THE JOURNAL OF Organic Chemistry

VOLUME 36, NUMBER 5

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MARCH 12, 1971

Photochemical Transformations of Phthaloyl Dixanthates and Phthaloic Bisdithiocarbamic Anhydrides

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Received March 31, 1970

The reaction of phthaloyl dichloride with potassium O-alkyl xanthates gave rise to the corresponding unsymmetrical phthaloyl dixanthates. Treatment of phthaloyl dichloride with dithiocarbamates, on the other hand, gave the symmetrical bisdithiocarbamic anhydrides. Photolysis of unsymmetrical phthaloyl dixanthates in benzene solution gave chiefly *trans*-biphthalyl, whereas symmetrical phthaloic bisdithiocarbamic anhydrides gave a mixture of *trans*-biphthalyl and the corresponding thiuram disulfides. No benzocyclobutenedione could be isolated from these runs. The thermal decomposition of unsymmetrical phthaloyl dixanthates yielded a mixture of several products, consisting of trans-biphthalyl, thiophthalic anhydride, carbonyl sulfide, and the corresponding O,S-dialkyl xanthates.

Photolysis of acyl xanthates are reported to give rise to the corresponding alkyl xanthates.² It has been shown that in these reactions the CO-S bond of the acyl xanthates undergoes homolytic fission giving rise to acyl and xanthate radicals. These acyl radicals are decarbonylated at appropriate temperatures to give alkyl radicals which then combine with xanthate radicals giving rise to the corresponding alkyl xanthates. By taking advantage of the fact that primary acyl radicals are decarbonylated only slowly, it has been possible to synthesize α diketones through the photolysis of the corresponding xanthates. Thus, the photolysis of di-O-ethyl S, S-glutaryl xanthate, for example, has been shown to give a satisfactory yield of cyclopentane-1,2-dione.² As aroyl xanthates are also reasonably stable at room temperatures, we argued that the photolysis of a xanthate such as symmetrical di-O-alkyl S,S-phthaloyl dixanthate (IV) should lead to the formation of benzocyclobutenedione, through the intramolecular coupling of the intermediate aroyl radical.

Acvl and aroyl xanthates are conveniently prepared by the treatment of potassium O-alkyl xanthates with the corresponding acid chlorides in acetone solution at low temperatures.² In a preliminary communication,³ we have shown that the reaction of potassium O-ethyl xanthate with phthaloyl dichloride in acetone solution does not give rise to the expected symmetrical di-O-ethyl S,S-phthaloyl dixanthate (IVb), but the unsymmetrical phthaloyl dixanthate (VIb) (Scheme I). In the present investigation, we have examined the reactions of several potassium alkyl xanthates with

symmetrical phthaloyl dichloride (I) with a view to studying the nature of the products formed in these cases.

Treatment of potassium O-methyl xanthate with I in ether solution around 0° gave a 78% yield of a product, identified as unsymmetrical di-O-methyl S,Sphthaloyl dixanthate (VIa), mp 120°. The identity of this product was confirmed on the basis of analytical results and spectral data. The infrared spectrum of VIa showed a carbonyl absorption at 1780 cm^{-1} , characteristic of γ -lactones. The nmr spectrum of VIa showed a multiplet centered around τ 2.86 (4 H) due to the phenyl protons and a singlet at τ 6.31 (6 H) due to the methoxyl protons. The multiplet due to the aromatic protons showed a characteristic ABCD pattern, as would be expected for the unsymmetrical structure VIa. Further evidence concerning the unsymmetrical structure VIa for this xanthate was derived from its conversion to phthalide, on treatment with Raney nickel.

The reason why the unsymmetrical phthaloyl dixanthate VIa is formed from the reaction of I with potassium O-methyl xanthate was not very apparent. Knapp⁴ had reported that an unsymmetrical diphenyl dithiolphthalate is formed when I is treated with a mixture of phenyl thiolacetate and anhydrous aluminum chloride. The formation of the unsymmetrical isomer has been explained in terms of the reaction of the unsymmetrical phthaloyl dichloride (II), which is assumed to be formed from I, under the influence of aluminum chloride.⁵ However, it is very doubtful that

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

⁽³⁾ A. Shah, S. N. Singh, and M. V. George, Tetrahedron Lett., 3983 (1968).

⁽⁴⁾ W. Knapp, Monatsh. Chem., 58, 176 (1931); Chem. Abstr., 26, 436 (1932).

⁽⁵⁾ E. Ott, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 528.





in the reaction of I with potassium O-methyl xanthate, the acid chloride is undergoing isomerization to the unsymmetrical derivative, especially in the absence of any catalyst such as aluminum chloride. A more probable explanation for the formation of VIa is indicated in Scheme I. In this scheme, we assume that the alkyl xanthate reacts with I to give the symmetrical di-Omethyl S,S-phthaloyl dixanthate (IVa), which undergoes an intramolecular rearrangement to the unsymmetrical isomer VIa, through the bicyclic 3,2,1 transition state V.⁶ With a view to finding out whether the symmetrical dixanthate IVa is initially formed in the reaction, as shown in Scheme I, we have examined the absorption spectrum of the product mixture, soon after mixing together the symmetrical phthaloyl dichloride and potassium O-methyl xanthate in a 1:2 ratio in ether solution around 0°. The absorption spectrum was characterized by the presence of two maxima at 288 m μ $(\epsilon 19,700)$ and 394 (70), respectively. Of these, the weak absorption around 394 m μ is characteristic of all acyl and aroyl xanthates containing the C = OSC-(=S)OR chromophore.² It was further observed that the absorption maximum at 394 m μ of a freshly formed solution of the dixanthate IVa disappeared after a few hours, and a new absorption maximum was observed at 364 m μ (ϵ 95), characteristic of the unsymmetrical dixanthate VI.³ These findings are in support of the view that the symmetrical dixanthate IVa is

actually formed at first, which then rapidly isomerizes to the unsymmetrical derivative VIa.

Our next objective was to examine the reaction of II with potassium O-methyl xanthate, with a view to studying the mode of this reaction. Treatment of an acetone solution of II with excess of potassium O-methyl xanthate around 5° gave a 70% yield of the unsymmetrical dixanthate VIa. The formation of VIa could be by the attack of the nucleophile on the carbonyl carbon (path a) or by a direct displacement on the carbon atom, attached to the chlorine atoms (path b), as shown in Scheme I. With a view to distinguishing between these two possible modes of reactions, we have examined the uv spectrum of the product mixture, immediately after mixing together II and potassium O-methyl xanthate in a 1:2 ratio in ether solution. If the reaction is proceeding through path a, then one would expect the initial formation of the symmetrical dixanthate IVa, which can be characterized by the absorption maximum at $394 \text{ m}\mu^2$ On the other hand, if path b is the preferred mode, then one would expect the formation of VIa directly. The uv spectrum of an ether solution of the product mixture, on treatment of II with potassium O-methyl xanthate, showed an absorption maximum at 394 m μ (ϵ 94), indicating thereby that the symmetrical dixanthate IIa is initially being formed in this reaction, which then undergoes thermal isomerization as shown in Scheme I.

With a view to finding out whether the symmetrical dixanthates of type IV (Scheme I) can be stabilized by changing the alkyl substituent on the xanthate,

⁽⁶⁾ For some examples of reactions in which such bicyclic 3,2,1 transition states have been suggested, see (a) M. S. Newman and C. Courduvelis J. Amer. Chem. Soc., 86, 2942 (1964); 88, 781 (1966); (b) M. S. Newman, N. Gill, and B. Darre, J. Org. Chem., 31, 2713 (1966).





we have examined the reactions of I with different O-alkyl xanthates. Treatment of I with potassium O-n-propyl xanthate, for example, gave a 50% yield of di-O-n-propyl S,S-phthaloyl dixanthate (VIc), mp $81-82^{\circ}$. The same dixanthate was obtained in a 60% yield, on treatment of the unsymmetrical phthaloyl dichloride with potassium O-n-propyl xanthate. Similarly, the reactions of I with potassium O-n-butyl xanthate and potassium O-benzyl xanthate gave in each case the corresponding unsymmetrical dixanthates VId and VIe, respectively, in yields ranging between 65 and 82%. Both the unsymmetrical dixanthates VId and VIe were also obtained in 66 and 70% yields, respectively, when II was treated with the corresponding potassium O-alkyl xanthates.

In our further efforts at preparing the symmetrical dixanthates of type IV, we have examined the reactions of I with a few dithiocarbamates. The reaction of I with pyrrolidinedithiocarbamate, for example, gave a 68% yield of a product, mp 140-141°, identified as symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa) (Scheme II). The identity of IXa was confirmed on the basis of analytical results and spectral data. The infrared spectrum of IXa showed a characteristic absorption band at 1675 cm^{-1} due to the C=O group and a band at 1471 cm⁻¹ due to the C=S group. The ultraviolet absorption spectrum of IXa was characterized by two absorption maxima at 290 m μ (ϵ 31,100) and 410 (400). The absorption characteristics of IXa are quite similar to those of the analogous benzoic piperidinedithiocarbamic anhydride.⁷ The nmr spectrum of IXa showed two broad

singlets at τ 7.83 (8 H) and 6.1 (8 H). Of these, the peak at τ 7.83 is assigned to the methylene protons away from the nitrogen atoms, whereas the one at τ 6.1 is due to the methylene protons adjacent to the nitrogen atoms of the pyrrolidine rings. The aromatic protons appeared as a multiplet centered around τ 2.31 (4 H), characteristic of an A₂B₂ system.

Further evidence concerning the symmetrical structure for IXa was derived by its conversion to *o*-phthalaldehyde, on treatment with Raney nickel.

In the formation of the unsymmetrical dixanthate VIa from the reaction of I and potassium O-methyl xanthate, we had suggested that initially the symmetrical dixanthate IVa is being formed which then isomerizes to VIa. It would be reasonable therefore to assume that the symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa), should also be capable of undergoing thermal isomerization to an unsymmetrical derivative. Refluxing a solution of IXa in dry benzene for 1 hr gave a 70% yield of a product, mp 161-162°, and identified as unsymmetrical phthaloic bis(pyrrolidinedithiocarbamic) anhydride (XIa). The identity of XIa was confirmed on the basis of analytical data and spectral evidences. The infrared spectrum of XIa showed a strong absorption band at 1786 $\rm cm^{-1}$ due to the C=O group present in a γ -lactone ring.

The uv spectrum of XIa was characterized by the presence of two absorption maxima at $284 \text{ m}\mu$ ($\epsilon 14,900$) and 330 (90). The nmr spectrum of XIa showed two broad singlets at τ 7.82 (8 H) and 6.36 (8 H), due to the methylene protons of the pyrrolidine rings. The aromatic protons appeared as a multiplet centered around τ 2.52 (4 H) and characteristic of an ABCD pattern.

The transformation of the symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa) to the unsymmetrical isomer XIa may also be proceeding through a bicyclic 3,2,1 transition state (X) as shown in Scheme II. By taking advantage of the fact that IXa shows a characteristic absorption band around 410 m μ , it has been possible to study the kinetics of the isomerization of IXa spectrophotometrically. Table I summarizes the rate data for three different

TABLE I FIRST-ORDER RATE CONSTANTS FOR THE ISOMERIZATION OF IXA TO XIA

	Temp,	
Solvent	°C	k1 (sec -1)
Benzene	40	$2.18 imes10^{-5}$
Benzene	45	$4.63 imes10^{-5}$
Benzene	50	$6.55 imes10^{-5}$

temperatures, 40, 45, and 50° . These results show that the isomerization of IXa to XIa obeys the firstorder rate law and the value for $\Delta H_a = 22$ kcal mol⁻¹. The calculated entropy of activation at 50°, ΔS_{50° = -9.7 eu, suggests an ordered transition state for the isomerization of IXa, in agreement with the suggested mechanism.

Our next objective was to study the reaction of the unsymmetrical phthaloyl dichloride (II) with aminedithiocarbamates with a view to understanding the mode of these reactions. Treatment of an acetone solution of II with pyrrolidinedithiocarbamate gave a 60% of the symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa). The formation of the symmetrical isomer IXa in this reaction clearly indicates that the preferred mode of attack of the nucleophile is on the carbonyl carbon of II and not on the carbon atom attached to the halogen atoms (Scheme II). This is analogous to the reaction of O-alkyl xanthates with II proceeding through path a, as shown in Scheme I.

In continuation of our studies, we have examined the reactions of a few other aminedithiocarbamates with both I and II. The reactions of I with piperidinedithiocarbamate, dimethylaminedithiocarbamate, and diethylaminedithiocarbamate gave the corresponding symmetrical phthaloic aminedithiocarbamic anhydrides IXb, IXc, and IXd in yields ranging between 50 and 76%. Symmetrical phthaloic aminedithiocarbamic anhydrides IXa and IXb were also obtained when II was treated with the corresponding aminedithiocarbamates.

It was mentioned earlier that the symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa) undergoes isomerization to the unsymmetrical derivative XIa on refluxing in benzene solution for 1 hr. Our attempts at bringing about similar isomerizations of the symmetrical phthaloic aminedithiocarbamic anhydrides IXb, IXc, and IXd to the corresponding unsymmetrical derivatives were, however, unsuccessful. In each case, the compound decomposed with the loss of carbon disulfide to the corresponding phthalamide, as shown in Scheme III. Thus, on refluxing, a benzene solution of IXb for 1 hr gave a 90% yield of phthaloyl dipiperidide (XIIb).⁸ Similarly, IXc and



IXd, on refluxing in benzene for 1 hr, gave N, N, N', N'tetramethylphthalamide (XIIc)⁸ and N, N, N', N'-tetraethylphthalamide (XIId),⁹ respectively.

Our next aim was to study the reaction of I with a mixture of nucleophiles, with a view to preparing mixed xanthates and aminedithiocarbamic anhydrides. Treatment of an ether solution of I and a mixture of potassium O-methyl xanthate and piperidinedithiocarbamate in equimolar proportions gave a mixture of products consisting of 25% of the unsymmetrical dixanthate VIa and 45% of the symmetrical aminedithiocarbamic anhydride IXb. None of the mixed xanthate could be isolated from this run.

In an earlier communication,³ we had reported the thermal and photochemical transformations of an unsymmetrical phthaloyl dixanthate such as VIb. In the present studies we have examined both the thermal and photochemical reactions of few unsymmetrical phthaloyl dixanthates such as VIa, VIc, VId, and VIe with a view to studying the nature of the products formed in these reactions.

Photolysis of VIa in benzene solution at room temperature gave a 38% yield of trans-biphthalyl (XXI), mp 352-54°, as the only isolable product. Under similar conditions, the photolysis of other unsymmetrical phthaloyl dixanthates such as VIc, VId, and VIe gave XXI in yields ranging between 34 and 41%. The formation of XXI in the photolysis of unsymmetrical phthaloyl dixanthates suggests that in all these cases the fragmentation may be taking place through a C-S bond fission giving rise to the radical intermediate XIII, which then gives rise to the carbene intermediate XIV through a second C-S bond fission. Dimerization of XIV would lead to trans-biphthalyl (XXI) (Scheme IV). It has not been possible to isolate either benzocyclobutenedione (XVII) or other dimeric products such as XVIII, XIX, or XX from these reactions.¹⁰ A similar type of photochemical trans-formation involving a C-S bond fission is reported in the case of 9,9-dixanthogenyl xanthene.¹¹

It is interesting to note that the C-S bond fission of the type postulated for the fragmentation of acyl and aroyl xanthates² has also been suggested for the photolysis of dithiocarbamic anhydrides.^{7,12} Thus, in the photolysis of benzoic piperidinedithiocarbamic anhydride,⁷ a mixture of products such as benzoic acid, benzoyl piperidide, benzoyl cyclopentamethylenethio-

 (11) A. Schönberg and U. Sodtke, *ibid.*, 4977 (1967).
 (12) E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron*, 21, 2857 2865 (1965).

⁽⁹⁾ P. B. Corbiere, French Patent 866,229 (1941); Chem. Abstr., 43, 5038 (1949).

⁽¹⁰⁾ For the formation of several dimeric products in the photolysis of benzocyclobutenedione, see (a) R. F. C. Brown and R. K. Solly, Tetrahedron Lett., 169 (1966); (b) H. A. Staab and J. Ipaktschi, ibid., 583 (1966).



carbamyl disufide, and cyclopentamethylene thiuram bisulfide are formed. A free-radical mechanism has been suggested to account for the formation of these products.

In the present investigation we have examined the photolysis of a few symmetrical phthaloic bisaminedithiocarbamic anhydrides with a veiw to studying the nature of the products formed in these reactions. The photolysis of symmetrical bis(pyrrolidinedithiocarbamic anhydride) (IXa), for example, gives rise to a mixture of trans-biphthalyl (XXI, 30%) and pyrrolidyl thiuram disulfide (XXIIIa, 75%). The formation of both XXI and XXIIIa can be explained on the basis of C-S bond fission in IXa, giving rise to the radical intermediates XVI and XXII, respectively (Scheme V). The diradical species can isomerize to the carbene intermediate XIV, which then undergoes dimerization to give trans-biphthalyl (XXI). The formation of the thiuram disulfide XXIIIa may arise through the dimerization of the radical species XXII.

Similarly, the photolysis of other symmetrical phthaloic bisaminedithiocarbamic anhydrides such as IXb, IXc, and IXd gave, in each case, *trans*-biphthalyl and the corresponding thiuram disulfides, XXIIIb, XXIIIc, and XXIIId, respectively.

It is noteworthy that the photolysis of unsymmetrical phthaloic bis(pyrrolidinedithiocarbamic) anhydride (XIa) also gives rise to a mixture of *trans*-biphthalyl (XXI, 50%) and pyrrolidyl thiuram disulfide (XXIIIa, 75%). The formation of *trans*-biphthalyl from XIa suggests that both XIa and the unsymmetrical phthaloyl dixanthates undergo similar type of fragmentation reactions (Scheme IV).

Thermal decomposition of acyl xanthates are reported to give rise to a mixture of products.^{2,13,14} Thus, ethyl phenylacetyl xanthate, for example, decomposes on heating to give a mixture of ethyl phenylacetate and carbon disulfide and a mechanism involving a four-membered, cyclic transition state has been suggested for this reaction.² During the present investigation, we have examined the thermal decomposition of several umsymmetrical phthaloyl dixanthates with a view to studying the nature of the products formed in these reactions. Heating unsymmetrical di-O-methyl phthaloyl dixanthate (VIa) to around 230-240° for about 30 min, for example, gave rise to a mixture of products which include thiophthalic anhydride (XXV, 68%), O,S-dimethyl xanthate (XXVIa, 30%), and carbonyl sulfide (XXVII, 76%), identified through its piperidinium salt¹⁵ (Scheme VI).

Similarly, the thermal decompositions of unsym-

- (13) G. Bulmer and F. G. Mann, J. Chem. Soc., 677 (1945).
- (14) T. Taguchi and M. Nako, Tetrahedron, 18, 245 (1962).
- (15) J. Parrod, C. R. Acad. Sci., Ser. C, 234, 1062 (1952); Chem. Abstr., 47, 1606 (1953).



metrical phthaloyl dixanthates VIc, VId, and VIe gave rise to a mixture of thiophthalic anhydride, carbonyl sulfide, and the corresponding O,S-dialkyl xanthates (XXVIc-e). It is interesting to note that in the decomposition of unsymmetrical phthaloyl dixanthates such as VIb, VIc, and VId. small amounts of trans-biphthalyl (XXI) could also be isolated. The formation of XXI in the thermal decomposition of these dixanthates suggests that a minor mode of decomposition is through the carbene intermediate XIV which dimerizes to give trans-biphthalvl. The exact nature of the pyrolytic decomposition of the unsymmetrical phthaloyl dixanthates is not very clearly understood. A probable mechanism, which accounts for the formation of products such as carbonyl sulfide (XXVII), thiophthalic anhydride (XXV), and O.Sdialkyl xanthates (XXVIa-e), is one which involves a cyclic concerted process as shown in Scheme VI. The formation of phthalic thioanhydride may be through a rearrangement of the initially formed thionphthalic anhydride (XXIV).¹⁶

In contrast to the thermal decomposition of unsymmetrical phthaloyl dixanthates, the dithiocarbamic anhydrides give chiefly the corresponding amides and carbon disulfide.^{7,8,12}

Experimental Section

All melting points are uncorrected and were taken on a Koffler hot stage. Ir spectra were determined on a Perkin-Elmer Model 137 Infracord spectrometer and uv spectra were determined on a Beckman DB spectrophotometer. Nmr traces were recorded on a Varian HR-100 spectrometer, using tetramethylsilane as internal standard. All irradiation experiments were carried out using a Hanovia, medium-pressure, mercury lamp (450 W). Kinetic studies were carried out spectrophotometrically, using a Beckman DU spectrophotometer.

(16) C. M. Sharts and D. W. Fong, J. Org. Chem., 32, 3709 (1967).



Potassium O-methyl xanthate, mp 185-186°, potassium O-npropyl xanthate, mp 237-238°, potassium O-n-butyl xanthate, 261-262°, and potassium O-benzyl xanthate, mp 179-180°, were prepared by reported procedures.¹⁷ Dimethylaminedithiocarbamate,¹⁸ mp 136°, and diethylaminedithiocarbamate,¹⁵ mp 81°, pyrrolidinedithiocarbamate,¹² mp 152°, and piperidinedithiocarbamate,⁷ mp 169-170°, were prepared by standard procedures. Symmetrical phthaloyl dichloride, bp 132-133° (10 mm), and unsymmetrical phthaloyl dichloride, mp 87-88°, were prepared by reported procedures.⁶

Unsymmetrical Di-O-alkyl S,S-Phthaloyl Dixanthates.—In a typical run, 0.09 mol of potassium O-alkyl xanthate was slowly added to a solution of 0.02 mol of symmetrical phthaloyl dichloride in 30 ml of diethyl ether, maintained around 5°. The mixture was stirred for 30 min and then was treated with water to remove any unchanged potassium O-alkyl xanthate. Removal of the solvent under vacuum gave the product which was recrystallized from a mixture (1:1) of methylene chloride and petro-leum ether (bp 40-60°). Table II summarizes the percentage yields and the physical data of the different unsymmetrical di-O-alkyl S,S-phthaloyl dixanthates.

Treatment of Di-O-methyl S,S-Phthaloyl Dixanthate (VIa) with Raney Nickel.—A mixture of VIa (0.4 g, 0.001 mol) and Raney nickel (2 g) was refluxed in acetone (20 ml) for 8 hr. Removal of the unchanged nickel and the solvent gave 0.1 g (62%) of phthalide, which melted at 75°, after recrystallization from methylene chloride. There was no depression in the melting point when mixed with an authentic sample.¹⁹

point when mixed with an authentic sample.¹⁹ **Photolysis of Di-O-alkyl** S,S-Phthaloyl Dixanthates.—In a typical run, a solution of di-O-methyl S,S-phthaloyl dixanthate (1.5 g, 0.004 mol) in benzene (200 ml) was irradiated for 1 hr at room temperature. Removal of the solvent gave a product which on treatment with methylene chloride gave 0.22 g (38%) of trans-biphthalyl (XXI), which melted over the range 352–354° (lit.^{10a} mp 352–354°), on recrystallization from acetic acid. The ir spectrum (KBr) of XXI showed a strong absorption band at 1789 cm⁻¹ due to a carbonyl group (γ -lactone). The uv spectrum of XXI (CH₂Cl₂) was characterized by the following absorption maxima: 250 m μ (ϵ 13,900) (shoulder), 260 (18,000), 272 (18,800) (shoulder), 292 (9300), 294 (42,00), 307 (16,600), 316 (11,100), 325 (13,000), 363 (36,200), 376 (30,300), and 382 (26,400).

Anal. Caled for C₁₆H₈O₄: C, 72.70; H, 3.01. Found: C, 72.68; H, 3.34.

Similarly, the photolyses of VIc, VId, and VIe in benzene solution gave *trans*-biphthalyl (XXI) as the only isolable product in each case, in yields ranging between 34 and 41%.

⁽¹⁷⁾ I. S. Shupe, J. Ass. Offic. Agr. Chem., 25, 495 (1942); Chem. Abstr., 86, 4670 (1942).

⁽¹⁸⁾ R. H. Sahasrabudhey and K. L. Radhakrishnan, J. Indian Chem. Soc., 31, 853 (1954).

⁽¹⁹⁾ J. H. Gardner and C. A. Naylor, Jr., "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 526.

TABLE II	
UNSYMMETRICAL DI-O-ALKYL S,S-PHTHALOYL D	IXANTHATES

	Yield.		Calco	d, %	Foun	ıd, %	Infrared, cn C==0	1-1 (KBr)	
Compd	%	Mp, °C	С	H	С	H	$(\gamma$ -lactone)	C = S	Uv, λ_{\max} , m μ (ϵ)
VIa	78	119 - 120	41.61	2.89	41.90	2.72	1780	1040	288 (22,100), 364 (100)
VIc	50	81-82	47.75	4.47	47.75	4.45	1782	1030	288 (31,900), 366 (120)
VId	88	60-61	50.23	5.10	50.33	5.22	1770	1030	290 (25,000), 366 (130)
VIe	65	124 - 125	57.83	3.61	57.87	3.76	1785	1020	290 (25,500), 368 (100)

Thermal Decomposition of Di-O-alkyl S,S-Phthaloyl Dixanthates.—In a typical run, 2 g (0.005 mol) of di-O-methyl S,Sphthaloyl dixanthate was heated around 230-240° for 20 min in a 10-ml round-bottomed flask, provided with a nitrogen inlet and a 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 g (76%) of piperidinium 1-piperidinecarbothiolate, mp 112°, which showed no depression in its melting point when mixed with an authentic sample.¹⁵

The pyrolyzed residue was treated with petroleum ether (bp $60-80^{\circ}$) to give 0.65 g (68%) of thiophthalic anhydride (XXV), mp 110° (mmp). The petroleum ether-soluble fraction was chromatographed over alumina to give 0.2 g (30%) of O,S-dimethyl xanthate (XXVIa), identified through a comparison of its ir spectrum with that of an authentic sample.²⁰

Di- \bar{O} -n-propyl S,S-phthaloyl dixanthate (1 g, 0.002 mol) was heated around 230-240° for 30 min under a stream of nitrogen and the evolved gases were bubbled through a 10% solution of piperidine in ether. The precipitated salt on recrystallization from a mixture (1:1) of methylene chloride and ether gave 0.25 g (43%) of piperidinium 1-piperidinecarbothiolate, mp 112° (mmp). Work-up of the pyrolyzed residue as in the previous case gave 0.02 g (6%) of trans-biphthalyl, mp 352-354° (mmp), 0.27 g (67%) of thiophthalic anhydride, mp 110° (mmp), and 0.3 g (70%) of O,S-di-n-propyl xanthate (XXVIc), identified by comparison of its infrared spectrum with that of an authentic sample.²¹

Similarly, heating VId (2 g, 0.004 mol) around 230-240° for 30 min gave carbonyl sulfide which when absorbed in an ether solution of piperidine gave 0.35 g (32%) of piperidinium 1-piperidine-carbothiolate, mp 112° (mmp). Work-up of the pyrolyzed residue as in the earlier cases gave 0.15 g (25%) of *trans*-biphthalyl, mp 352-354° (mmp), 0.12 g (16%) of thiophthalic anhydride, mp 110° (mmp), and 0.5 g (52%) of *O*,S-di-*n*-butyl xanthate (XXVId), identified by a comparison of its infrared spectrum with that of an authentic sample.²²

In a separate run, 2 g (0.004 mol) of VIe was heated around 230-240° for 30 min and the carbonyl sulfide that was evolved was absorbed in 10% piperidine in ether to give 0.8 g (83%) of piperidinium 1-piperidinecarbothiolate, mp 112° (mmp). The pyrolyzed residue, on work-up as in the previous cases gave 0.32 g (50%) of thiophthalic anhydride, mp 110° (mmp), and 0.7 g (63%) of O,S-dibenzyl xanthate (XXVIe), identified through a comparison of its ir spectrum with that of an authentic sample.²⁰

Reaction of Unsymmetrical Phthaloyl Dichloride with Potassium O-Alkyl Xanthates.—In a typical run, 0.59 g (0.004 mol) of potassium O-methyl xanthate was treated with a solution of 0.3 g (0.001 mol) of II in acetone (10 ml) around 0°. Removal of the solvent under vacuum gave a product which was extracted with methylene chloride. The methylene chloride extract was washed with water and dried over anhydrous sodium sulfate, and the solvent removed under vacuum to give 0.35 g (70%) of unsymmetrical di-O-methyl S,S-phthaloyl dixanthate, which melted at 119-120° (mmp), on recrystallization from a mixture (1:1) of methylene chloride and petroleum ether (bp 40-60°).

Similarly, the reactions of potassium O-n-propyl xanthate, potassium O-n-butyl xanthate, and potassium O-benzyl xanthate with II gave the unsymmetrical xanthates VIc, mp 81-82° (60%), VId, mp 60-61° (66%), and VIe, mp, 124-125° (70%). Phthaloic Bis(pyrrolidinedithiocarbamic anhydride) (IXa).—A solution of 6.5 g (0.03 mol) of pyrrolidinedithiocarbamate in ether (50 ml) was gradually added to an ether solution of I (2.5 g, 0.012 mol in 50 ml) at 5°, over a period of 30 min. The reaction mixture was washed with water to remove any unchanged pyrrolidinedithiocarbamate, and the ether solution was dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave a product which was recrystallized from a mixture (1:1) of ether and methylene chloride to give 3.5 g (68%) of symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa), mp 140–141°. The ir spectrum (KBr) of IXa showed absorption bands at 1675 (C=O) and 1471 cm⁻¹ (C=S). The uv spectrum (CH₂Cl₂) of IXa was characterized by the following absorption maxima: 290 m μ (ϵ 31,100) and 410 (400). Anal. Calcd for C₁₈H₂₀N₂O₂S₄: C, 50.94; H, 4.72; N, 6.60.

Anal. Calcd for $C_{18}H_{20}N_2O_2S_4$: C, 50.94; H, 4.72; N, 6.60. Found: C, 51.24; H, 4.70; N, 6.61. Treatment of Symmetrical Phthaloic Bis(pyrrolidinedithio-

Treatment of Symmetrical Phthaloic Bis(pyrrolidinedithiocarbamic anhydride) with Raney Nickel.—A mixture of 0.42 g (0.001 mol) of IXa and 2 g of Raney nickel in 25 ml of alcohol was stirred under reflux for 8 hr. Removal of the solvent and unchanged nickel gave a residue which on treatment with a solution of 2,4-dinitrophenylhydrazine gave 0.12 g (30%) of o-phthalaldehyde 2,4-dinitrophenylhydrazone, mp 265° (lit.²³ mp 270°), after recrystallization from ethanol

Anal. Calcd for $C_{20}H_{14}N_{\circ}O_8$: C, 48.58; H, 2.83; N, 22.76. Found: C, 48.83; H, 3.00; N, 22.55.

Photolysis of Symmetrical Phthaloic Bis(pyrrolidinedithiocarbamic anhydride) (IXa).—A solution of (0.8 g, 0.002 mol) of IXa in dry benzene (175 ml) was irradiated for 1 hr around 5°. Removal of the solvent under vacuum gave a residue which on treatment with methylene chloride gave 0.07 g (30%) of transbiphthalyl, mp $352-354^{\circ}$ (mmp), after recrystallization from acetic acid.

Removal of the solvent from the methylene chloride- soluble fraction gave 0.35 g (75%) of pyrrolidyl thiuram disulfide (XXIIIa), mp 144°, on recrystallization from a mixture (1:1) of ether and methylene chloride. There was no depression in the melting point of XXIIIa when mixed with an authentic sample.¹³

Thermal Isomerization of Symmetrical Phthaloic Bis(pyrrolidinedithiocarbamic anhydride) (IXa) to the Unsymmetrical Derivative XIa.--A solution of 0.5 g (0.001 mol) of IXa in dry benzene (25 ml) was refluxed for 1 hr. Removal of the solvent under vacuum gave 0.35 g (70%) of unsymmetrical phthaloic bis(pyrrolidinedithiocarbamic) anhydride (XIa), which melted at 161-162°, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether (bp 40-60°). The infrared spectrum of XIa showed an absorption band at 1786 cm⁻¹ (C=O, γ -lactone). The uv spectrum (CH₂Cl₂) was characterized by the following absorption maxima: 284 m μ (ϵ 14,900) and 330 (90). The nmr spectrum (CDCl₃) of XIa showed two multiplets at τ 6.36 (8 H) and 7.82 (8 H), respectively, due to the methylene protons of the pyrrolidine ring. Of these two multiplets, the one at τ 6.36 is assigned to the methylene protons near to the nitrogen atoms, whereas the multiplet at τ 7.82 is assigned to the methylene protons away from the nitrogen atoms. The aromatic protons appeared as a separate multiplet centered around τ 2.52 (4 H) and characteristic of an ABCD pattern.

Anal. Calcd for $C_{18}H_{20}N_2O_2S_4$: C, 50.94; H, 4.71; N, 6.60. Found: C, 50.64; H, 4.60; N, 6.55.

Photolysis of Unsymmetrical Phthaloic Bis(pyrrolidinedithiocarbamic) anhydride (XIa).—A solution of XIa (0.7 g, 1.6 mmol) in benzene (175 ml) was irradiated for 1 hr. Removal of the solvent under vacuum gave a residue which was treated with methylene chloride to give 0.11 g (50%) of *trans*-biphthalyl, mp $352-354^{\circ}$ (mmp), after recrystallization from acetic acid.

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The methylene chloride soluble portion gave 0.33 g (70%) of pyrrolidyl thiuram disulfide (XXIIIa), mp 144-145° (mmp), after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether (bp 40-60°).

Reaction of Unsymmetrical Phthaloyl Dichloride with Pyrrolidinedithiocarbamate.—Treatment of a solution of 3 g (0.013 mol) of pyrrolidinedithiocarbamate in acetone (25 ml) with an acetone solution of II (1 g, 0.005 mol in 25 ml) around 5° and work-up in the usual manner gave 1.2 g (60%) of symmetrical phthaloic bis(pyrrolidinedithiocarbamic anhydride) (IXa), mp 140–141° (mmp), after recrystallization from methylene chloride.

Symmetrical Phthaloic Bis(piperidinedithiocarbamic anhy-dride) (IXb).—Treatment of a mixture of 10 g (0.04 mol) of piperidinedithiocarbamate and 3.8 g (0.018 mol) of I in ether (100 ml) around 5° and work-up as in the case of IXa gave 5.7 g (68%) of symmetrical phthaloic bis(piperidinedithiocarbamic anhydride) (IXb), which melted at 132-133° (lit.⁸ mp 123°), after recrystallization from a mixture (1:1) of ether and methylene chloride. The ir spectrum (CCl₄) of IXb showed absorption bands at 1684 (C=0) and 1471 cm⁻¹ (C=S). The uv spectrum (CH₂Cl₂) of IXb was characterized by the following absorption maxima: 296 m μ (ϵ 18,700) and 410 (500). The nmr spectrum (CDCl₃) of IXb showed two broad singlets centered around τ 5.89 (8 H) and 8.27 (12 H), due to the methylene protons situated near the nitrogen atoms and those situated away from the nitrogen atoms in the piperidine rings, respectively. In addition, the spectrum showed a symmetrical multiplet centered around $\tau 2.5$ (4 H), due to the aromatic protons, characteristic of an A_2B_2 pattern.

Anal. Calcd for $C_{20}H_{24}N_2O_2S_4$: C, 53.09; H, 5.31; N, 6.19. Found: C, 53.23; H, 5.22; N, 6.30.

Treatment of IXb with Raney Nickel.—A mixture of IXb (0.4 g, 0.8 mmol) and Raney nickel (2 g) in ethanol (20 ml) was refluxed for 10 hr. Removal of the solvent and unchanged nickel gave a product which on treatment with a solution of 2,4-dinitrophenylhydrazine gave 0.12 g (30%) of *o*-phthaldehyde 2,4-dinitrophenylhydrazone, mp 265° (mmp), after recrystallization from ethanol.

Photolysis of Symmetrical Phthaloic Bis(piperidinedithiocarbamic anhydride) (IXb).—A solution of 1.5 g (0.003 mol) of IXb in dry benzene (175 ml) was irradiated for 1 hr at 5°. Removal of the solvent under vacuum gave a product which on treatment with methylene chloride gave 0.2 g (46%) of *trans*biphthalyl, mp 352-354° (mmp), after recrystallization from acetic acid.

Removal of the solvent from the methylene chloride soluble fraction gave 0.4 g (40%) of cyclopentamethylene thiuram disulfide (XXIIIb), mp 130° (mmp). The identity of XXIIIb was further confirmed by a comparison of its infrared spectrum with that of an authentic sample.²⁴

Attempted Isomerization of IXb.—A solution of 0.5 g (0.001 mol) of IXb in benzene (25 ml) was refluxed for 45 min. Removal of the solvent under vacuum gave a product which was recrystallized from a mixture (1:1) of methylene chloride and petroleum ether (bp $40-60^{\circ}$) to give 0.3 g (90%) of phthaloyl dipiperidide, mp 65-66° (lit.⁸ mp 54°). The infrared spectrum of this product showed an absorption band at 1640 cm⁻¹, characteristic of an amide carbonyl group.

this product showed an absorption band at 1010 the , the acteristic of an amide carbonyl group. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 72.00; H, 8.00; N, 9.33. Found: C, 72.38; H, 8.31; N, 8.95.

Reaction of Unsymmetrical Phthaloyl Dichloride with Piperidinedithiocarbamate.—A solution of 2 g (0.008 mol) of piperidine)dithiocarbamate in acetone (20 ml) was treated with an acetone solution of II (0.8 g, 0.004 mol) around 5°. Work-up of the mixture as in the earlier cases gave 0.75 g (44%) of symmetrical phthaloic piperidinedithiocarbamate, mp 132–133° (mmp).

Symmetrical Phthaloic Bis(dimethylaminedithiocarbamic anhydride) (IXc).—Treatment of a mixture of 6 g (0.036 mol) of dimethylaminedithiocarbamate with 3 g (0.014 mol) of I in ether (150 ml) around -30° and work-up as in the earlier cases gave 2.7 g (50%) of symmetrical phthaloic bis(dimethylaminedithiocarbamic anhydride) (IXc), mp 115–116° (lit.⁸ mp 107°), after recrystallization from methylene chloride. The ir spectrum of IXc showed absorption bands at 1686 (C=O) and 1493 cm⁻¹ (C=S). The uv spectrum (CH₂Cl₂) of IXc was characterized by the following absorption maxima: 290 m μ (ϵ 32,900) and 410 (600). Anal. Caled for $C_{14}H_{18}N_2O_2S_4$: C, 45.16; H, 4.30; N, 7.52. Found: C, 45.41; H, 4.40; N, 7.40.

Photolysis of Phthaloic Bis(dimethylaminedithiocarbamic anhydride) (IXc).—Irradiation of a solution of 1 g (0.002 mol) of IXc in benzene (175 ml) for 1 hr at 5° and work-up of the reaction as in the earlier cases gave 0.13 g (37%) of *trans*-biphthalyl, mp $352-354^{\circ}$ (mmp), and 0.3 g (48%) of tetramethyl thiuram disulfide (XXIIIc), mp 154° (mmp).

Attempted Isomerization of IXc.—A solution of 0.5 g (0.001 mol) of IXc in dry benzene (25 ml) was refluxed for 1 hr. Removal of the solvent under vacuum and recrystallization of the product from a mixture (1:1) of methylene chloride and petroleum ether (bp 40–80°) gave 0.25 g (83%) of N,N,N',N'-tetramethylphthalamide, mp 121–122° (lit.⁸ mp 121–122°). The ir spectrum of this product showed an absorption band at 1640 cm⁻¹, characteristic of an amide carbonyl group.

Anal. Caled for $C_{12}H_{16}N_2O_2$: C, 65.45; H, 7.27; N, 12.72. Found: C, 65.11; H, 7.10; N, 12.80. Symmetrical Phthaloic Bis(diethylaminedithiocarbamic an-

Symmetrical Phthaloic Bis(diethylaminedithiocarbamic anhydride) (IXd).—A solution of diethylaminedithiocarbamate (4.5 g, 0.02 mol) in ether (75 ml) was treated with an ether solution of I (2 g, 0.01 mol, in 50 ml) around 30°. The reaction mixture was worked up in the usual manner to give 3.2 g (76%) of IXd, mp 86–87°, after recrystallization from methylene chloride. The ir spectrum (KBr) of IXd showed absorption bands at 1686 (C==O) and 1476 cm⁻¹ (C==S). The uv spectrum (ethanol) of IXd was characterized by the following absorption maxima: 290 m μ (ϵ 24,300) and 410 (250). The nmr spectrum (CDCl₃) of IXd showed a triplet centered around τ 8.69 (12 H) due to the methyl protons and a quartet centered around τ 6.1 (8 H) due to the methylene protons. In addition, the spectrum showed a multiplet centered around τ 2.37 (4 H) due to the aromatic protons, characteristic of an A₂B₂ pattern.

Anal. Calcd for $C_{18}H_{24}N_2O_2S_4$; C, 50.46; H, 5.6; N, 6.54. Found: C, 50.23; H, 5.6; N, 6.72.

Photolysis of Symmetrical Phthaloic Bis(diethylaminedithiocarbamic anhydride) (IXd).—A solution of 1 g (0.002 mol) of IXd in 175 ml of dry benzene was irradiated for 1 hr at 5°. Removal of the solvent under vacuum gave a product which was treated with methylene chloride to give 0.1 g (33%) of transbiphthalyl, mp $352-354^{\circ}$ (mmp).

Removal of the solvent from the methylene chloride soluble portion gave 0.2 g (34%) of tetraethyl thiuram disulfide (XXIIId), mp 71-72°, after recrystallization from methylene chloride. There was no depression in the melting point of XXIIId when mixed with an authentic sample.^{24,25}

Attempted Isomerization of IXd.—A solution of 0.5 g (0.001 mol) of IXd in dry benzene (25 ml) was refluxed for 1 hr. Removal of the solvent under vacuum and recrystallization of the product from a mixture (1:1) of methylene chloride and petro-leum ether (bp 40-60°) gave 0.22 g (64%) of N, N, N', N'-tetraethylphthalamide, mp 39–40° (lit.⁹ mp 38°). The ir spectrum of the product showed an absorption band at 1645 cm⁻¹, characteristic of an amide carbonyl group.

Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.56; H, 8.75; N, 10.21. Found: C, 69.72; H, 8.55; N, 10.00. Reaction of Symmetrical Phthaloyl Dichloride with a Mixture

Reaction of Symmetrical Phthaloyl Dichloride with a Mixture (1:1) of Potassium O-Methyl Xanthate and Piperidinedithiocarbamate.—To a solution of 4 g (0.02 mol) of I in ether (25 ml), maintained at 5°, was added an ether solution (50 ml) of a mixture of potassium O-methyl xanthate (3 g, 0.02 mol) and piperidinedithiocarbamate (5 g, 0.02 mol), over a period of 30 min. Removal of the solvent under vacuum gave a residue which was washed with water to remove all unchanged xanthate and piperidinedithiocarbamate. Treatment of this residue with ether (50 ml) gave an ether-soluble portion, which on recrystallization from a mixture (1:1) of methylene chloride and petroleum ether (bp $40-60^\circ$) gave 4.0 g (45%) of symmetrical phthaloic bis(piperidinedithiocarbamic anhydride) (IXb), mp 143-144° (mmp).

Removal of the solvent from the ether-soluble portion gave a product which was recrystallized from methylene chloride to give 1.7 g (25%) of unsymmetrical di-O-methyl S,S-phthaloyl dixanthate (VIa), mp 119-120° (mmp). None of the mixed product could be isolated from this run.

Registry No.—VIa, 27193-06-2; VIc, 27193-07-3; VId, 27193-08-4; VIe, 27193-09-5; IXa, 27193-10-8;

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IXb, 27193-11-9; IXc, 27193-12-0; IXd, 27193-13-1; XIa, 27193-14-2; XXI, 482-23-5; XXIIIa, 496-08-2.

Acknowledgment.-The authors are grateful to Dr. A. Shah for partial experimental assistance. We thank Mr. A. H. Siddiqui for his help in microanalysis. One of the authors (S. N. S.) is grateful to the authorities of the Indian Institute of Technology, Kanpur, for the award of a Senior Research Assistantship.

Organic Disulfides and Related Substances. 31. **Possible Anchimeric Involvement of an Ortho Carboxylate Moiety** in Disproportionation of Unsymmetrical o-Carboxyphenyl Disulfides¹

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Received August 17, 1970

Disproportionation of 2-(phenyldithio)benzoic acid (2) to phenyl disulfide and 2,2'-dithiodibenzoic acid is much faster for the salt than for the acid. Among the facts which suggest that the o-carboxylate moiety of the salt anchimerically facilitates disproportionation are the following: an increase in rapidity with increasing pH near pH 7; decreased rapidity for the meta isomer; lack of a marked effect of dilution; inhibition of disproportionation by N-ethylmaleimide (through trapping of benzenethiolate ion) but acceleration by addition of thiolate ion; accordance with expectation as to the relative rapidity of disproportionation of other dithiobenzoic acids; and, evidence for existence and consistent reactions of o-sulfenobenzoic acid anhydride (5a) as an unstable intermediate generated by anchimeric displacement of benzenethiolate ion by the o-carboxylate moiety.

1

o-(2-Protoaminoethyldithio)benzoate (1) is active as an antiradiation drug.² That the methyl ester, the



meta isomer, and the para isomer of 1 showed no significant antiradiation activity^{2a} led us to suspect anchimeric involvement of the carboxylate moiety of 1 with the disulfide linkage. In a similar vein, inactivity of the cyclohexyl analog of 1^{2b} is understandable, since this analog is believed to have trans substituents, which should resist anchimeric involvement. This suspicion of anchimeric involvement was strengthened during work with a phenyl counterpart (2) of 1, since the sodium salt of 2 (3) disproportionated far more readily to the two symmetrical disulfides than did 2 itself (eq 1).³

$$2 + OH^{-} \xrightarrow{-H_{3}O}$$

$$o - \overline{O_{2}CC_{6}H_{4}SSC_{6}H_{5}} \xrightarrow{2} \frac{1}{2} (o - \overline{O_{2}CC_{6}H_{4}S})_{2} + \frac{1}{2} (C_{6}H_{5}S)_{2} \quad (1)$$

This paper further supports the probability of such an anchimeric involvement in the reaction of eq 1.

The extent of disproportionation of 2 proved to be highly dependent on the pH of the solution (Table I). At pH 14 disproportionation is 95% complete in 0.6 hr (calculated as usual).⁴ Attack of the hydroxyl ion on

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		TABLE	I		
	pH	Dependen	CE OF THE		
	Dispropor	TIONATION	OF DISULI	FIDE 2^a	
pH^b	Time, hr	%°	$_{\mathrm{p}\mathrm{H}^{b}}$	Time, hr	%°
14	0.6	95	6.8	164	31
8.5	48	81	6.8	73	31
8.5	24	70	6.8	56	26
8.5	3	39	6.8	24	14
8.5	2	32	6.4	216	25
7.6	24	46	6.4	44	17
7.6	24	45^d	6.4	24	13
7.6	24	39*	6.4	18	12
7.6	24	3'	6.4	2	3
7.6	24	390	6.4	24	100^{h}
			i	i	$<\!\!2$

^a In 10 ml of H₂O (except as noted) at 25-26°; solutions resulted in each instance. ^b Measured both before and after the reaction; not more than 0.4 pH unit change in 216 hr and no reaction, not more than 0.4 pH unit enarge in 210 hr and no change in 72 hr. "Disproportionation, %"; see ref 4. "Con-taining 10 mol % of N-ethylmaleimide (4). "Containing 31 mol % of 4. "Containing 115 mol % of 4. "In 100 ml of H₂O. "Containing 10 mol % of C₆H₈S-Na⁺(6). 'After being dissolved completely in 100 ml % of C₆H₈S-Na⁺(6). completely in 10 ml of AcOH and heated for 119 hr at 100°, 2 was recovered unchanged.³

the disulfide bond may be a major path of reaction at high pH.⁵ At much lower values of pH, on the other hand, the notable increase in disproportionation with increasing pH points toward increasing anchimeric involvement of carboxylate ion with the disulfide moiety. For example, with a 24-hr reaction period, Table I shows that for the pH sequence 6.4, 6.8, 7.6, and 8.5, the sequence in "disproportionation, %" was 13, 14, 46, and 70.

Disproportionation reactions of disulfides can be homolytic, heterolytic, or some combination of these pathways.⁶ Although 2 also may be subject to light-induced disproportionation,³ the carboxylate-assisted re-

^{(1) (}a) Paper XXX: L. Field and P. R. Engelhardt, J. Org. Chem., 35, 3647 (1970). (b) This investigation was supported by Public Health Service Research Grant AM11685 from the National Institute of Arthritis and Metabolic Diseases. (c) Abstracted from the Ph.D. Dissertation of P. M. G., Jr. (Vanderbilt University, May 1970), which may be consulted for further details. (d) Reported in part at the Southeastern Region Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968, Abstracts, p 98, and at the IVth Symposium on Organic Sulfur, Venice, Italy, June 1970.

⁽⁵⁾ For a discussion of the effect of base on symmetrical disulfides and of the resistance of sodium 2.2'-dithiodibenzoate to attack by OH⁻ even at high pH, however, see J. P. Danehy and K. N. Parameswaran, J. Org. Chem., 33, 568 (1968).

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