189° obtained by oxidizing an acetic acid solution of the sulfide with the calculated quantity of chromic anhydride in acetic acid.

2,5-(Di-*p*-bromophenyl)-3,4-dihydroxythiophene-1-dioxide.—This compound was prepared as described previously. The reaction mixture was allowed to reflux three hours and stand overnight (89%), m.p. 241–243°. Recrystallization from an ethanol–water mixture gave a m.p. 249–250°.

Anal. Calcd. for $C_{16}H_{10}Br_2O_4S$: C, 41.95; H, 2.19. Found: C, 41.93; H, 2.11.

The quinoxaline was prepared by refluxing in a 1:1 alcohol–acetic acid solution for 2.5 hours. A precipitate formed on addition of water (28%), m.p. 242° dec. Recrystallization from toluene gave a m.p. 245° dec. of light yellow crystals.

Anal. Calcd. for $C_{22}H_{14}Br_2N_2O_2S$: N, 5.26. Found: N, 5.44.

The dibenzoate was prepared using the pyridine procedure. Recrystallization from 95% ethanol gave yellow crystals, m.p. 205–206°.

Anal. Calcd. for $C_{30}H_{18}Br_2O_6S$: C, 54.09; H, 2.72. Found: C, 54.06; H, 2.81.

Ethyl Sulfonyldiacetate.—Ethyl thiodiacetate was prepared according to the procedure of Overberger, Mallon and Fine.[13] By adding the ethyl chloroacetate to the sodium sulfide in acetone at such a rate that the temperature remains below 30°, a 10% higher yield of product can be obtained than that previously reported.

In a 3-l. beaker were placed 206 g. (1 mole) of ethyl thiodiacetate, 100 ml. of acetic acid and 700 ml. of water. The mixture was stirred vigorously with a mechanical stirrer and 220 g. of powdered potassium permanganate was added in small amounts so that the temperature did not exceed 30°. The dark colored mixture was stirred for another 2 to 3 hours and then allowed to stand overnight. The mixture was cooled to 0° in an ice-bath and a sufficient amount of sodium bisulfite was added to it keeping the temperature below 15°. Sulfuric acid (18 *N*) was added at 0° with stirring at such a rate to ensure that the temperature of the reaction mixture did not rise above 30° until the manganese dioxide dissolved and a clear solution was obtained. The solution was then extracted with ether in a continuous extractor; the ethereal solution was concentrated and the residual liquid fractionally distilled under reduced pressure. The bulk of the material distilled at 154° (2 mm.) and solidified on cooling, m.p. 33–34°, 216 g. (90.0%) (b.p. 178–181° (5 mm.), d^{27} 1.258, $n^{25}\text{D}$ 1.4562, 92% by esterification).[3b]

Anal. Calcd. for $C_8H_{14}O_6S$: C, 40.33; H, 5.92; S, 13.45. Found: C, 40.20; H, 6.27; S, 13.43.

The amide was prepared from the ester by stirring with an excess of concentrated ammonium hydroxide until the mixture became a solid mass. The reaction mixture was stirred with water and the solid removed by filtration. The solid was washed with hot alcohol and dried, m.p. 222.5–223.5° (dec.), rate of heating 2°/min. after 200° (browning without melting at 200°)[4] (226°).[5]

Anal. Calcd. for $C_4H_8N_2O_4S$: N, 15.6; S, 17.8. Found: N, 15.5; S, 17.9.

***n*-Octyl Thiodiacetate**.—Thiodiacetic acid was prepared according to the procedure of Barkenbus and Landis.[14] In a 500-ml. flask fitted with a reflux condenser were added 60 g. (0.4 mole) of thiodiacetic acid, 208 g. (1.6 mole) of *n*-octanol and 14 ml. of concentrated sulfuric acid. The mixture was refluxed about 3 hours, cooled, washed with water and then extracted with ether. The ethereal layer was washed with 5% sodium bicarbonate solution followed by washing with water. The ether solution was dried over anhydrous magnesium sulfate and the residual liquid after removal of the ether fractionally distilled. The first fraction consisted of 75 g. of *n*-octanol distilling at 92° (20 mm.). The main fraction of ester distilled at 197–202° (2.5 mm.), 212° (2.8 mm.), 124.5 g., (83.2%). An analytical sample of the *n*-octyl thiodiacetate was prepared by redistillation at 178–180° (0.2 mm.), $n^{24}\text{D}$ 1.4620, $d^{25}{}_4$ 0.9739. Kyrides, *et al.*,[15] gave a b.p. 360–365° (atm.), but no yield or analysis was given.

Anal. Calcd. for $C_{20}H_{38}O_4S$: C, 64.13; H, 10.23. Found: C, 63.96; H, 10.29.

Preparation of *n*-Octyl Sulfonyldiacetate.[16]—In an identical manner to that described for the preparation of ethyl sulfonyldiacetate, 145 g. (0.357 mole) of *n*-octyl thiodiacetate, 500 ml. of water, 70 ml. of acetic acid and 95 g. of powdered potassium permanganate, gave 144.5 g. (92.1%) of *n*-octyl sulfonyldiacetate, b.p. 185° (10^{-2} mm.), $n^{25}\text{D}$ 1.4573, $d^{25}{}_4$ 1.0327.

Anal. Calcd. for $C_{20}H_{38}O_4S$: C, 59.08; H, 9.42. Found: C, 59.34; H, 9.50.

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[11] W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green and Company, London, 1948, p. 98.

[12] C. L. Jackson and G. T. Hartshorn, *Am. Chem. J.*, **5**, 267 (1883).

[13] C. G. Overberger, H. J. Mallon and R. Fine, THIS JOURNAL, **72**, 4958 (1950).

[14] E. Barkenbus and P. S. Landis, *ibid.*, **70**, 684 (1948).

[15] L. P. Kyrides, W. Groves and F. B. Zienty, U. S. Patent 2,262,686, November 11, 1941.

[16] The octyl esters were prepared by Dr. Joginder Lal.