Photochemical and Thermal Transformations of *O*-Alkyl *S*-Phthalidyl Xanthates and Dithiocarbamoyl Phthalides

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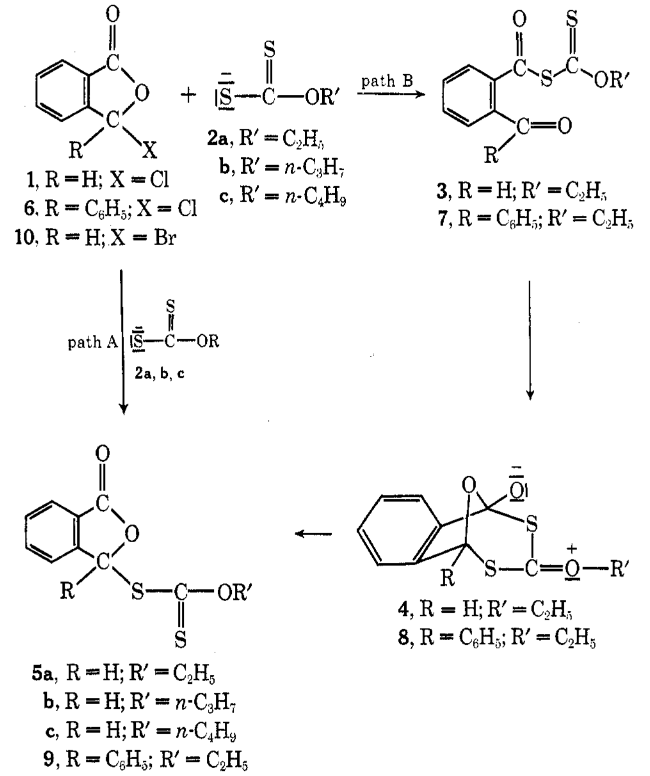
The reaction of 3-chlorophthalide, 3-bromophthalide, and 3-chloro-3-phenylphthalide with potassium *O*-alkyl xanthates gave the corresponding *O*-alkyl *S*-(3-phthalidyl) xanthates. Dithiocarbamates, on the other hand, gave the corresponding 3-dithiocarbamoyl phthalides. Photolysis of both *O*-alkyl *S*-(3-phthalidyl) xanthates and 3-dithiocarbamoyl phthalides gave *meso*-dihydrobiphthalide as the chief product in each case. The thermal decomposition of these substances, on the other hand, gave a mixture of products consisting of carbonyl sulfide, thiophthalic anhydride, 3,3′-monothiobiphthalide, 3,3′-dithiobiphthalide, and isocoumarino[4,3-*c*]isothiocoumarin. The thermal and photochemical decomposition of *O*-ethyl *S*-(3-phenylphthalidyl) xanthate gave rise to 3,3′-diphenylbiphthalide as the chief product. The same product was obtained from the thermal and photochemical decompositions of 3-dithiocarbamoyl-3-phenylphthalides.

In earlier communications[2,3] we had reported the reactions of both symmetrical and unsymmetrical phthaloyl dichlorides with several potassium *O*-alkyl xanthates and dithiocarbamates which led to the synthesis of phthaloyl dixanthates and bisdithiocarbamic anhydrides. In the reaction of symmetrical phthaloyl dichloride with potassium *O*-methyl xanthate, for example, the unsymmetrical di-*O*-methyl *S*,*S*-phthaloyl dixanthate was formed as the major product. It was shown that in this reaction the symmetrical di-*O*-methyl *S*,*S*-phthaloyl dixanthate is formed initially which then rapidly rearranges to the unsymmetrical isomer. The reaction of dithiocarbamates with both symmetrical and unsymmetrical phthaloyl dichlorides, on the other hand, gave the corresponding symmetrical phthaloic bisdithiocarbamic anhydrides, in each case. In continuation of our studies, we have examined the reactions of a few monohalophthalides with potassium *O*-alkyl xanthates and dithiocarbamates, with a view to examining the nature of the products formed in these reactions.

Treatment of potassium *O*-ethyl xanthate with an acetone solution of 3-chlorophthalide (**1**) gave a product which was identified as *O*-ethyl *S*-phthalidyl xanthate (**5a**), mp 107–108°. The identity of this product was confirmed on the basis of analytical results and spectral data. The ir spectrum of **5a** showed a carbonyl absorption at 1770 cm^{-1}, characteristic of a γ-lactone. The nmr spectrum of **5a** showed a multiplet centered around δ 7.9 (5 H) due to the four aromatic protons and one tertiary proton attached to the 3 position of the phthalide nucleus. In addition, the spectrum showed a quartet centered around δ 4.89 (2 H) due to the methylene protons and a triplet at δ 1.42 (3 H) due to the methyl protons of the alkyl side chain.

The formation of **5a** may be rationalized in terms of a direct displacement of the chloride ion (path A) or through the attack of the nucleophile on the carbonyl carbon (path B) as shown in Scheme I. If the reaction is proceeding through path B, then one would expect the formation of the intermediate aldehydo xanthate **3**, which can then rearrange to **5a** through a bicyclo[3.2.1] transition state **4**.[4] With a view to finding out whether the intermediate **3** is formed in the reaction or not, we have examined the absorption spectrum of the product mixture, immediately after mixing together the chlorophthalide **1** and potassium *O*-ethyl xanthate in a 1:1 ratio, in acetone solution around 5°. The absorption spectrum of this mixture was characterized by the presence of a maximum at 390 nm (ϵ 80), characteristic of acyl and aroyl xanthates containing the –C(=O)SC(=S)– chromophore.[2,3,5] Further, it was observed that the absorption maximum at 390 nm of a freshly formed solution of **3** gradually disappeared, and a new absorption maximum at 362 nm (ϵ 50) was observed due to the formation of **5a**. In this connection it might be mentioned that a similar absorption maximum around 360 nm was observed in all the unsymmetrical phthaloyl dixanthates that we have ex-

SCHEME I



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(1) To whom enquiries should be addressed.

(2) A. Shah, S. N. Singh, and M. V. George, *Tetrahedron Lett.*, 3983 (1968).

(3) S. N. Singh and M. V. George, *J. Org. Chem.*, **36**, 615 (1971).

(4) For some examples involving bicyclo[3.2.1] transition states, see (a) ref 3; (b) M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, **86**, 2942 (1964); **88**, 781 (1966); (c) M. S. Newman, N. Gill, and B. Darre, *J. Org. Chem.*, **31**, 2713 (1966); (d) M. S. Newman and L. K. Lala, *ibid.*, **32**, 3225 (1967); (e) M. S. Newman, S. S. Gupte, and S. Sankarappa, *ibid.*, **35**, 2757 (1970).

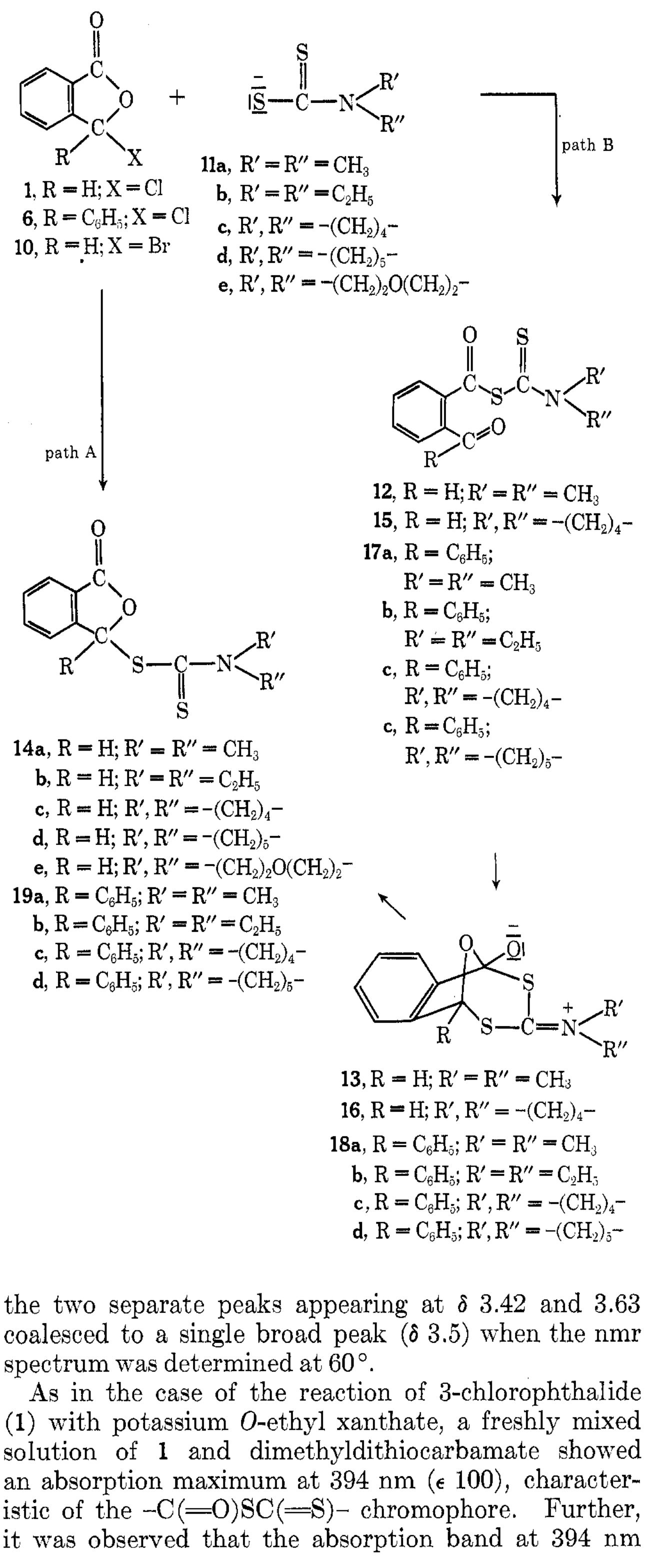
(5) D. H. R. Barton, M. V. George, and M. Tomoeda, *J. Chem. Soc.*, 1967 (1962).

amined earlier.[3] These observations support the view that the reaction of **1** with potassium *O*-ethyl xanthate proceeds through B, as shown in Scheme I.

With a view to studying the mode of displacement in a few other phthalide derivatives, we have examined the reactions of 3-chloro-3-phenylphthalide and 3-bromophthalide with different potassium *O*-alkyl xanthates. Treatment of potassium *O*-ethyl xanthate with an acetone solution of 3-chloro-3-phenylphthalide (**6**), for example, gave a 60% yield of *O*-ethyl *S*-(3-phenylphthalidyl) xanthate (**9**), mp 88°. It has been observed that a freshly formed solution of **9** shows an absorption maximum at 392 nm (ε 75), characteristic of the -C(=O)SC(=S)- chromophore present in the intermediate xanthate **7** (Scheme I). The absorption maximum at 392 nm gradually disappeared, and a new absorption band was observed at 366 nm, characteristic of the rearranged xanthate **9**. It is therefore inferred that the reaction of potassium *O*-ethyl xanthate with **6** proceeds through path B (Scheme I) and is similar to the reaction of 3-chlorophthalide. The reaction of potassium *O*-ethyl xanthate with 3-bromophthalide (**10**), on the other hand, gave rise to a 88% yield of **5a**. It is interesting to note that, even when this reaction was carried out at low temperatures (−30°), we could not detect the formation of any aldehydo xanthate (**3**). It appears that the nucleophilic substitution in this case is proceeding through path A, involving a direct displacement of the halide ion. This difference in the mode of reactions between 3-chlorophthalide and 3-bromophthalide may be attributed to the greater ease with which benzyl bromides undergo displacement reactions when compared to the corresponding chlorides. Similarly, the reactions of potassium *O*-*n*-propyl xanthate and potassium *O*-*n*-butyl xanthate with **10** resulted in the formation of *O*-*n*-propyl *S*-(3-phthalidyl) xanthate (**5b**) and *O*-*n*-butyl *S*-(3-phthalidyl) xanthate (**5c**) in 80 and 75% yields, respectively.

Our next objective was to examine the reactions of 3-chlorophthalide, 3-chloro-3-phenylphthalide, and 3-bromophthalide with different dithiocarbamates with a view to studying the nature of the products formed in these reactions. The reaction of 3-chlorophthalide (**1**) with dimethyldithiocarbamate (**11a**), for example, gave a 62% yield of a product, mp 186–187°, identified as 3-[(dimethylthiocarbamoyl)thio]phthalide (**14a**), based on analytical results and spectral data. The ir spectrum of **14a** showed an absorption band at 1750 cm^{-1}, characteristic of a γ-lactone carbonyl group. The uv spectrum of **14a** showed an absorption maximum at 340 nm (ε 90), characteristic of unsymmetrical phthaloic dithiocarbamic anhydrides.[3] The nmr spectrum of **14a** showed a multiplet centered around δ 7.9 (5 H) due to the four aromatic protons and the tertiary proton attached to the 3 carbon of the phthalide nucleus. In addition, the spectrum showed two singlets at δ 3.42 (3 H) and 3.63 (3 H), respectively, due to the two methyl groups of the dithiocarbamate group. The magnetic nonequivalence of these two methyl groups is attributed to the restricted rotation about the C–N bond in **14a**, similar to the restricted rotation that is observed in amides.[6] Further, it was observed that the two separate peaks appearing at δ 3.42 and 3.63 coalesced to a single broad peak (δ 3.5) when the nmr spectrum was determined at 60°.

SCHEME II



As in the case of the reaction of 3-chlorophthalide (**1**) with potassium *O*-ethyl xanthate, a freshly mixed solution of **1** and dimethyldithiocarbamate showed an absorption maximum at 394 nm (ε 100), characteristic of the -C(=O)SC(=S)- chromophore. Further, it was observed that the absorption band at 394 nm disappeared on keeping the solution at room temperature for a couple of hours, and a new absorption maximum at 340 nm (ε 90), characteristic of thiocarbamoyl phthalides, was observed. The initial appearance of the absorption maximum at 394 nm is attributed to the formation of the unstable benzoic dithiocarbamic anhydride intermediate **12** which then rapidly rearranges to **14a** through the bicyclo[3.2.1] transition state **13**, as shown in Scheme II (path B).

Similarly, the reaction of tetramethylenedithiocarbamate (**11c**) with **1** gave rise to a 64% yield of 3-[(tetramethylenethiocarbamoyl)thio]phthalide (**14c**).

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(6) For some relevant examples for the restricted rotation in amides, see (a) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); (b) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

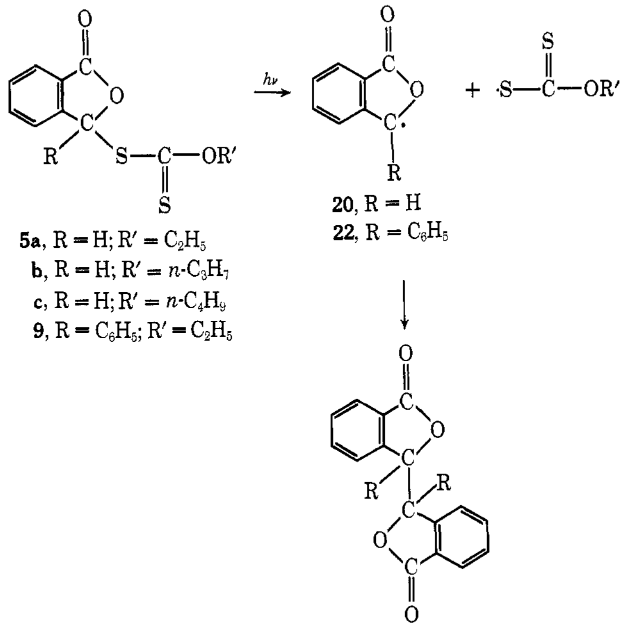
In the reaction of 3-chloro-3-phenylphthalide (**6**) with dimethyldithiocarbamate, a 60% yield of 3-phenylphthalidyl dimethyldithiocarbamate (**19a**) was formed as the chief product. Based on the appearance of an absorption maximum at 392 nm (ϵ 150) in a freshly mixed solution of **6** and **11a**, it has been inferred that this reaction proceeds through path B, as shown in Scheme II. Similarly, the reaction of diethyldithiocarbamate (**11b**), tetramethylenedithiocarbamate (**11c**), and pentamethylenedithiocarbamate (**11d**) with **6** gave rise to the corresponding phthalides, **19b**, **19c**, and **19d**, in yields ranging between 57 and 71%.

In continuation of our studies we have examined the reaction of 3-bromophthalide (**10**) with several dithiocarbamates to ascertain whether these reactions are analogous to those of *O*-alkyl xanthates. Treatment of an acetone solution of **10** with dimethyldithiocarbamate, for example, gave a 86% yield of **14a** as the only isolable product. The formation of **14a** in this reaction could arise by either a direct displacement of the bromide ion as per path A or through the attack on the carbonyl carbon as in path B (Scheme II). In order to distinguish between these two possible modes, we have examined the uv spectrum of the product mixture, immediately after mixing **10** and **11a** in acetone solution at 5°. The uv spectrum showed an absorption at 340 nm, characteristic of thiocarbamoyl phthalides, indicating thereby that the displacement reaction is proceeding through path A, as shown in Scheme II. Similarly, the reactions of **10** with diethyldithiocarbamate (**11b**), tetramethylenedithiocarbamate (**11c**), pentamethylenedithiocarbamate (**11d**), and oxydiethylenedithiocarbamate (**11e**) gave the corresponding 3-[(dialkylthiocarbamoyl)thio]phthalides, **14b–e**, in yields ranging from 75 to 85%.

Earlier we had reported the thermal and photochemical fragmentations of several unsymmetrical phthaloyl dixanthates and symmetrical phthaloic bisdithiocarbamic anhydrides.[2,3] Photolysis of unsymmetrical phthaloyl dixanthates in benzene solution, for example, gave chiefly *trans*-biphthalide, whereas symmetrical phthaloic bisdithiocarbamic anhydrides gave a mixture of *trans*-diphthalide and the corresponding thiuram disulfides. The thermal decomposition of unsymmetrical phthaloyl dixanthates, on the other hand, yielded a mixture of several products, consisting of *trans*-diphthalide, thiophthalic anhydride, carbonyl sulfide, and the corresponding *O*,*S*-dialkyl xanthates. During the course of the present investigation, we have examined both the thermal and photochemical transformations of several *O*-alkyl *S*-(3-phthalidyl) xanthates and 3-[(dialkylthiocarbamoyl)thio]phthalides with a view to studying the mode of these transformations.

Photolysis of *O*-ethyl *S*-(3-phthalidyl) xanthate (**5a**) in benzene solution at room temperature gave a 25% yield of *meso*-dihydrobiphthalide (**21**), mp 270°, as the only isolable product. Under analogous conditions, the photolysis of *O*-*n*-propyl *S*-(3-phthalidyl) xanthate (**5b**) and *O*-*n*-butyl *S*-(3-phthalidyl) xanthate (**5c**) gave **21** in 20 and 35% yields, respectively. The formation of *meso*-dihydrobiphthalide (**21**) in the photolysis of *O*-alkyl *S*-(3-phthalidyl) xanthates suggests that the photofragmentation reactions may be proceeding through the initial scission of a C–X bond, leading to the formation of phthalidyl radical **20**, which then dimerizes to **21** as shown in Scheme III. A similar type of photochemical fragmentation of the C–S bond is reported in the case of unsymmetrical phthaloyl dixanthates[2,3] and 9,9-dixanthogenyl xanthene.[7]

Scheme III



5a, R = H; R′ = C_2H_5
b, R = H; R′ = n-C_3H_7
c, R = H; R′ = n-C_4H_9
9, R = C_6H_5; R′ = C_2H_5

20, R = H
22, R = C_6H_5

21, R = H
23, R = C_6H_5

If the photochemical transformation of **5a** to **21** is proceeding through a homolytic C–S bond fission, then one would expect that this process would be more facile in the case of a compound such as *O*-ethyl *S*-(3-phenylphthalidyl) xanthate (**9**), as the intermediate 3-phenylphthalidyl radical (**22**) would be more stable when compared to **20**. In accord with this view, we found that a benzene solution of **9** undergoes very ready photolysis giving rise to a 50% yield of *meso*-3,3′-diphenylbiphthalide.[8,9]

The thermal decomposition of *O*-alkyl *S*-phthalidyl xanthates is of interest in that a mixture of several products is formed in these cases. Heating a sample of *O*-ethyl *S*-phthalidyl xanthate (**5a**), for example, to *ca.* 230–240° for *ca.* 20 min gave rise to a mixture of products consisting of a 33% yield of carbonyl sulfide (**26**), identified through its piperidinium salt,[10] a 14% yield of phthalic thioanhydride (**32**), and a yellow product, mp 324–325°. Both analytical results and the presence of two molecular ion peaks at *m*/*e* 280 and 296, respectively, in the mass spectrum indicated that this mixture consists of compounds having the molecular formulas $C_{16}H_8O_3S$ and $C_{16}H_8O_2S_2$. The ir spectrum of this product showed four distinct carbonyl absorption bands at 1786, 1736, 1695, and 1647 cm^{-1}, indicating the presence of γ- and δ-lactones and thiolactones.[11] The uv spectrum of this mixture showed several absorption maxima, indicating that the

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[7] A. Schönberg and U. Sodtke, *Tetrahedron Lett.*, 4977 (1967).

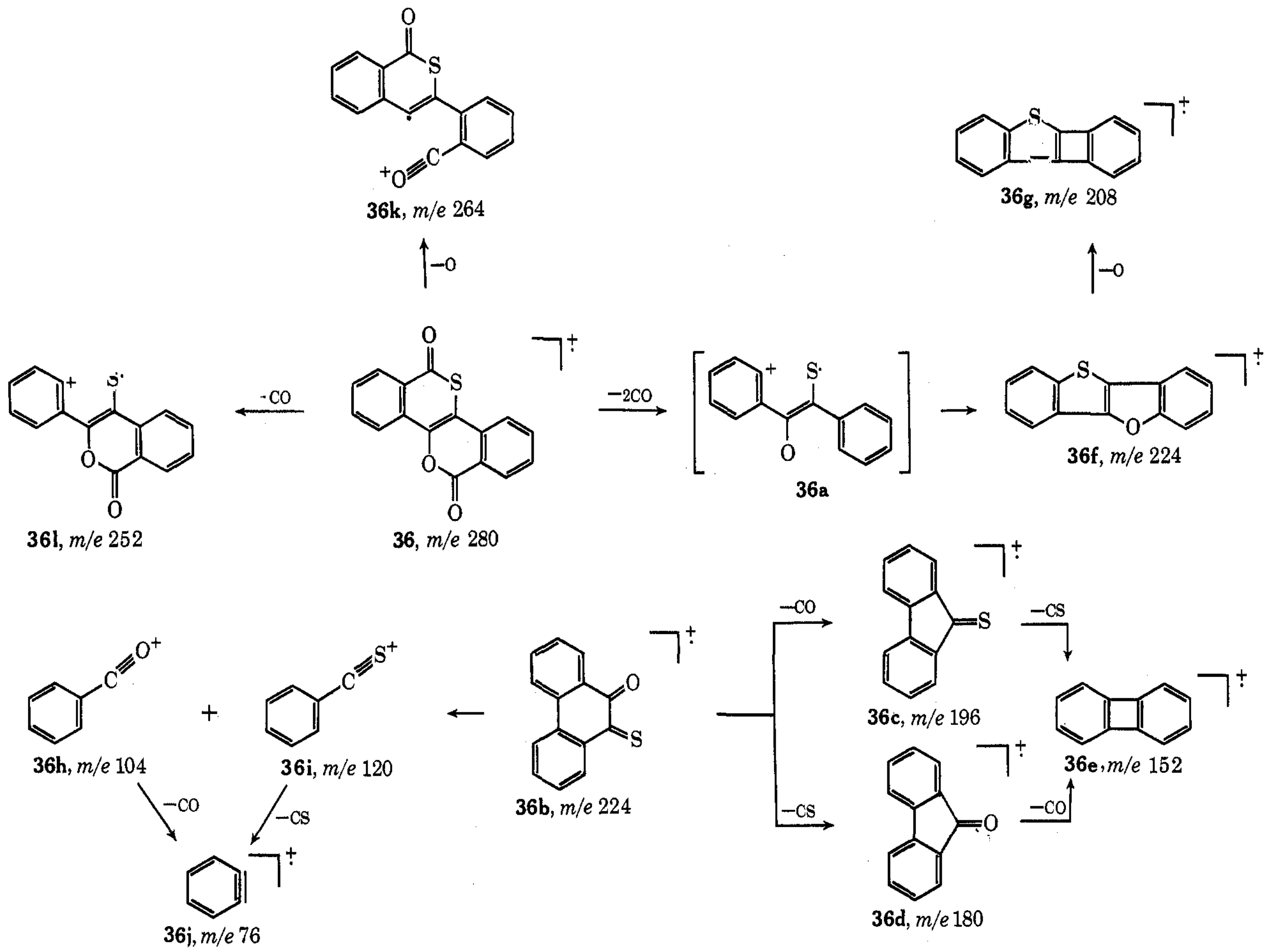
[8] On the basis of analogy to **21**, the meso configuration is assigned to **23**.

[9] For an earlier report on the formation of 3,3,-diphenylbiphthalide, see M. Renson, *Bull. Soc. Chim. Belg.*, **70**, 77 (1961); *Chem. Abstr.*, **55**, 18852 (1961).

[10] J. Parrod, *C. R. Acad. Sci.*, 234 (1952); *Chem. Abstr.*, **47**, 1606 (1953).

[11] J. H. Markgraf, C. I. Heller, and H. L. Avery, III, *J. Org. Chem.*, **35**, 1588 (1970).

SCHEME IV



components are extensively conjugated. The extreme insolubility of this mixture in most of the common organic solvents has prevented a satisfactory separation into its components. However, when a dilute solution of this product in methylene chloride was tested on a tlc plate, we could detect the presence of at least three components. It might be mentioned in this connection that Markgraf and coworkers[11] have reported the formation of a similar reaction mixture when they treated phthalic thioanhydride with tris(dimethylamino)phosphine. A similar mixture of products is also reported to be formed in the reaction of triethyl phosphite with a mixture of phthalic thioanhydride and phthalic anhydride.[12] Comparison of Markgraf's reaction mixture[13] with ours on a tlc plate indicated that two of the components, namely, 2-thio-3,3′-biphthalide (**35**) and isocoumarino[4,3-*c*]isothiocoumarin (**36**), were common constituents. Further confirmation of the identities of these compounds has been made by separating both the constituents **35** and **36** from our reaction mixture, employing preparative tlc and comparing their ir and uv spectra with those of the authentic samples.[13,14]

Additional evidence concerning the structure of **36** was derived from electron impact studies. The mass spectrum of **36** showed the molecular ion peak at *m/e* 280. Other peaks were observed at *m/e* 264, 252, 224, 196, 180, 152, 120, 104, and 76, which could be due to some of the fragments shown in Scheme IV. The species at *m/e* 224, 196, 180, and 152 are formulated as ions corresponding to monothiophenanthrenequinone (**36b**), thiofluorenone (**36c**), fluorenone (**36d**), and biphenylene (**36e**), respectively. The occurrence of the *m/e* 208 species is assigned to the fragment **36g**, which is probably formed by the loss of two molecules of carbon monoxide from **36**. Other peaks at *m/e* 120, 104, and 76 could be due to the fragments **36i**, **36h**, and **36j**, respectively. A peak at *m/e* 252 may be assigned to the fragment **36l**, arising through a loss of carbon monoxide from **36**, whereas the peak at *m/e* 264 could be assigned to the fragment **36k**, formed by the loss of an oxygen atom from **36**, as shown in Scheme IV. It might be mentioned in this connection that an analogous mode of fragmentation has been observed in the case of both biphthalide and bithiophthalide.[14b]

The exact mode of formation of the products **26**, **32**, **35**, **36**, and **37** in the thermal decomposition of **5a** is not very clear. A probable route to the formation of these products is indicated in Scheme V. In this scheme, we assume that the products such as 2-thio-3,3′-biphthalide (**35**), isocoumarino[4,3-*c*]isothiocoumarin (**36**), and 2,2′-dithio-3,3′-diphthalide (**37**) are formed from the reaction between the two carbene intermediates **25** and **29**, which can exist in equilibrium

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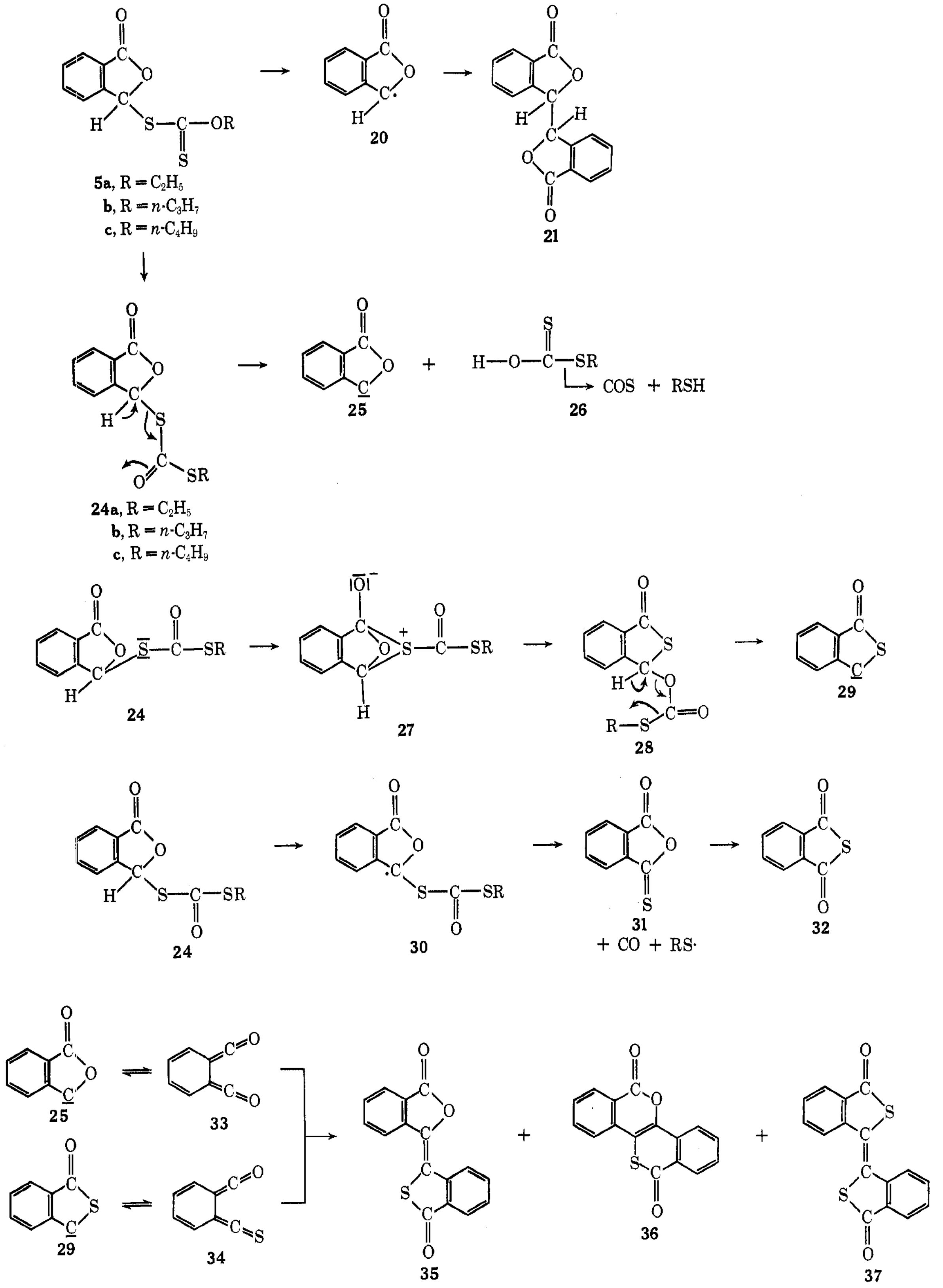
[12] C. W. Bird and D. Y. Wong, *Chem. Commun.*, 932 (1969).

[13] We thank Dr. J. H. Markgraf for very kindly sending us a sample of the mixture of products obtained from the reaction of phthalic thioanhydride with tris(dimethylamino)phosphine.[11]

[14] (a) We thank Dr. C. W. Bird, who has kindly sent us the spectral data of compound **35**, which he obtained by extensive fractional recrystallization of a product formed in the reaction of phthalic thioanhydride with tris(dimethylamino)phosphine;[11] (b) C. W. Koch and J. H. Markgraf, *J. Heterocycl. Chem.*, **8**, 225 (1971).

Scheme V



with their diketene isomers **33** and **34**, respectively.[15] The formation of the carbene **25** may occur through a free-radical process involving the intermediate **20** or through a cyclic concerted process involving **24a**, which in itself is a rearranged product of **5a**.[16] The decomposition of **24a** as in this scheme would also account for the formation of carbonyl sulfide, which has been identified as one of the products in the thermal decomposition of **5a**. The formation of the carbene **29**, on the other hand, is postulated through a concerted process involving the decomposition of **28**, which is

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[15] For some examples of such dimerizations, see (a) R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966); (b) H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966).

[16] For some examples of this type of rearrangement, see T. Taguchi and H. Nakao, *Tetrahedron*, **18**, 245 (1962).

presumed to be a transformation product of **24** and involving the bicyclo[2.2.1] transition state **27**. The occurrence of phthalic thioanhydride in this reaction may be rationalized in terms of the free-radical intermediate **30**, which can fragment further to give the thionphthalic anhydride (**31**), and the rearrangement of **31** leads to **32**.[17]

Similarly, the thermal decompositions of *O*-*n*-propyl *S*-phthalidyl xanthate (**5b**) and *O*-*n*-butyl *S*-phthalidyl xanthate (**5c**) gave carbonyl sulfide, phthalic thioanhydride, and a mixture of products consisting of **35**, **36**, and **37** in each case.

The thermal decomposition of *O*-ethyl *S*-(3-phenylphthalidyl) xanthate (**9**), on the other hand, gave a 76% yield of 3,3′-diphenylbiphthalide (**23**) as the only isolable product. A probable route to the formation of **23** is through the radical intermediate **22**, arising through a homolytic fragmentation of **9** (Scheme III). It is interesting to note that both the thermal and photochemical transformations of **9** lead to the same product **23**. The relative stabilities of the phthalidyl radicals **20** and **22** would account for the difference in behavior between the thermal decompositions of **5a** and **9**.

The C–S type of bond fission occurring in the photolysis of acyl and aroyl xanthates has also been postulated in the photofragmentation of dithiocarbamic anhydrides.[3,18] In the photolysis of symmetrical bispyrrolidine dithiocarbamic anhydride, for example, a mixture of *trans*-biphthalide and bis(tetramethylene)-thiuram disulfide are formed. The formation of these products has been explained in terms of a homolytic fragmentation of the C–S bond leading to radical intermediates.

During the course of the present investigation we have examined both the thermal and photochemical transformations of 3-[(dialkylthiocarbamoyl)thio]-phthalides with a view to studying the nature of the products formed in these reactions. Photolysis of a benzene solution of 3-[(dimethylthiocarbamoyl)thio]-phthalide (**14a**), for example, gave a 27% yield of *meso*-3,3′-dihydrobiphthalide (**21**) as the only isolable product. Similarly, the photolysis of 3-[(diethylthiocarbamoyl)thio]phthalide (**14b**), 3-[(tetramethylenethiocarbamoyl)thio]phthalide (**14c**), 3-[(pentamethylenethiocarbamoyl)thio]phthalide (**14d**), and 3-[(oxydiethylenethiocarbamoyl)thio]phthalide (**14e**) gave **21** in each case and in yields ranging between 25 and 40%. The photolysis of 3-phenylphthalidyl dimethyldithiocarbamate (**19a**), on the other hand, gave a 50% yield of 3,3′-diphenylbiphthalide (**23**). Similarly, the photolysis of 3-phenylphthalidyl diethyldithiocarbamate (**19b**), 3-phenylphthalidyl tetramethylenedithiocarbamate (**19c**), and 3-phenylphthalidyl pentamethylenedithiocarbamate (**19d**) gave, in each case, **23** in yields ranging between 45 and 57%.

The formation of 3,3′-dihydrobiphthalide (**21**) in the photolysis of 3-[(dialkylthiocarbamoyl)thio]phthalides **14a–e** and 3,3′-diphenylbiphthalide (**23**) in the photolysis of 3-phenylphthalidyl dialkyldithiocarbamates **19a–d** may be rationalized in terms of the initial C–S bond fission leading to the generation of the phthalide radicals **20** and **22**, respectively, through reaction paths similar to those indicated in Scheme III.

The thermal decomposition of the 3-[(dialkylthiocarbamoyl)thio]phthalides **14a–e** gave, in each case, a mixture of products consisting of 2-thio-3,3′-diphthalide (**35**), isocoumarino[4,3-*c*]thiosocoumarin (**36**), and 2,2′-dithio-3,3′-biphthalide (**37**) in yields ranging between 12 and 17%. The formation of the mixture of products consisting of **35**, **36**, and **37** in these cases indicates that both *O*-alkyl *S*-phthalidyl xanthates and 3-[(dialkylthiocarbamoyl)thio]phthalides undergo a similar type of thermal transformation.

The thermal decomposition of 3-phenylphthalidyl dialkyldithiocarbamates **19a–d** gave, in each case, 3,3′-diphenylbiphthalide in yields ranging between 60 and 80%. It is interesting to note that, as in the case of *O*-ethyl *S*-(3-phenylphthalidyl) xanthate, both the thermal and photochemical transformations of 3-phenylphthalidyl dialkyldithiocarbamates give rise to the same product, in each case.

Experimental Section

All melting points are uncorrected and were taken on a Mel-Temp melting point apparatus. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord spectrometer and uv spectra were determined on a Beckman DB spectrometer. The nmr spectra were determined either on a Varian A-60D or HR-100 spectrometer, using tetramethylsilane as an internal standard.

All irradiation experiments were carried out using a Hanovia medium-pressure mercury lamp (450 W).

Starting Materials.—Potassium *O*-ethyl xanthate, mp 185–186°, potassium *O*-*n*-propyl xanthate, mp 237–238°, and potassium *O*-*n*-butyl xanthate, mp 261–262°, were prepared by known procedures.[19] Dimethyldithiocarbamate,[20] mp 136°, diethyldithiocarbamate,[20] mp 152°, tetramethylenedithiocarbamate,[18] mp 152°, pentamethylenedithiocarbamate,[18] mp 169–170°, and oxydiethylenedithiocarbamate,[18] mp 180–182°, were prepared by reported procedures. 3-Chlorophthalide,[21] mp 61°, 3-bromophthalide,[22] mp 78–80°, and 3-chloro-3-phenylphthalide,[23] mp 60°, were prepared in good yields as per standard reports.

Reaction of 3-Chlorophthalide (1) with Potassium *O*-Ethyl Xanthate (2a).—To a solution of **1** (0.42 g, 0.0025 mol) in acetone (20 ml), maintained around 5°, was gradually added **2a** (0.4 g, 0.0025 mol) in small portions and with constant stirring. After removal of the solvent from the reaction mixture, the residue was treated with excess of water to remove any unchanged **2a** and recrystallized from a mixture (1:1) of ethanol and methylene chloride to give 0.42 g (66%) of *O*-ethyl *S*-(3-phthalidyl) xanthate (**5a**), mp 107–108°.

Anal. Calcd for $C_{11}H_{10}O_3S_2$: C, 51.96; H, 3.93. Found: C, 52.59; H, 4.03.

The ir spectrum (KBr) of **5a** showed an absorption band at 1770 cm^{-1} due to the carbonyl group (γ-lactone) and another band at 1040 cm^{-1} due to the C=S group.

The uv spectrum of **5a**(CH_2Cl_2) was characterized by the following absorption maxima: 278 nm (ε 12,600) and 362 (50).

Reaction of 3-Bromophthalide (10) with Potassium *O*-Alkyl Xanthates (2a–c).—In a typical run, a solution of **2a** in acetone (0.019 mol in 25 ml) was slowly added to an acetone solution of **10** (0.018 mol in 25 ml), maintained around 5°. The addition was completed in about 30 min, during which period the mixture was kept stirred. Removal of the solvent under vacuum and treatment of the residue with water to remove any unchanged **2a** gave a 88% yield of **5a**, mmp 107–108°.

Under similar conditions, the reaction of **10** with **2b** gave a 80% yield of *O*-*n*-propyl *S*-(3-phthalidyl) xanthate (**5b**), mp

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(17) For examples of this type of transformation, see C. M. Sharts and D. W. Fong, *J. Org. Chem.*, **32**, 3709 (1967).

(18) E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron*, **21**, 35, 2857, 2865 (1965).

(19) I. S. Shupe, *J. Ass. Offic. Agr. Chem.*, **25**, 495 (1942); *Chem. Abstr.*, **36**, 4670 (1942).

(20) R. H. Sahasrabudhey and K. L. Radhakrishnan, *J. Indian Chem. Soc.*, **31**, 853 (1954).

(21) S. Gabriel, *Ber.*, **49**, 1612 (1916).

(22) I. A. Koten and R. J. Sauer, "Organic Syntheses," Vol. 42, V. Boekelhide, Ed., Wiley, New York, N. Y., 1962, p 26.

(23) H. C. Martin, *J. Amer. Chem. Soc.*, **38**, 1143 (1916).

92°, after recrystallization from a mixture (1:1) of ethanol and methylene chloride.

Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.73; H, 4.47. Found: C, 53.46; H, 4.38.

The ir spectrum (KBr) of **5b** showed absorption bands at 1770 (C=O, γ-lactone) and 1050 cm^{-1} (C=S).

The uv spectrum (CH_2Cl_2) of **5b** was characterized by the following absorption maxima: 278 nm (ε 12,800) and 364 (50).

In an analogous manner, the reaction of **10** with **2c** gave a 75% yield of *O*-*n*-butyl *S*-(3-phthalidyl) xanthate (**5c**), mp 90°, after recrystallization from a mixture (1:1) of ethanol and methylene dichloride.

Anal. Calcd for $C_{13}H_{14}O_3S_2$: C, 55.31; H, 4.96. Found: C, 55.20; H, 4.68.

The ir spectrum (KBr) of **5c** showed absorption bands at 1765 and 1040 cm^{-1} due to the C=O group (γ-lactone) and the C=S group, respectively.

The uv spectrum of **5c** (CH_2Cl_2) showed the following absorption maxima: 278 nm (ε 15,850) and 364 (130).

Photolysis of *O*-Alkyl *S*-(3-Phthalidyl) Xanthates.—In a representative run, a solution of **5a** (1.0 g, 0.004 mol) in benzene (200 ml) was irradiated for 30 min at room temperature. Removal of the solvent under vacuum gave a product which on treatment with a small quantity of acetone gave 0.13 g (25%) of *meso*-3,3′-dihydrobiphthalide (**21**), which melted at 270° (lit.[24] mp 269°), on recrystallization from acetic acid.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.76. Found: C, 72.33; H, 4.04.

The ir spectrum (KBr) of **21** showed an absorption band at 1765 cm^{-1} due to a γ-lactone carbonyl group.

The uv spectrum (CH_2Cl_2) of **21** showed the following absorption maxima: 238 nm (ε 1350), 276 (3650), 284 (3750), 296 (900), 308 (900), 362 (2050), 376 (1680), and 384 (1450).

In identical runs, the photolysis of **5b** and **5c** gave **21** in 20 and 35% yields, respectively.

Thermal Decomposition of *O*-Alkyl *S*-(3-Phthalidyl) Xanthates.—In a typical run, 4.0 g (0.016 mol) of **5a** was heated at *ca.* 230–240° for 20 min in a 10-ml round-bottomed flask provided with a nitrogen inlet and a water-cooled condenser. The gaseous products were bubbled through a 10% solution of piperidine in diethyl ether. The precipitated piperidinium salt was filtered and recrystallized from a mixture (1:1) of methylene chloride and diethyl ether to give 1.2 g (33%) of piperidinium 1-piperidine carbothiolate, mp 112°, which showed no depression in its melting point when mixed with an authentic sample.[9]

The pyrolyzed mixture was extracted with methylene chloride to give a methylene chloride soluble fraction, which after removal of the solvent and recrystallization from a mixture (1:1) of methylene chloride and petroleum ether (bp 60–80°) gave 0.35 g (14%) of phthalic thioanhydride (**32**), mmp 110°.

The methylene chloride insoluble product gave 0.2 g of a yellow solid, mp 324–325°. Our attempts to purify this sample by recrystallization from common organic solvents were unsuccessful, in view of its very low solubility.

Anal. Calcd for $C_{16}H_8O_3S$: C, 68.57; H, 2.86. Calcd for $C_{16}H_8O_2S_2$; C, 64.86; H, 2.70. Found: C, 68.69; H, 2.79.

The ir spectrum (KBr) of the yellow mixture showed absorption bands at 1786 (γ-lactone C=O), 1695 (γ-thiolactone C=O), 1736 (δ-lactone C=O), and 1647 cm^{-1} (δ-thiolactone C=O).

The uv spectrum (CH_2Cl_2) was characterized by the following absorption maxima: 384 nm (ε 13,000), 372 (13,800), 306 (4830), 284 (4560), 270 (6100).

The mass spectrum of the yellow mixture showed prominent peaks at *m/e* 296, 280, 264, 252, 240, 236, 232, 224, 208, 195, 196, 180, 163, 153, 120, 104, 76, and 50.

Treatment of the yellow product with boiling methylene chloride could bring a small quantity of it in solution and testing this dilute solution on a tlc plate revealed the presence of at least three components. The top spot on the tlc plate showed no fluorescence under a uv lamp, whereas the middle spot and the bottom spot showed blue and green fluorescence, respectively. Employing preparative tlc, we have been able to separate the components from a small quantity of the mixture.

Extraction of the top spot on the tlc plate with methylene chloride gave a light yellow solid, mp 350°, which showed no depression in its melting point with an authentic sample of **37**.[10]

The ir spectrum (KBr) of **37** showed an absorption band at 1700 cm^{-1} due to the C=O group in a γ-thiolactone[10] and was identical with that of an authentic sample.

The uv spectrum (CH_2Cl_2) of **37** was characterized by the following absorption maxima: 292 nm (ε 4740), 304 (5200), 316 (4750), and 400 (19,750).

Extraction of the middle spot on the tlc plate with methylene chloride gave a yellow solid, mp 339–340°, which showed no depression in its melting point when mixed with an authentic sample of 2-thio-3,3′-biphthalide (**35**).[10]

The ir spectrum (KBr) of **35** showed two absorption bands at 1792 and 1704 cm^{-1} due to the C=O groups in γ-lactone and γ-thiolactone, respectively. The ir spectrum was superimposable on that of an authentic sample of **35**.

The uv spectrum (CH_2Cl_2) of **35** was characterized by the following absorption maxima: 274 nm (ε 5700), 300 (6550), 314 (6700), 380 (21,850) and 392 (20,850).

Extraction of the bottom spot on the tlc plate with methylene chloride gave a pale yellow solid, mp 340°, which showed no depression in its melting point when mixed with an authentic sample of **36**.[10]

The ir spectrum (KBr) of **36** showed two absorption bands at 1754 and 1667 cm^{-1} due to the C=O groups in δ-lactone and δ-thiolactone, respectively. The ir spectrum of **36** was identical with that of an authentic sample.

The uv spectrum (CH_2Cl_2) of **36** was characterized by the following absorption maxima: 272 nm (ε 42,000) (shoulder), 284 (26,900), 308 (32,750) (shoulder), 320 (48,700), 356 (54,600), 370 (66,350), and 386 (50,400).

Further confirmation of the structure of **36** was derived from its mass spectrum, which showed the molecular ion peak at *m/e* 280.

The pyrolysis of **5b** under similar conditions gave a 24% yield of carbonyl sulfide, identified through its piperidinium salt (mp 112°), 16% of phthalic thioanhydride, mmp 110°, and 9% yield of the mixture consisting of **35**, **36**, and **37**, as identified on a tlc plate. Similarly, the thermal decomposition of **5c** gave a 30% yield of carbonyl sulfide, a 25% yield of phthalic thioanhydride, and a 15% yield of the mixture consisting of **35**, **36**, and **37**.

Reaction of 3-Chloro-3-phenylphthalide (6) with Potassium *O*-Ethyl Xanthate (2a).—To an acetone solution (20 ml) of **6** (2.5 g, 0.1 mol) maintained around 5° was added 1.6 g (0.01 mol) of **2a**, in small portions and with stirring, over a period of 30 min. Removal of the solvent under vacuum gave a product which was treated with water to remove any unchanged **2a** and was recrystallized from a mixture (1:1) of methylene chloride and methanol to give 2.1 g (60%) of *O*-ethyl *S*-(3-phenylphthalidyl) xanthate (**9**), mp 88°.

Anal. Calcd for $C_{17}H_{14}O_3S_2$: C, 61.81; H, 4.24. Found: C, 61.89, H, 4.27.

The ir spectrum (KBr) of **9** showed an absorption band at 1786 cm^{-1} due to the C=O group (γ-lactone).

The uv spectrum (CH_2Cl_2) of **9** was characterized by the following absorption maxima: 284 nm (ε 17,050) and 366 (50).

The nmr spectrum ($CDCl_3$) of **9** showed a multiplet centered around δ 7.5 (9 H) due to the aromatic protons, a quartet at δ 4.17 (2 H) due to the methylene protons, and a triplet at δ 0.9 (3 H) due to the methyl protons.

Photolysis of *O*-Ethyl 3-(Phenylphthalidyl) Xanthate (9).—A solution of 0.5 g (0.0015 mol) of **9** in benzene (200 ml) was irradiated at room temperature for 30 min. Removal of the solvent under vacuum gave a product which on recrystallization from a mixture (1:1) of methylene chloride and ethanol gave 0.15 g (50%) of 3,3′-diphenylbiphthalide (**23**), mp 285–286° (lit.[8] mp 293°).

Anal. Calcd for $C_{28}H_{18}O_4$: C, 80.38; H, 4.30. Found: C, 80.24; H, 4.14.

The ir spectrum (KBr) of **23** showed a single C=O absorption at 1783 cm^{-1}, due to a γ-lactone grouping.

The uv spectrum (CH_2Cl_2) of **23** showed the following absorption maxima: 280 nm (ε 3550) and 288 (3820).

Thermal Decomposition of *O*-Ethyl 3-(Phenylphthalidyl) Xanthate (9).—Heating 0.66 g (0.002 mol) of the xanthate **9** at *ca.* 200° for 20 min and work-up of the pyrolyzed residue by treatment with ethanol in the usual manner gave 0.32 g (76%) of **23**, mmp 285–286°.

Reaction of 3-Chlorophthalide (1) or 3-Bromophthalide (10) with Dithiocarbamates (11a–e).—In a representative run, 0.01 mol of **11a** was added to a solution of **1** in acetone (0.01 mol in 25 ml), maintained around 5°, over a period of 30 min. Removal of the solvent under vacuum gave a product which was

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[24] K. F. Cohen, J. T. Pinhey, and R. J. Smith, *Tetrahedron Lett.*, 4729 (1968).

TABLE I

3-[(DIALKYLTHIOCARBAMOYL)THIO]PHTHALIDES

Compd	Yield, %	Mp, °C	Calcd, %			Found, %			Ir, cm^{-1} (KBr), C=O (γ-lactone)	Uv, λ_{max}, nm (ε)
			C	H	N	C	H	N		
14a	62,[a] 86[b]	186–187	50.00	4.54	5.78	50.27	4.53	5.56	1750	282 (11,850), 340 (90)
14b	85[b]	121–122	55.51	5.33	4.96	55.30	5.28	5.25	1760	284 (11,350), 340 (120)
14c	64,[a] 64	175–176	55.91	4.65	5.0	56.16	4.60	5.09	1750	284 (13,100), 334 (100)
14d	75[b]	115–116	57.33	5.11	4.77	57.54	5.41	4.58	1760	286 (16,650), 340 (100)
14e	78[b]	167–168	52.88	4.40	4.74	52.65	4.23	4.67	1750	288 (14,800), 350 (130)

[a] In the reaction of **1** with dithiocarbamates. [b] In the reaction of **10** with dithiocarbamates.

TABLE II

3-PHENYLPHTHALIDYL DIALKYLDITHIOCARBAMATES

Compd	Yield, %	Mp, °C	Calcd, %			Found, %			Ir, cm^{-1} (KBr), C=O (γ-lactone)	Uv, λ_{max}, nm (ε)
			C	H	N	C	H	N		
19a	60	135–136	62.00	4.55	4.25	61.82	4.84	4.00	1770	286 (10,100), 360 (70)
19b	71	135–136	63.86	5.32	3.92	64.17	5.30	3.85	1773	290 (7,650), 364 (60)
19c	57	149–150	64.22	4.78	3.94	64.33	4.64	3.88	1776	290 (11,550), 366 (70)
19d	70	135–136	65.04	5.14	3.79	65.06	5.13	4.10	1770	290 (11,100), 366 (90)

washed with excess of water to remove any unchanged **11a** and recrystallized from a mixture (1:1) of ethanol and methylene chloride. Table I summarizes the percentage yields and the physical data of the different 3-[(dialkylthiocarbamoyl)thio]-phthalides (**14a–e**).

Photolysis of 3-[(Dialkylthiocarbamoyl)thio]phthalides (14a–e).—In a typical run, a solution of 1 g (0.004 mol) of **14a** in benzene (200 ml) was irradiated for 1 hr at room temperature. Removal of the solvent under vacuum gave a product which on recrystallization from acetic acid gave 0.11 g (27%) of *meso*-3,3′-dihydrobiphthalide (**21**), mmp 270°.

Under identical conditions, the photolysis of **14b** gave a 40% yield of **21**, whereas the photolysis of **14c**, **14d**, and **14e** gave 25, 27, and 25% yields of **21**, respectively.

Thermal Decomposition of 3-[(Dialkylthiocarbamoyl)thio]-phthalides (14a–e).—In a typical run, 0.25 g (0.001 mol) of **14a** was heated at *ca.* 230–240°, under a nitrogen atmosphere, for 20 min. The evolved gases were passed into a 10% solution of piperidine in diethyl ether. No piperidinium salt of either COS or CS_2 precipitated out. Work-up of the pyrolyzed residue as in the case of *O*-alkyl *S*-phthalidyl xanthates resulted in the isolation of 0.018 g (12%) of a mixture of **35**, **36**, and **37**, melting over the range 324–325°, as identified by tlc comparison.

Under identical conditions, the thermolysis of **14b** (14%), **14c** (15%), **14d** (14%), and **14e** (17%) gave, in each case a mixture of products consisting of **35**, **36**, and **37**, in yields indicated in parentheses.

Reaction of 3-Chloro-3-Phenylphthalide (6) with Dithiocarbamates (11a–d).—In a representative run, 0.01 mol of **11a** was added to an acetone solution of **6** (0.01 mol, 20 ml), maintained around 5°, for a period of 45 min. Removal of the solvent under vacuum gave a product which was washed with excess of water to remove any unreacted **11a** and recrystallized from a mixture (1:1) of ethanol and methylene chloride. Table II summarizes the physical data of the different 3-phenylphthalidyl dialkyldithiocarbamates (**19a–d**).

Photolysis of 3-Phenylphthalidyl Dialkyldithiocarbamates (19a–d).—In a typical run, a solution of 0.66 g (0.002 mol) of **19a** in benzene (175 ml) was irradiated for 1 hr at room temperature. Removal of the solvent under vacuum and work-up of the mixture in the usual manner gave 0.21 g (50%) of 3,3′-diphenylbiphthalide (**23**), mmp 285–286°, after recrystallization from a mixture (1:1) of ethanol and methylene chloride.

In similar experiments, the photolysis of **19b**, **19c**, and **19d** gave **23** in 57, 57, and 45% yields, respectively.

Thermal Decomposition of 3-Phenylphthalidyl Dialkyldithiocarbamates (19a–d).—In a typical run, 0.33 g (0.001 mol) of **19a** was heated at *ca.* 200° under nitrogen atmosphere for 20 min. The pyrolyzed residue was treated with a small quantity of ethanol to give 0.15 g (72%) of 3,3′-diphenylbiphthalide (**23**) mmp 285–286° on recrystallization from a mixture (1:1) of ethanol and methylene chloride.

Under similar conditions, the thermal decomposition of **19b** (80%), **19c** (70%), and **19d** (60%) gave **23** in each case, in yields indicated in parentheses.

Registry No.—**5a**, 32819-73-1; **5b**, 32819-74-2; **5c**, 32819-75-3; **9**, 32785-00-5; **14a**, 32819-76-4; **14b**, 32958-89-7; **14c**, 32819-77-5; **14d**, 32851-12-0; **14e**, 32819-78-6; **19a**, 32785-01-6; **19b**, 32819-79-7; **19c**, 32785-02-7; **19d**, 32819-80-0; **21**, 4281-21-4; **35**, 32819-82-2; **36**, 23667-34-7; **37**, 32819-84-4.