[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Dimetalation of Phenoxathiin and Phenoxathiin-10-dioxide by Organometallic Compounds

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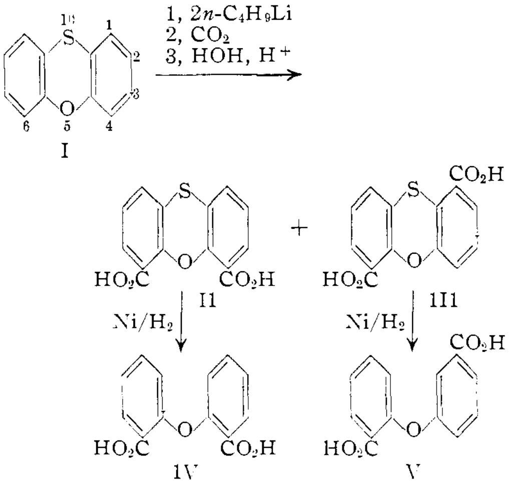
Phenoxathiin and phenoxathiin-10-dioxide are exceptionally susceptible to dimetalation by organolithium compounds. The interaction of phenoxathiin and *n*-butyllithium yields 1,6- and 4,6-dilithiophenoxathiin. Under milder conditions phenoxathiin-10-dioxide is dimetalated to produce 1,9-dilithiophenoxathiin-10-dioxide. Upon carbonation the organolithium compounds were converted to the corresponding dicarboxylic acids which were identified by cleavage to dicarboxydiphenyl ethers.

The only known, direct method of introducing a functional group into the 4-position of the phenoxathiin nucleus is by metalation with organolithium compounds.[2] The resulting 4-phenoxathiinyllithium has been allowed to react with carbon dioxide, O-methylhydroxylamine, oxygen and iodine to give 4-carboxy-,[2] 4-amino-,[2] 4-hydroxy-[3] and 4-iodophenoxathiin,[4] respectively. Though the crude products have been obtained in good yields, large losses were incurred during isolation of the pure compounds. It is shown that the losses may have been due to the presence of interfering disubstitution products resulting from dilithiophenoxathiins.

The ease of dimetalation of phenoxathiin (I) would have been unexpected if the related oxygen and sulfur heterocycles, dibenzofuran and dibenzothiophene, had been taken as model compounds for this reaction. The dimetalation of dibenzofuran has been effected by the very reactive organosodium compounds,[5] but not by organolithium reagents. In this Laboratory an excellent yield of 4-dibenzothiophenecarboxylic acid was obtained, but no dimetalation product was isolated when dibenzothiophene was treated with 2.2 equivalents of *n*-butyllithium. The behavior of phenoxathiin toward organolithium compounds is analogous to that of dibenzo-*p*-dioxin. Two dilithio derivatives of this heterocycle were formed upon treatment with 2.5 equivalents of *n*-butyllithium.[6] The metalation was limited to the formation of the monolithio derivative only when methyllithium was employed as the metalating agent.

On the basis of the assumption that *n*-butyllithium would metalate phenoxathiin only in the positions which are *ortho* to the hetero atoms, there are four phenoxathiindicarboxylic acids which would result upon carbonation of the dimetalation products. They are the 1,4-, 1,6-, 1,9- and 4,6- derivatives. One of the positions *ortho* to the oxygen is known to be especially reactive since monometalation occurs at the 4-position.

The two phenoxathiindicarboxylic acids prepared simultaneously by way of dimetalation of phenoxathiin were obtained in yields of 8.9 and 34.7%. The acid melting at 266–267° was proved to be the 4,6- derivative II when it yielded 2,2′-dicarboxydiphenyl ether (IV) upon desulfurization with Raney nickel. Though the phenoxathiindicarboxylic acid (III) melting at *ca.* 350° dec. was obtained in the lower yield, it was the more interesting of the two isomers. This acid was also a product when phenoxathiin-10-oxide was treated with *n*-butyllithium at room temperature. The higher-melting isomer yielded 2,3′-dicarboxydiphenyl ether[7,8] (V) upon hydrogenolysis with Raney nickel. This product could be obtained upon cleavage of either 1,6- or 3,6-phenoxathiindicarboxylic acid. It was not considered likely that the 3,6-diacid could have been formed by way of dimetalation of phenoxathiin since the 3-position is not *ortho* to a hetero atom. Therefore, dimetalation of phenoxathiin by organometallic compounds occurs at the 1,6- and 4,6-positions.



The interaction of one equivalent of *n*-butyllithium with phenoxathiin, followed by carbonation, afforded a 76.2% yield (based upon 4-phenoxathiincarboxylic acid) of crude acid. From this mixture there were isolated yields of 36.9 and 1.4% of 4-phenoxathiincarboxylic acid and 1,6-phenoxathiindicarboxylic acid, respectively. In the dimetalation experiments in which the yields of crude acids averaged *ca.* 90% the yield of pure 4,6-diacid was approximately four times that of the 1,6-diacid. Therefore, it would be expected that some of the 4,6-diacid was formed in the monometalation experiment, even though none was isolated. This dicarboxylic acid probably escaped

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[1] Shell Research Fellow, 1954–1955.

[2] H. Gilman, M. W. Van Ess, H. B. Willis and C. G. Stuckwisch, THIS JOURNAL, **62**, 2606 (1940).

[3] H. Gilman and D. L. Esmay, *ibid.*, **76**, 5787 (1954).

[4] J. F. Nobis and N. W. Burske, *ibid.*, **76**, 3034 (1954).

[5] H. Gilman and R. V. Young, *ibid.*, **57**, 1121 (1935).

[6] H. Gilman and C. G. Stuckwisch, *ibid.*, **65**, 1461 (1943).

[7] M. Tomita, *J. Pharm. Soc. Japan*, **57**, 391 (in German, 76) (1937) [*C. A.*, **33**, 2117 (1939)].

[8] R. Anschutz, W. Stoltenhoff and F. Voeller, *Ber.*, **58**, 1736 (1925).

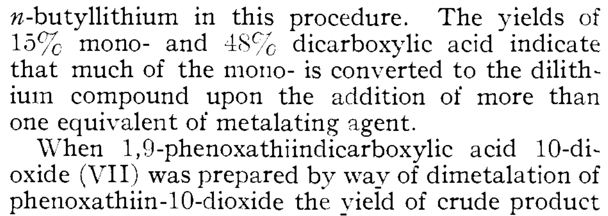
isolation since it is less soluble than the 4-acid but more soluble than the 1,6-diacid. It is estimated that at least 85% of the *n*-butyllithium effected metalation in the experiment in which a 76.2% yield of crude product was obtained. Calculations based upon these two figures indicate that the crude mixture probably consisted of six moles of 4-phenoxathiincarboxylic acid per mole of phenoxathiindicarboxylic acids.

Phenylcalcium iodide behaved toward phenoxathiin in a manner similar to that of the organolithium compounds. This property could not have been predicted with certainty in view of the anomalous metalation of dibenzothiophene[9] by this reagent. When the metalation of phenoxathiin by phenylcalcium iodide[2] was first performed the reaction appeared anomalous because the carbonation product was not the expected 4-acid but was an unidentified acid. In the present work both acids were isolated and the latter was shown to be 4,6-phenoxathiindicarboxylic acid.

Shirley and Lehto[10] showed that *n*-butyllithium metalated phenoxathiin-10-dioxide (VI) in the 1-position by proving that the carbonation product was 1-phenoxathiincarboxylic acid 10-dioxide. The workers stated that the yield of this acid could not be increased above 46% by increasing the amount of *n*-butyllithium from 1 to 1.5 equivalents. We find that it would be detrimental to use an excess of *n*-butyllithium in this procedure. The yields of 15% mono- and 48% dicarboxylic acid indicate that much of the mono- is converted to the dilithium compound upon the addition of more than one equivalent of metalating agent.

When 1,9-phenoxathiindicarboxylic acid 10-dioxide (VII) was prepared by way of dimetalation of phenoxathiin-10-dioxide the yield of crude product was 92.5%. Though this mixture undoubtedly contained a considerable amount of monocarboxylic acid, it is likely that the extent of dimetalation was much greater than the 52.2% yield of pure 1,9-diacid indicates. There are two reasons why the yield of pure dicarboxylic acid in this experiment was only slightly greater than that obtained when 1.5 equivalents of *n*-butyllithium were employed. In the latter case a slightly higher reaction temperature and an improved method of separation of the acids were used.

We established the structure of 1,9-phenoxathiindicarboxylic acid 10-dioxide by desulfurizing the compound to 3,3′-dicarboxydiphenyl ether[7] (VIII).



The isolation of this cleavage product is considered to be adequate proof that the acid is the 1,9-derivative even though two other phenoxathiindicarboxylic acids, the 1,7- and the 3,7-derivatives, would also yield the same product. It is unlikely that metalation occurred in the 7-position, one which is not *ortho* to either the sulfone group or the ether linkage.

Attempts were made to limit the metalation of phenoxathiin and phenoxathiin-10-dioxide to the formation of the monolithium derivatives. Some dimetalation of phenoxathiin took place when *n*-butyllithium was used at −20° (6 hr.) to room temperature (1.5 hr.). Methyllithium showed the greatest promise as a monometalating agent for phenoxathiin since no interfering dimetalation occurred even though two equivalents of the reagent were employed at the temperature of refluxing ether. Though the crude 4-phenoxathiincarboxylic acid was obtained in a low yield (11.6%), it was in a relatively high state of purity. However, phenoxathiin-10-dioxide, being more easily metalated than the unoxidized heterocycle, gave a mixture of a mono- and a dicarboxylic acid after treatment with one equivalent of methyllithium.

Experimental[11]

Metalation of Phenoxathiin. (a) With Two Equivalents of *n*-Butyllithium.—To a refluxing, stirred solution of 40.0 g. (0.20 mole) of phenoxathiin in 100 ml. of anhydrous ether was added 373 ml. of a 1.17 *M* ethereal solution (0.44 mole) of *n*-butyllithium[12] and the mixture was stirred at the reflux temperature for 40 hr. The reaction mixture was poured jet-wise into a stirred slurry of ether and Dry Ice and the resultant mixture was allowed to stand until the ether was evaporated. The dry solid was pulverized and extracted with petroleum ether (b.p. 60–70°) in a Soxhlet extractor. Following removal of the residual solvent, the salt mixture from the Soxhlet thimble was dissolved in water. The solution was stirred with Norit A, filtered and acidified with dilute (1:10) hydrochloric acid.

The crude, yellow acid mixture, 54.5 g. (95%), melting range 221–275°, was extracted with benzene in a Soxhlet extractor in order to remove the more soluble 4-phenoxathiincarboxylic acid. No attempt was made to isolate this acid. Removed from the Soxhlet thimble was 46.0 g. of benzene-insoluble solid which melted over the range 240–267°. The solid was dissolved in 10% potassium hydroxide solution and to the vigorously stirred, pale orange solution was added slowly enough dilute acetic acid to precipitate most of the dull yellow acid. Following collection of the product, which weighed 33.0 g. and melted over the range 260–283°, the filtrate was further acidified with dilute hydrochloric acid. The bright canary-yellow product weighed 16.0 g. and melted over the range 295–316°. (Since a total of 49.0 g. was obtained, there may have been *ca.* 3 g. of occluded salts.) The material melting over the range 260–283° was redissolved in dilute potassium hydroxide solution and the partial acidification process was repeated. There was collected 24.6 g. of dull yellow material, melting range 256–266°, and 4.4 g. of bright yellow solid melting over the range 267–318°. The last batch was combined with the 16-g. fraction and the mixture was digested with 60% acetic acid. Upon filtration of the acetic acid suspension there was collected 9.6 g. of yellow solid which melted over the range 318–332°. The acetic acid filtrate was cooled and there was obtained 2.9 g. of yellow crystals melting over the range 246–267°.

Crystallization from 60% acetic acid of the material melting over the range 256–267° gave three fractions having the following weights and melting ranges: 5.1 g., 264–268°;

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(9) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *J. Org. Chem.*, **3**, 120 (1938).

(10) D. A. Shirley and E. A. Lehto, THIS JOURNAL, **77**, 1841 (1955).

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

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

14.9 g., 267–270°; and 2.1 g., 253–260°. The first two fractions, 20.0 g., represented a 34.7% yield of relatively pure 4,6-phenoxathiindicarboxylic acid. An analytical sample, one which had been successively recrystallized from glacial acetic acid and methyl ethyl ketone with no change in melting point, melted at 266–267°.

Anal. Calcd. for $C_{14}H_8O_5S$: C, 58.33; H, 2.80; S, 11.12; neut. equiv., 144. Found: C, 58.31, 58.52; H, 2.99, 2.90; S, 11.01, 11.08; neut. equiv., 144, 146.

The material which melted over a range at temperatures above 300° was recrystallized from a large volume of aqueous acetone. There were obtained fractions with the following weights and melting ranges: 5.1 g., 340–346°; 0.9 g., 334–339°; and 3.9 g., 318–324°. Decomposition accompanied melting in all three cases. The weight of 5.1 g. represents an 8.9% yield of relatively pure 1,6-phenoxathiindicarboxylic acid. This material did not depress the melting points of a sample (m.p. 351–353° dec.) which was obtained by a subsequent recrystallization from methyl Cellosolve.

Anal. Calcd. for $C_{14}H_8O_5S$: S, 11.12; neut. equiv., 144. Found: S, 11.04, 10.97; neut. equiv., 144.5, 141.5.

(b) **With One Equivalent of *n*-Butyllithium.**—To a stirred solution of 20.0 g. (0.10 mole) of phenoxathiin in 300 ml. of anhydrous ether at 35° was added 50 ml. of a 1.06 *M* ethereal solution (0.05 mole) of *n*-butyllithium over a period of 45 minutes. Color Test II[13] was negative 45 minutes after the addition of this first half-molar equivalent. The second half-molar equivalent (0.05 mole) of *n*-butyllithium was added over a 30-minute period. Color Test II was negative 30 minutes after the completion of the addition, at which time the mixture was carbonated and worked up as in the preceding experiment.

Filtered from the petroleum ether extract was a small amount of yellow crystals which melted at 166–167°, leaving a residue. A mixture of this unknown material (believed to be a ketone) and a sample of 4-phenoxathiincarboxylic acid (m.p. 171–173°) melted over the range 142–150°, leaving a residue. Unsuccessful attempts were made to purify the small amount of yellow crystals. Upon concentration of the petroleum ether filtrate there was recovered 0.7 g. (3.8%) of phenoxathiin, m.p. and mixed m.p. 53–55°.

The crude, yellow acid mixture weighed 18.6 g. and melted over the range 151–165°. An attempt was made to separate the acids by extraction with ether, followed by recrystallization from glacial acetic acid. No separation was effected. The resultant mixture which weighed 14.4 g. was digested with benzene, a solvent which dissolved the monocarboxylic acid and left the dicarboxylic acid as a residue. Recrystallization of the dicarboxylic acid from methanol yielded 0.4 g. (1.4%) of 1,6-phenoxathiindicarboxylic acid, m.p. and mixed m.p. with an authentic specimen 348–350° dec.

Upon concentration of the benzene solution there was obtained 11.5 g. of yellow crystals, melting range 156–172°. Following two recrystallizations from benzene there was collected 9.8 g. of yellow crystals, m.p. 170–172°. A final recrystallization from glacial acetic acid yielded 9.1 g. (36.9%) of 4-phenoxathiincarboxylic acid, m.p. and mixed m.p. 171–173°.

(c) **With Methyllithium.**—To a stirred solution of 30.0 g. (0.15 mole) of phenoxathiin in 150 ml. of anhydrous ether was added 138 ml. of a 1.31 *M* ethereal solution (0.18 mole) of methyllithium.[14] After a 20-hour reflux period the mixture was carbonated and worked up as described in (a). There was obtained from the petroleum ether extract 26.3 g. (87.7% recovery) of phenoxathiin. The yield of crude product melting at 169–172° was 3.4 g. (9.3%). After one recrystallization from glacial acetic acid there was collected 2.7 g. of pure 4-phenoxathiincarboxylic acid, m.p. 171–173°.

When two molar equivalents of methyllithium were employed in the reaction the yield of crude product, m.p. 169–172°, was 11.6%.

(d) **With Phenylcalcium Iodide.**—To a stirred solution of 32.0 g. (0.16 mole) of phenoxathiin in 150 ml. of anhydrous ether was added 360 ml. of a 0.46 *M* ethereal solution (0.16 mole) of phenylcalcium iodide.[15] After a 38-hour reflux period the mixture was carbonated. When the dry carbonation mixture had been extracted with petroleum ether (b.p. 60–70°), the brown solid was removed from the Soxhlet thimble, the solvent was evaporated, the solid was stirred with water and the mixture was filtered. A water-insoluble, brown solid was collected and the filtrate was acidified. There was obtained 0.5 g. of pale yellow acid which melted over the range 160–165°. After recrystallization from 50% acetic acid there was isolated 0.1 g. of 4-phenoxathiincarboxylic acid, m.p. and mixed m.p. 169.5–171.5°.

The water-insoluble, brown solid was stirred with water and the mixture was acidified. Upon filtration there was obtained 2.8 g. of a sticky, brown material which was subsequently dissolved in hot ethanol, the solution treated with Norit A and filtered. When the solution was diluted with water, a black oil and yellow-brown crystal separated. The crystals were decanted from the oil, collected and recrystallized from 50% acetic acid. There was obtained 0.1 g. of yellowish-brown crystals, m.p. 253–256°. A mixture of this material and 4,6-phenoxathiindicarboxylic acid (m.p. 266–267°) melted at 259–261°. The infrared spectra, determined on Nujol mulls of the two samples, contained no significant differences.

A sample of the acid prepared by the original reaction of phenoxathiin with phenylcalcium iodide[2] was procured. A mixture of this material (m.p. reported 260–262°, found 258–259° dec.) and 4,6-phenoxathiindicarboxylic acid melted at 258–260° dec.

Preparation of 1,6-Phenoxathiindicarboxylic Acid from *n*-Butyllithium and Phenoxathiin-10-oxide.[16]—To a stirred suspension of 21.6 g. (0.10 mole) of phenoxathiin-10-oxide in 200 ml. of anhydrous ether was added 240 ml. of a 1.33 *M* ethereal solution (0.32 mole) of *n*-butyllithium over a period of 1.25 hr. After 5 hr. of stirring, the mixture was carbonated and worked up as in the preceding experiments.

Upon acidification of the salt solution there was collected a yellow acid which was contaminated by oily impurities. The latter were removed by digestion with petroleum ether (b.p. 60–70°). The greenish-yellow solid was digested with refluxing glacial acetic acid, and the suspension was filtered while hot. Removed from the filter paper was a yellow solid which was recrystallized from methyl Cellosolve to yield 2.3 g. (8.0%) of 1,6-phenoxathiindicarboxylic acid, m.p. and mixed m.p. 348–350° dec.

Metalation of Phenoxathiin-10-dioxide. (a) **With Two Equivalents of *n*-Butyllithium.**—To a stirred suspension of 46.4 g. (0.20 mole) of phenoxathiin-10-dioxide in 250 ml. of anhydrous ether at −45° was added 320 ml. of a 1.33 *M* ethereal solution (0.43 mole) of *n*-butyllithium. After 3 hr. at −45 ± 5° the mixture was allowed to warm to −10° over a period of 1 hr. The yellow-orange suspension was carbonated, the mixture was allowed to warm to room temperature and the ether was removed by decantation. The white solid was dissolved in water and the filtered solution was acidified to yield 55.1 g. of finely divided, white solid which melted over the range 336–342°. Concentration of the aqueous filtrate yielded an additional crop of 4.1 g. of product. The total weight of acid, 59.2 g., represented a 92.5% yield of crude 1,9-phenoxathiindicarboxylic acid 10-dioxide. After two recrystallizations from large volumes of methanol there was obtained 33.4 g. (52.2%) of 1,9-phenoxathiindicarboxylic acid 10-dioxide, m.p. 354–357° dec.

(b) **With One and One-half Equivalents of *n*-Butyllithium.**—To a stired suspension of 23.2 g. (0.10 mole) of phenoxathiin-10-dioxide in 200 ml. of anhydrous ether was added 155 ml. of a 0.97 *M* solution (0.15 mole) of *n*-butyllithium over a period of 30 minutes. The orange suspension was kept at ice-bath temperature during the addition and for a subsequent 4-hour period of stirring. The ice-bath was removed and stirring was continued for a 30-minute period, after which the mixture was carbonated. Following evaporation of the ether, the white solid was stirred with 1500 ml. of water, and the mixture was filtered. When the filtered salt solution was acidified, there was obtained 17.7 g. of product melting over the range 290–330°. The aqueous filtrate was made alkaline, concentrated to 400 ml., treated with Norit A and filtered. Upon acidification there formed 9.4 g. of product melting over the range 335–341°.

The mixture of 27.1 g. of white solid, melting range 290–341°, was digested with 400 ml. of refluxing ethyl acetate

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(13) H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).

(14) H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **55**, 1252 (1933).

(15) J. W. Morton, Jr., Ph.D. Thesis, Iowa State College, 1952.

(16) For the cleavage of phenoxathiin-10-oxide by *n*-butyllithium, see H. Gilman and S. H. Eidt, THIS JOURNAL, **78**, *in* press (1956).

and the hot mixture was filtered. Retained on the filter paper was 19.9 g. of slightly impure 1,9-phenoxathiindicarboxylic acid 10-dioxide, melting range 344–348°. Upon concentration of the ethyl acetate solution, there was obtained 5.8 g. of product melting over the range 212–222°. The higher-melting fraction was recrystallized twice from methanol to yield 15.4 g. (48.1%) of 1,9-phenoxathiindicarboxylic acid 10-dioxide, m.p. 350–352° dec. A mixed melting point with a sample of 1,9-phenoxathiindicarboxylic acid 10-dioxide obtained in the preceding experiment was not depressed.

After the low-melting fraction was recrystallized twice from 70% ethanol, there was obtained 4.1 g. (14.9%) of 1-phenoxathiincarboxylic acid 10-dioxide, m.p. 230–232°.

(c) **With One Equivalent of Methyllithium.**—To a stirred suspension of 23.2 g. (0.10 mole) of phenoxathiin-10-dioxide in 200 ml. of anhydrous ether at 0–5° was added 84 ml. of a 1.31 *M* solution (0.10 mole) of methyllithium over a period of 40 minutes. The pale orange suspension was stirred at ice-bath temperature for 2 hr. and then allowed to warm to room temperature over a period of 1 hr. Following carbonation and evaporation of the ether, the white solid was stirred with 500 ml. of water and the mixture was filtered. There was collected 16.5 g. (71.1% recovery) of crude phenoxathiin-10-dioxide, m.p. and mixed m.p. 142–146°. The aqueous filtrate was acidified to yield 8.6 g. of white solid melting over the range 217–240°. After successive recrystallizations from glacial acetic acid and 95% ethanol, there was obtained 5.0 g. (18.1%) of 1-phenoxathiincarboxylic acid 10-dioxide, m.p. and mixed m.p. 228–231°. The aqueous solution was concentrated and there was collected 0.9 g. (2.8%) of crude 1,9-phenoxathiindicarboxylic acid 10-dioxide, melting range 338–342° dec.

Preparation of 4-Phenoxathiincarboxylic Acid 10-Oxide.[17]—To a yellow, refluxing, stirred solution of 2.44 g. (0.01 mole) of 4-phenoxathiincarboxylic acid in 25 ml. of glacial acetic acid was added dropwise 5 ml. (0.03 mole) of dilute nitric acid (sp. gr. 1.2). After 2 hr. of refluxing the solution was poured into 80 ml. of an ice–water mixture. A finely divided, white solid was collected and dried. The 2.1 g. of product melted over the range 135–145°, but the melting range was indefinite and dependent upon the temperature of the bath when the sample was inserted and upon the rate of heating. After the product was recrystallized from *ca.* 100 ml. of benzene, there was collected 1.6 g. (61.5%) of 4-phenoxathiincarboxylic acid 10-oxide, m.p. 171–173°. Following a recrystallization from hot water the melting point of the crystals was again dependent upon the rate of heating of the bath. Samples melted immediately when placed in the bath at temperatures above 120°. After another recrystallization from benzene the white 4-phenoxathiincarboxylic acid 10-oxide melted sharply at 171–173°. A mixture of the product and the starting material melted over the range 128–137°.

Anal. Calcd. for $C_{13}H_8O_4S$: S, 12.32; neut. equiv., 260. Found: S, 12.02, 11.89; neut. equiv., 260, 262.

Preparation of 1,6-Phenoxathiindicarboxylic Acid 10-Dioxide.—A mixture consisting of 2.88 g. (0.01 mole) of 1,6-phenoxathiindicarboxylic acid, 20 ml. of glacial acetic acid and 6 ml. (0.06 mole) of 30% aqueous hydrogen peroxide was stirred at 106° for 2 hr. and allowed to stand overnight. There was collected 2.8 g. of white solid melting over the range 351–354° dec. Recrystallization from a large volume of methanol yielded 2.6 g. (80.5%) of fine, white needles of 1,6-phenoxathiindicarboxylic acid 10-dioxide, m.p. 351–353° dec. A mixture of the white needles and the dense, blunt, white crystals of 1,9-phenoxathiindicarboxylic acid 10-dioxide (m.p. *ca.* 350° dec.) melted over the range 324–334°.

Anal. Calcd. for $C_{14}H_8O_7S$: S, 10.01; neut. equiv., 160. Found: S, 9.86, 9.91; neut. equiv., 158, 161.

Preparation of 4,6-Phenoxathiindicarboxylic Acid 10-Dioxide.—One-hundredth mole of 4,6-phenoxathiindicarboxylic acid was oxidized according to the procedure in the preceding preparation. The crude product was 3.03 g. of white needles, m.p. 327–330° dec. After one recrystallization from a large volume of acetone–water, there was obtained 2.63 g. (82.3%) of 4,6-phenoxathiindicarboxylic acid 10-dioxide, m.p. 329–331° dec.

Anal. Calcd. for $C_{14}H_8O_7S$: S, 10.01; neut. equiv., 160. Found: S, 9.95, 9.94; neut. equiv., 161, 161.

Preparation of Dimethyl 4,6-Phenoxathiindicarboxylate.—To a cold, swirled ethereal solution of *ca.* 0.084 mole of diazomethane was added portionwise 4.03 g. (0.014 mole) of 4,6-phenoxathiindicarboxylic acid. Following evaporation of the ether, the crude product, m.p. 81–83°, was recrystallized twice from methanol to yield 3.52 g. (79.5%) of dimethyl 4,6-phenoxathiindicarboxylate, m.p. 82.5–83°.

Anal. Calcd. for $C_{16}H_{12}O_5S$: S, 10.13. Found: S, 9.72, 9.82.

Preparation of Dimethyl 1,6-Phenoxathiindicarboxylate.—The reaction was carried out according to the procedure in the preceding preparation. There was obtained 4.45 g. of yellow solid, melting range 136–140°, which was recrystallized three times from large volumes of methanol and one time from ethanol to yield 2.55 g. (57.5%) of dimethyl 1,6-phenoxathiindicarboxylate, m.p. 150.5–151.5°.

Anal. Calcd. for $C_{16}H_{12}O_5S$: S, 10.13. Found: S, 10.11, 10.08.

Preparation of Dimethyl 1,9-Phenoxathiindicarboxylate 10-Dioxide.—The reaction between 3.20 g. (0.01 mole) of 1,9-phenoxathiindicarboxylic acid 10-dioxide and *ca.* 0.06 mole of diazomethane yielded a white, ether-insoluble solid which was stirred with 5% sodium carbonate solution, and the insoluble solid was collected by filtration and washed with water. The filtrate was acidified and there was collected 0.80 g. (25.0% recovery) of starting material. The solid which was insoluble in sodium carbonate weighed 2.40 g. and melted over the range 167–225°. It was digested with 30 ml. of methanol and the hot mixture was filtered. Following crystallization there was collected 1.60 g. (46.0%) of dimethyl 1,9-phenoxathiindicarboxylate 10-dioxide, m.p. 170–171°.

Anal. Calcd. for $C_{16}H_{12}O_7S$: S, 9.20. Found: S, 9.07, 9.08.

Preparation of Diethyl 1,9-Phenoxathiindicarboxylate 10-Dioxide.—A mixture of 16.01 g. (0.05 mole) of 1,9-phenoxathiindicarboxylic acid 10-dioxide and 100 g. of hydrogen chloride in 200 g. of absolute ethanol was stirred at the reflux temperature for 16 hr. Following distillation of the ethanol the residual white solid was stirred with sodium bicarbonate solution and the mixture was filtered. There was collected 16.4 g. of crude ester, melting range 138–142°, which was recrystallized twice from dilute ethanol to yield 12.8 g. (68.1%) of diethyl 1,9-phenoxathiindicarboxylate 10-dioxide, m.p. 143–143.5°.

Anal. Calcd. for $C_{18}H_{16}O_7S$: S, 8.52. Found: S, 8.52, 8.42.

Hydrogenolysis[18] of 1,6-Phenoxathiindicarboxylic Acid.—A mixture of 2.88 g. (0.01 mole) of 1,6-phenoxathiincarboxylic acid, 750 ml. of 0.5% sodium carbonate solution and 30–35 g. of freshly prepared Raney nickel catalyst[19,20] was stirred at 70° for 30 minutes and filtered. After the nickel had been washed with four 50-ml. portions of 0.5% sodium carbonate solution and with three 50-ml. portions of water, the aluminum hydroxide was precipitated and removed by filtration. Upon acidification of the filtrate there was obtained 1.40 g. of white solid melting over the range 218–229°. The mother liquor was extracted with ether and the ethereal extract was concentrated to yield 1.05 g. of pale yellow solid. The material was subjected to vacuum sublimation and there was obtained a white sublimate melting over the range 108–112°. The yellow color and high melting range of the residue indicated that it was principally unreacted starting material.

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[17] The only analytical datum reported for 4-phenoxathiincarboxylic acid 10-dioxide (m.p. 183–184°,[2] 189–190°[10]) was the experimental neutralization equivalent value of 261.[2] Since this value agrees with the theoretical value (260) for 4-phenoxathiincarboxylic acid 10-oxide, it was deemed advisable to prepare the 10-oxide acid.

(18) The hydrogenolysis–desulfurization method described herein, one which employs Raney nickel in dilute sodium carbonate solution, was modeled after the procedures reported in the following articles: S. A. Harris, R. Mozingo, D. E. Wolf, A. N. Wilson and K. Folkers, THIS JOURNAL, **67**, 2102 (1945); F. F. Blicke and D. G. Sheets, *ibid.*, **70**, 3768 (1948), and **71**, 4010 (1949).

(19) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

(20) The catalyst had been prepared in the usual manner except that the final heating of the reaction mixture after the addition of the alloy was carried out for 2 hr. at 50–80°.

The 1.40 g. of white solid was recrystallized successively from acetone–water, acetone–benzene and ethanol–water to yield 0.24 g. of 2,3′-dicarboxydiphenyl ether, m.p. 220–221°. The melting points reported for this acid are 202°[7] and 215°.[8] A mixture of the product and an authentic specimen[21] of 2,3′-dicarboxydiphenyl ether (m.p. found 205–210°) melted over the range 208–215°. The infrared spectra of the two samples were superimposable.

Hydrogenolysis of 4,6-Phenoxathiindicarboxylic Acid.—A mixture of 2.00 g. (0.007 mole) of 4,6-phenoxathiindicarboxylic acid, 600 ml. of 0.5% sodium carbonate solution and 25–30 g. of Raney nickel was stirred at 75° for 1.25 hr., filtered and worked up as in the preceding experiment. There was collected 1.5 g. of white solid melting over the range 109–230°.

When a solution of ferric chloride was added to a sample of the crude acid, there resulted a purple color which was of the same hue as that given by a salicylic acid blank. Authentic samples of benzoic acid[22] and 2,2′-dicarboxydiphenyl ether gave negative ferric chloride tests. It was believed that the reaction mixture contained benzoic acid, salicylic acid and 2,2′-dicarboxydiphenyl ether, the first two acids having been produced by cleavage of the diphenyl ether linkage.

The mixture was subjected to vacuum sublimation at 100–120°, yielding 1.12 g. of sublimate, melting range 112–129°. The residue was successively recrystallized from water and a mixture of benzene and methyl ethyl ketone to yield 0.20 g. (11.2%) of 2,2′-dicarboxydiphenyl ether, m.p. and mixed m.p. with an authentic specimen 227–229°. The infrared spectra of the product and the authentic specimen were identical.

Hydrogenolysis of 1,9-Phenoxathiindicarboxylic Acid 10-Dioxide.—A mixture of 3.20 g. (0.01 mole) of 1,9-phenoxathiindicarboxylic acid 10-dioxide, 750 ml. of 0.5% sodium carbonate solution and *ca.* 40 g. of Raney nickel was stirred at 75° for 30 minutes, filtered and worked up according to the procedure used for the 1,6-diacid. There was collected 2.03 g. of white product, melting range 103–237°, and, upon further concentration of the aqueous filtrate, 0.34 g., melting range 108–289°. The larger fraction was digested with hot water and the hot suspension was filtered. Collected from the filter paper was 0.72 g. of crude product, m.p. 244–247°, which was recrystallized twice from acetone–water to yield 0.43 g. (16.7%) of 3,3′-dicarboxydiphenyl ether, m.p. 249–250°. A mixture of this product and an authentic specimen[20] of 3,3′-dicarboxydiphenyl ether (m.p. reported[8] 243–245°, found 247–251°) melted at 247–250°. The infrared spectra of the two samples were superimposable.

Dimetalation of Dibenzothiophene by *n*-Butyllithium (Attempted).[23]—An ethereal solution of dibenzothiophene and 2.2 molar equivalents of *n*-butyllithium was stirred at the reflux temperature for 36 hr. and then carbonated. Color Test II was negative at the time of carbonation. Following hydrolysis and acidification there was obtained a 90.9% yield of crude acid melting over the range 237–245°. The following fractions were separated after extraction with methanol: 35.4% of exceptionally pure 4-dibenzothiophenecarboxylic acid, m.p. 255–255.5° (identified by a mixed m.p. determination); 22.2%, m.p. 250–252°; and 16.7%, melting range 244–250°.

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[21] Kindly provided by Dr. M. Tomita.

[22] Benzoic acid was isolated and identified as one of products from one run of the hydrogenolysis of 1,9-phenoxathiindicarboxylic acid 10-dioxide.

[23] This work is described in the Ph.D. Thesis of D. L. Esmay.

[CONTRIBUTION NO. 385 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Thermal Addition of Monoölefins to Dienophiles

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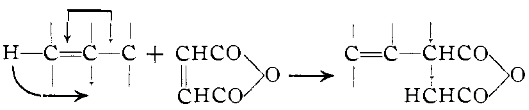
Olefins containing at least 3 carbons have been shown to add to α,β-unsaturated nitriles, esters and ketones at elevated temperatures to form δ,ϵ-unsaturated nitriles, esters and ketones, respectively. When the double bond of the initial product is terminal, a second molecule of the α,β-unsaturated compound can add, producing an unsaturated bifunctional product. Structures of the products indicate that the addition proceeds through the formation of a quasi-6-membered ring.

Several workers[1] have reported that non-conjugated olefinic compounds add to maleic anhydride at elevated temperatures. The uncatalyzed thermal addition of such monoölefins as butenes to maleic anhydride was first reported by Alder[2] to proceed by addition of allylic hydrogen across the double bond of maleic anhydride with the olefinic double bond remaining intact. More recent studies on the addition to maleic anhydride of methyl undecylenate,[3] methylenecyclohexane[4] and other olefins[5] demonstrate that the addition proceeds by direct attachment of the maleic anhydride to an olefinic carbon atom followed by double bond migration and transfer of a hydrogen to saturate the anhydride.



Addition of allylbenzene to aryl maleic anhydrides has been described,[6] but the utility of other dienophiles in this thermal addition reaction has not been reported.

We have investigated the scope of the reaction with regard to α,β-unsaturated compounds known to be dienophiles in the Diels–Alder diene addition and have also studied the influence of various olefinic structures. Thermal adducts with propylene and higher olefins have been obtained from a variety of known dienophiles including acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone, ethyl vinyl sulfone, acrylic acid and diethyl vinylphosphonate. Olefins examined include propylene, the butenes,

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[1] E. A. Bevan, *Oil and Colour Chem. Assoc.*, **34**, 1939 (1940); E. T. Clocker, U. S. Patent 2,188,882, 1940; W. G. Bickford, P. Krauczunas and D. H. Wheeler, *Oil and Soap*, **19**, 23 (1942).

[2] K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76B**, 27 (1943).

[3] J. Ross, A. I. Gebhart and J. F. Gerecht, THIS JOURNAL, **68**, 1373 (1946).

[4] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

[5] K. Alder and H. A. Dortmann, *Ber.*, **85**, 556 (1952).

[6] C. S. Rondestvedt and A. H. Filbey, *J. Org. Chem.*, **19**, 548 (1954).