CHAPTER - III

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF DI-O-ALKYL-S,S-PHTHALOYL DIXANTHATES

3.1 Abstract

The reaction of an ether solution of symmetrical phthaloyl dichloride with potassium-O-alkylxanthates gave rise to the corresponding unsymmetrical phthaloyl dixanthates, whereas using acetone as the solvent, the dixanthate was formed along with the considerable yield of thiophthalic anhydride. Similarly, the acetone solution of symmetrical phthaloyl dichloride when treated with excess of potassium-O-alkylxanthates resulted in the formation of anhydrosulfide of alkylxanthic acid and thiophthalic anhydride. The same products could also be obtained from the reaction of unsymmetrical phthaloyl dixanthates and potassium-O-alkylxanthates. Photolysis of unsymmetrical phthaloyl dixanthates in benzene solution gave chiefly trans-biphthalyl. 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-dialkylxanthates. Reactions of unsymmetrical phthaloyldixanthates with hydrazine hydrate and hydrogen peroxide have also been studied.

3.2 Results and Discussion

Acyl and aroyl xanthates are conveniently prepared by the treatment of potassium-O-alkyl xanthates with the corresponding acid chlorides in acetone at low temperature.[1] It has been shown that the reaction of potassium-O-ethylxanthate with phthaloyl dichloride in acetone solution does not give rise to the expected symmetrical di-O-ethyl S,S-phthaloyldixanthate, but the unsymmetrical phthaloyl dixanthate.[2]

In the present investigation, we have examined the reactions of several potassium-O-alkylxanthates derived from secondary alchols with symmetrical phthaloyl dichloride (1) with a view to studying the nature of the products formed in these cases.

Treatment of potassium-O-isopropylxanthate with 1 in ether solution around 0° gave 42%, yield of a product, identified as unsymmetrical di-O-isopropyl S,S-phthaloyldixanthate (5a). 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 1780 cm^{-1}, characteristic of γ-lactone. The NMR spectrum of 5a

(Fig. 1) shows a multiplet centered around 7.7 ppm (4H) due to the phenyl protons and two doublets at 1.4 ppm (12H) due to methyl protons. The multiplet due to the aromatic protons shows a characteristic ABCD pattern, as would be expected for the unsymmetrical structure 5a. Further evidence concerning the structure of 5a was derived from the conversion of 5a to phthalide, on treatment with Raney-Nickel.

The reason why the unsymmetrical phthaloyl dixanthate 5a is formed from the reaction of 1 with potassium-O-isopropylxanthate, was not very apparent. A probable explanation for the formation of 5a is indicated in Scheme 1.

In this scheme, we assume that the alkyl xanthate reacts with 1 to give the symmetrical di-O-isopropyl S,S-phthaloyldixanthate (3a), which undergoes an intramolecular rearrangement to the unsymmetrical isomer 5a, through the bicyclic [3,2,1] transition state.[3] With a view to finding out whether the symmetrical dixanthate 3a is initially formed in the reaction, as shown in Scheme 1, we have examined the absorption spectrum of the product mixture, soon after mixing together the symmetrical phthaloyldichloride and

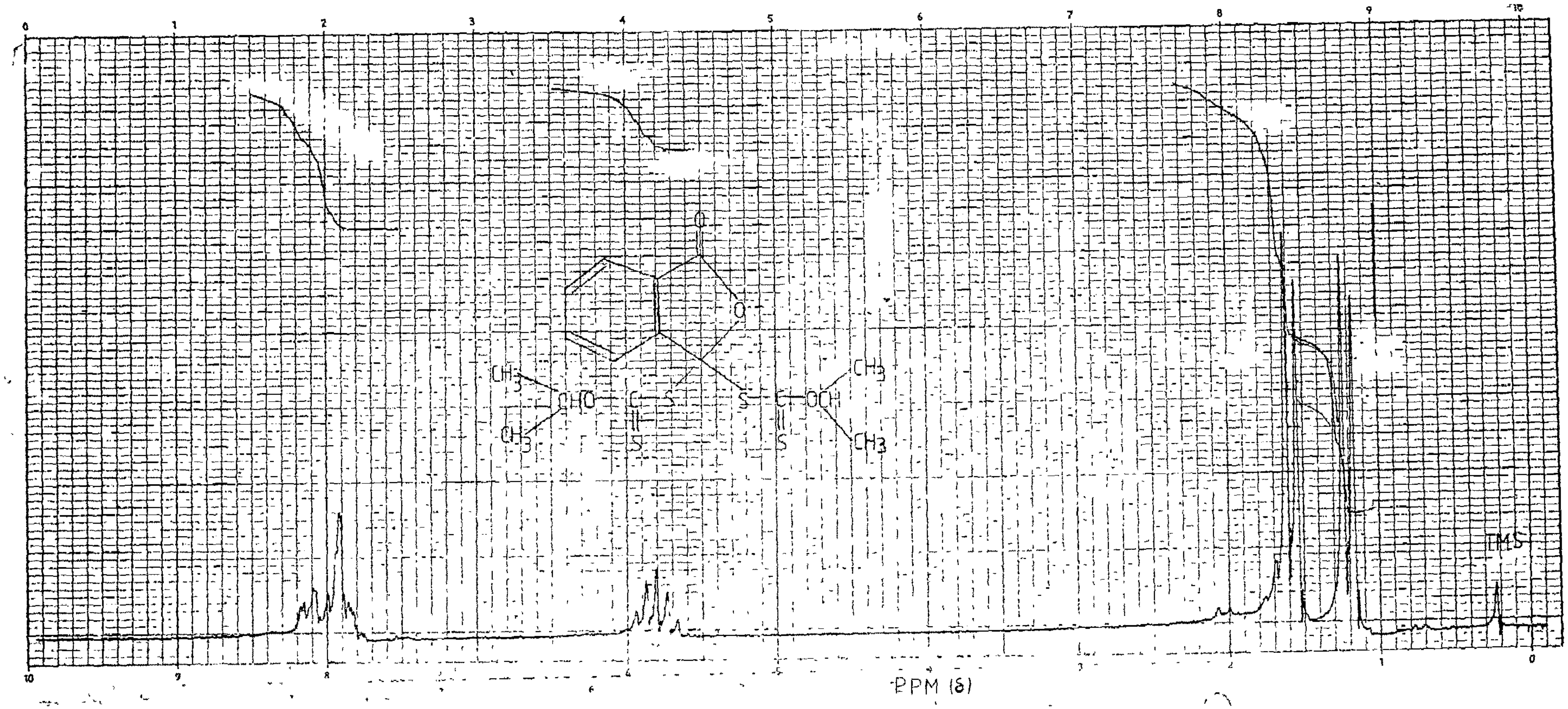
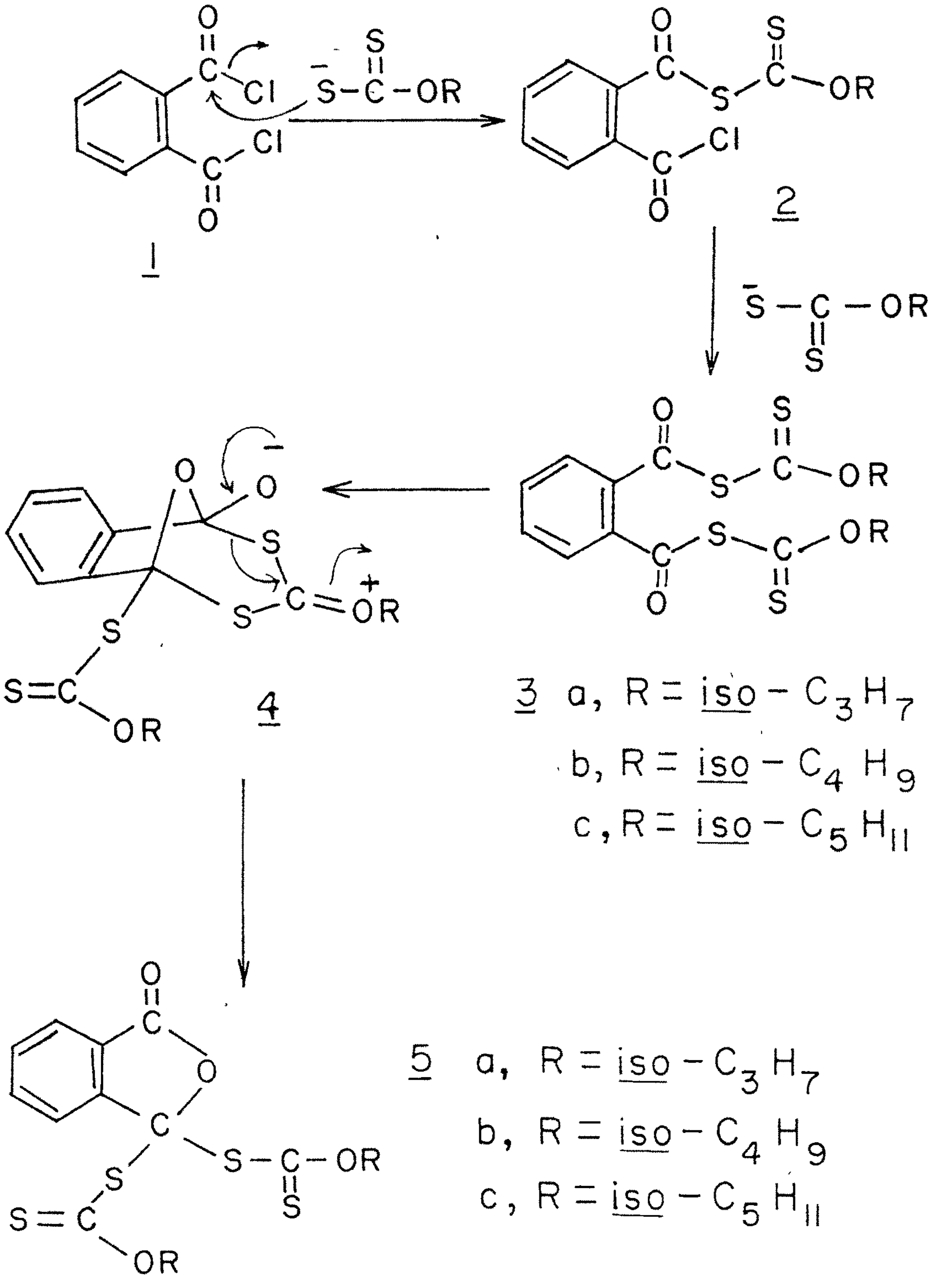


Fig. 1 NMR Spectrum (90 mcs) of unsymmetrical di-O-isopropyl S,S-phthaloyl dixanthate (5a)

SCHEME-I



1

2

4

3 a, R = iso – C_3H_7
b, R = iso – C_4H_9
c, R = iso – C_5H_{11}

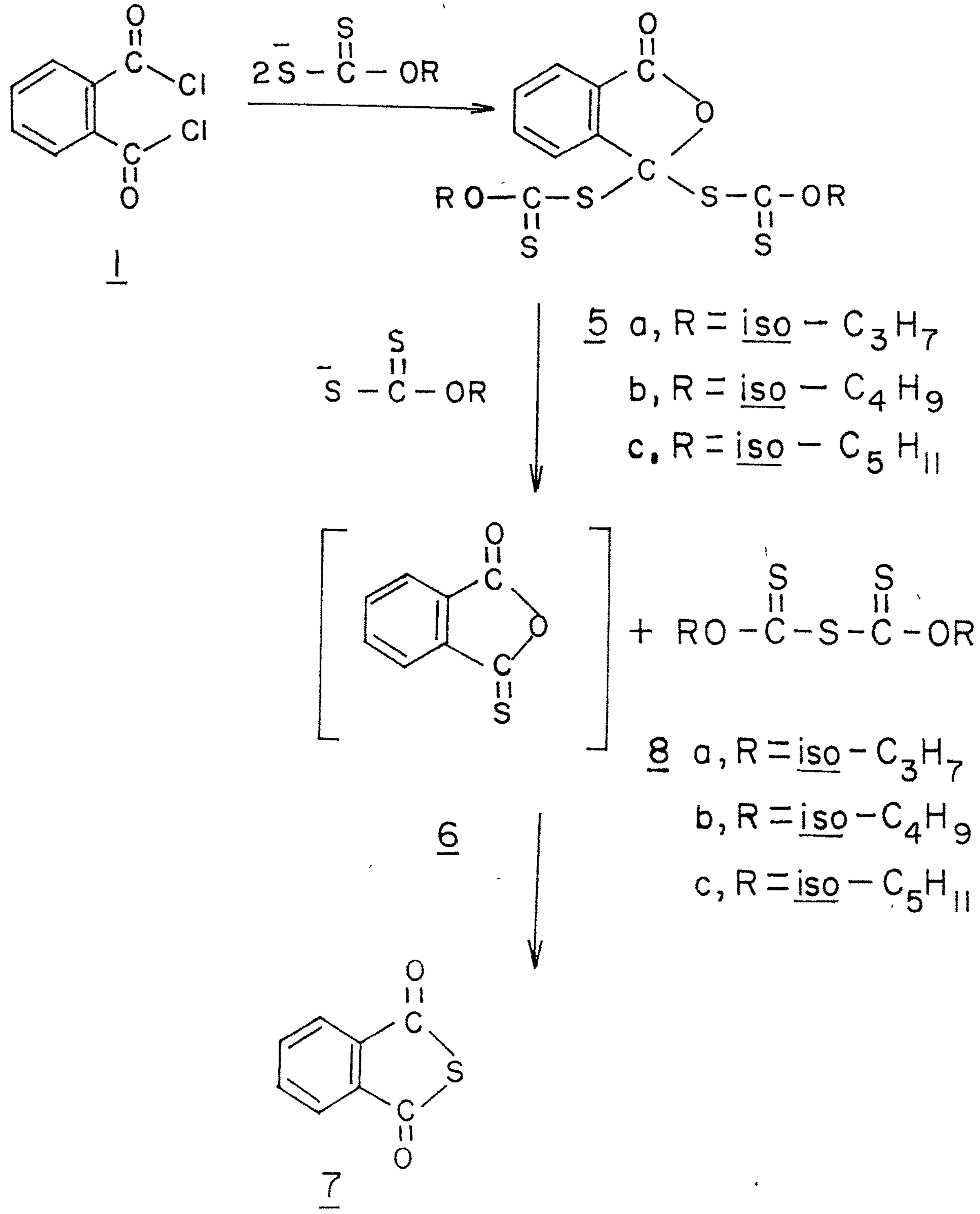
5 a, R = iso – C_3H_7
b, R = iso – C_4H_9
c, R = iso – C_5H_{11}

potassium-O-isopropylxanthate in 1:2 ratio, in ether solution, around 0°. The absorption spectrum was characterised by the presence of two absorption maxima at 288 nm and 394 nm respectively. Of these, the weak absorption band around 394 nm is characteristic of all acyl and aroyl xanthates containing the  $-\overset{\overset{O}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-OR$ chromophore.[1] It was further observed that the absorption maximum at 394 nm of a freshly prepared solution of the dixanthate 3a, disappeared after a few hours and a new absorption maximum was observed at 365 nm, characteristic of the unsymmetrical dixanthate 5a[2]. These findings are in support of the view that the symmetrical dixanthate 3 is actually formed at first, which then rapidly isomerises to the unsymmetrical derivative 5.

With a view to finding out whether the symmetrical dixanthate of the type 3 (Scheme 1) can be stabilized by changing the alkyl substituent on the xanthate, we have examined the reactions of 1 with different-O-alkylxanthates. Treatment of 1 with potassium-O-isobutylxanthate, for example, gave 43% yield of di-O-isobutyl S,S-phthaloyl dixanthate (5b). Similarly, the reaction of 1 with potassium-O-isoamylxanthate, gave 40% yield of unsymmetrical dixanthate 5c.

In continuation of our studies, we have examined the reaction of 1 with excess of potassium-O-alkylxanthates. These resulted in the formation of anhydrosulphide of alkylxanthic acid (8) and thiophthalic anhydride (7). Formation of anhydrosulphide of ethylxanthic acid was reported[4,5,6] from the reaction of potassium-O-ethylxanthate and ethyl chloroformate. Xanthic acid disulphides on treatment with KCN were reported[7] to give anhydrosulfides. Simmons et al.[8] have also reported the preparation of anhydrosulphide of ethylxanthic acid by the reaction of tetracyanodithiin with potassium-O-ethylxanthate. The direct formation of anhydrosulphide from the xanthate reaction was observed by Willcox,[9] during reaction of potassium-O-ethylxanthate and ether solution of acetyl chloride at room temperature. We have also examined the reaction of dixanthate 5 with potassium-O-alkyl xanthate and products isolated from the reaction mixture were same as in the reaction of 1 with excess of potassium-O-alkylxanthate. This supports the probable mechanism for the formation of anhydrosulfide (8) (Scheme 2). This indicates that anhydrosulfide (8) is formed through the formation of the dixanthate 5 and not directly from the reaction of 1 with excess of potassium-O-alkylxanthate. Our attempts to isolate,

SCHEME - 2



5 a, R = iso – C_3H_7
b, R = iso – C_4H_9
c, R = iso – C_5H_{11}

8 a, R = iso – C_3H_7
b, R = iso – C_4H_9
c, R = iso – C_5H_{11}

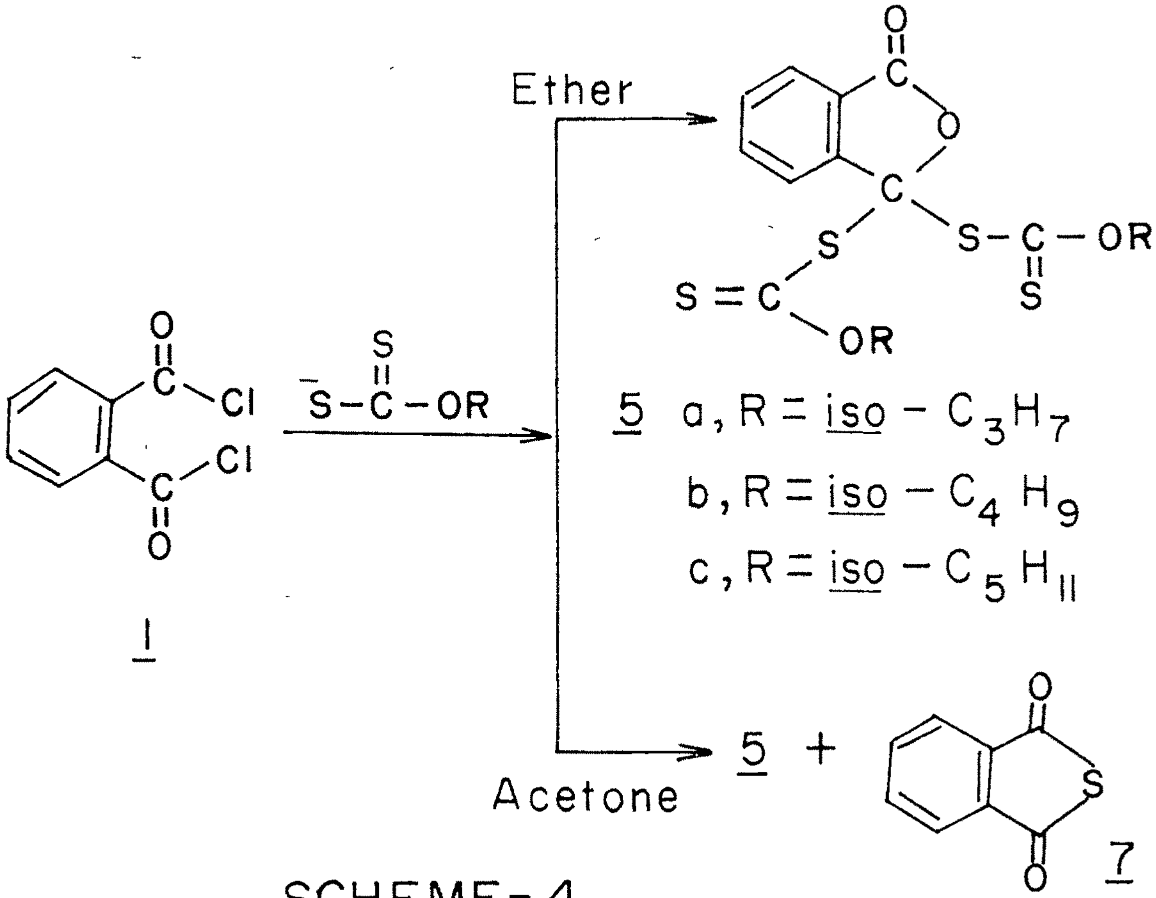
thionphthalic anhydride (6) from the reaction mixture were not successful which showed that thionphthalic anhydride (6) rapidly changes to thiophthalic anhydride[10] (7).

In continuation of this work, we have studied solvent effects in the synthesis of dixanthate 5. For example, acetone solution of 1, when treated with potassium-O-isopropylxanthate gave 46% of thiophthalic anhydride (7) and 14% of the dixanthate 5a. Whereas using ether as the solvent,[2] the dixanthates could be obtained in good yields (Scheme 3).

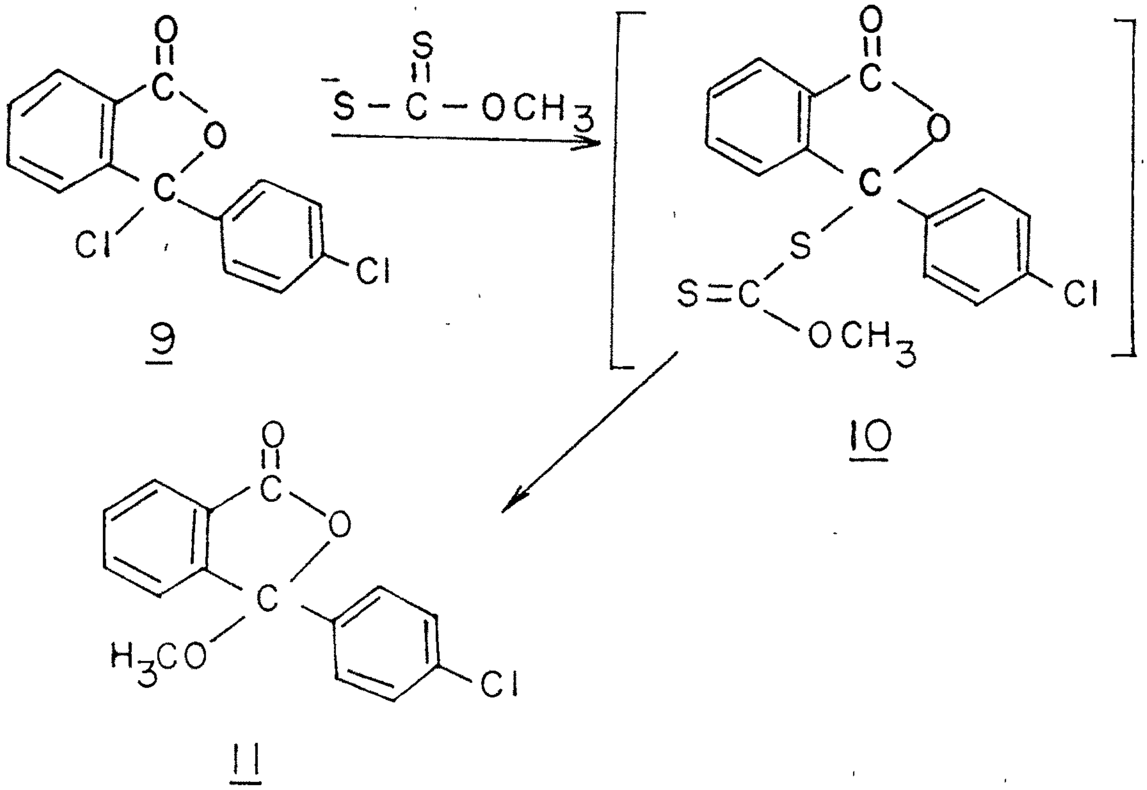
In our attempt to prepare substituted phthalyl xanthates, we have observed ready decomposition of O-methyl-S-(3-p-chlorophenylphthalyl)xanthate. For example, acetone solution of 3-chloro-3-(p-chlorophenyl)phthalide (9) when treated with potassium-O-methylxanthate at 60° for half an hour resulted in 3-methoxy-3-(p-chlorophenyl)phthalide (11) and not in expected xanthate 10 (Scheme 4).

A similar observation has been made by Willcox[11] and Richter[12] concerning the reaction of acid chloride and potassium-O-ethylxanthate. For example, O-ethyl-S-benzoylxanthate has been reported[12] to give ethyl

SCHEME-3



SCHEME-4



benzoate and carbon disulphide at 40°. This indicates that xanthate is formed first and then it decomposes to ester and carbon disulphide. During the reaction of **9** with potassium O-methylxanthate, we have observed the development of yellow colour of the solution during the reaction which slowly fades and results in the formation of **11** after removal of solvent. So we presume that the xanthate **10** was formed first which then decomposes to produce **11** and carbondisulphide.

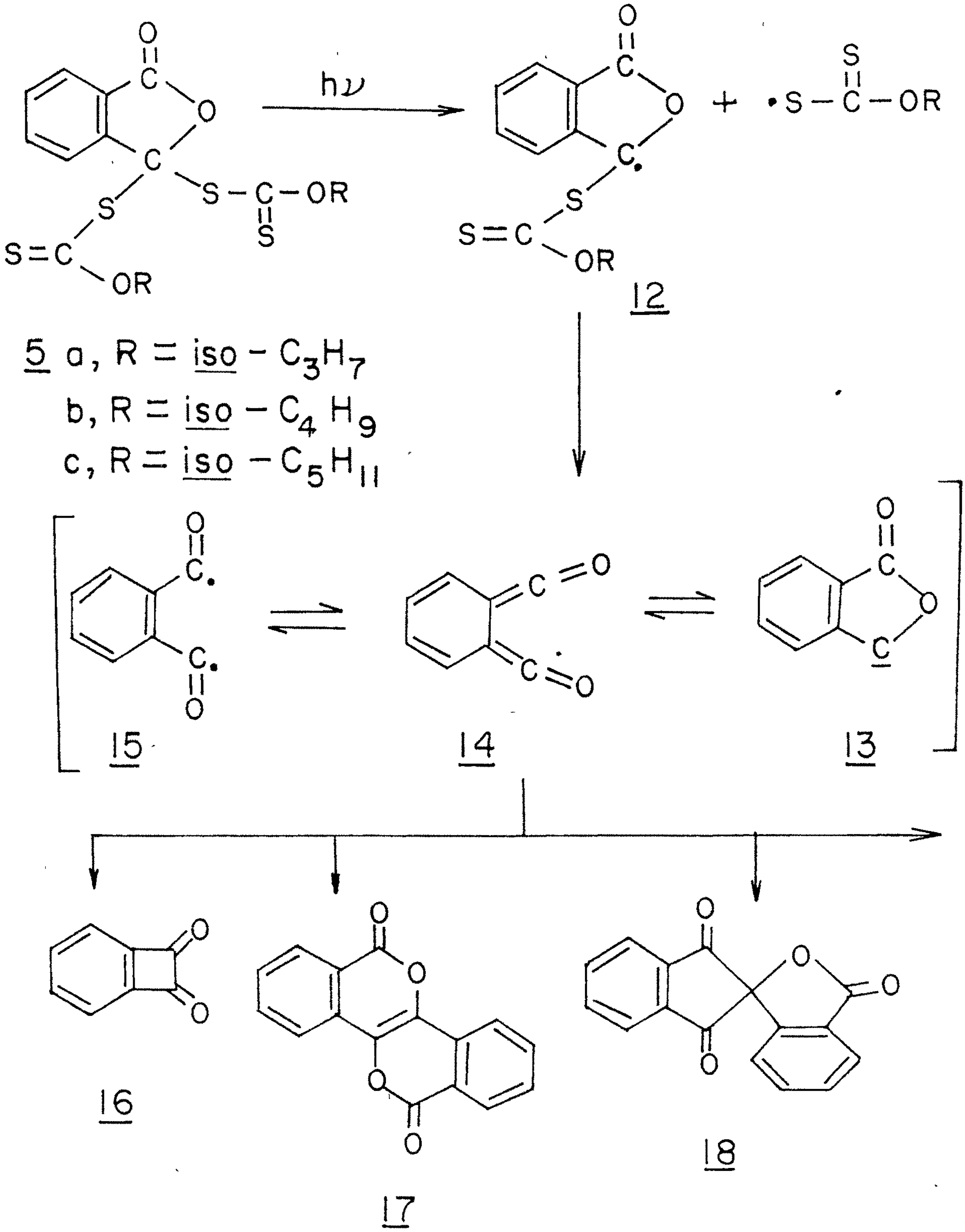
The thermal and photochemical transformation of an unsymmetrical phthaloyl dixanthate such as **5** has been reported earlier.[2] In the present studies, we have examined both the thermal and photochemical reactions of a few unsymmetrical phthaloyl dixanthates **5a**-c with a view to studying the nature of the products formed in these reactions.

Photolysis of acylxanthates are reported to give rise to the corresponding alkyl xanthates.[1] It has been shown that the photolysis of di-O-ethyl S,S-glutaryl xanthate gives a good yield of cyclopentane-1,2-dione.[1] A similar type of fragmentation have been reported in a few acyl[13] and aroyl xanthates[2,14,15] and dithiocarbamic anhydrides.[14,15,16] We have observed the fragmentation of C(S)-S bond in the photolysis of O-alkyl S-benzoyl xanthates.[17]

Photolysis of 5a in benzene solution at room temperature gave a 70% yield of trans-biphthalyl (20), as the only isolable product. Under similar conditions, the photolysis of other unsymmetrical phthaloyl dixanthates such as 5b and 5c gave 20 in yields ranging between 31-36%. The formation of 20 in the photolysis of unsymmetrical phthaloyl dixanthates suggests that the fragmentation may be taking place through a C-S bond fission giving rise to the radical intermediate 12, which then gives rise to the carbene intermediate 13, through a second C-S bond fission. Dimerisation of 13 would lead to trans-biphthalyl (20) (Scheme 5). It has not been possible to isolate either benzocyclobutenedione (16) or other dimeric products such as 17, 18, or 19 from this reaction.[18,19] A similar type of photochemical transformation involving C-S bond fission is reported in the case of 9,9-dixanthogenyl xanthene[20] and isomeric diaryl esters of dithiophthalic acid.[21,22]

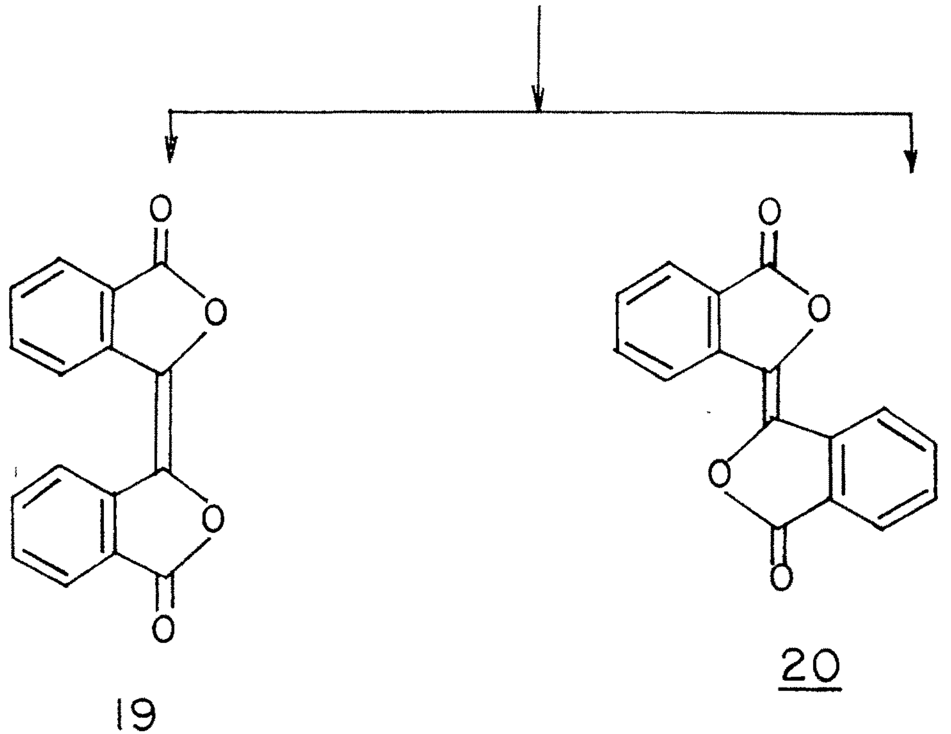
In order to study solvent effect in the photolysis of the dixanthate 5, we have also examined the photolysis of 5a in methanol at room temperature which resulted in the formation of trans-biphthalyl (20), as the only product in 61% yield.

SCHEME-5

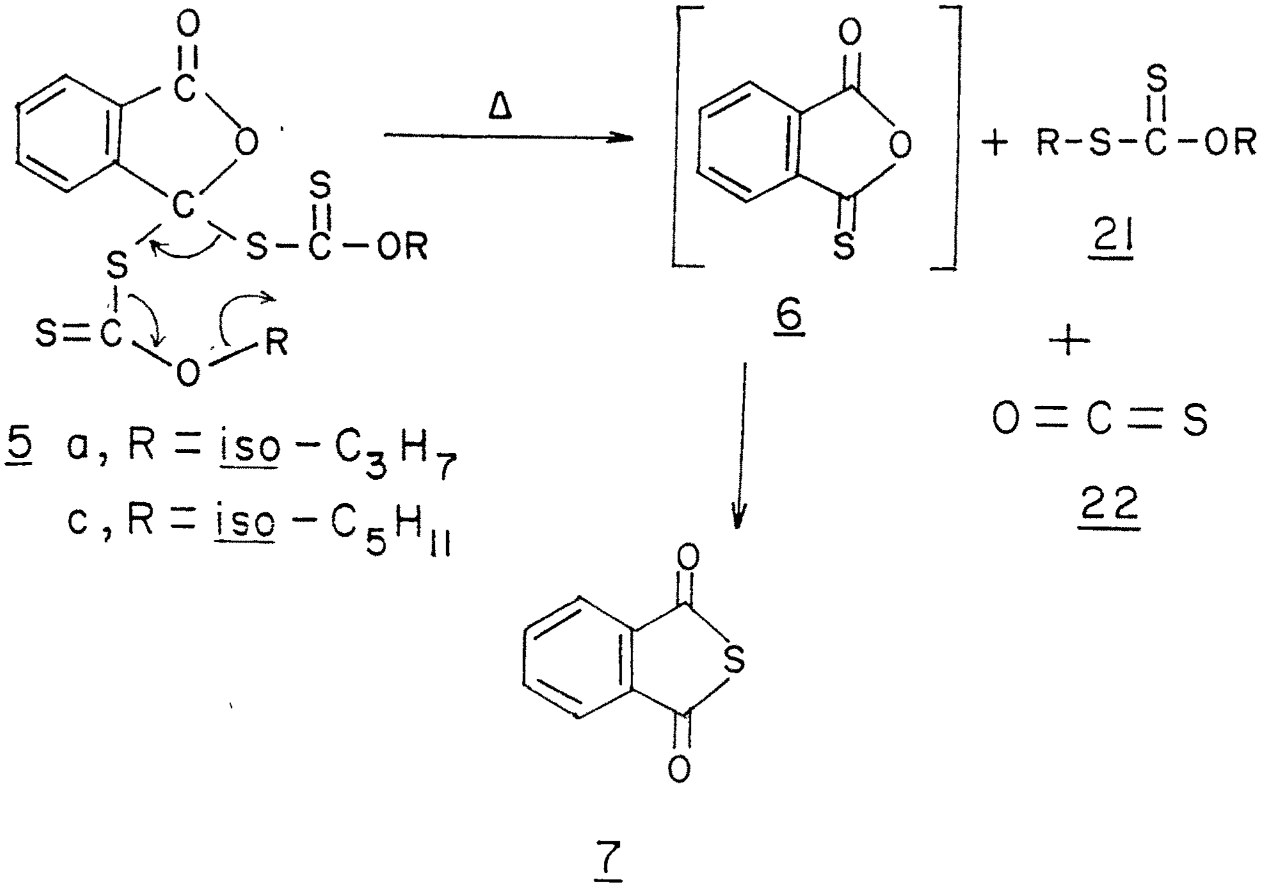


5 a, R = iso − C_3H_7
b, R = iso − C_4H_9
c, R = iso − C_5H_{11}

SCHEME -5 (Contd)



SCHEME-6



Thermal decomposition of acylxanthates are reported to give rise to a mixture of products.[1,23,24] Thus, ethylphenylacetylxanthate, for example, decomposes on heating to give a mixture of ethyl phenylacetate and carbon disulphide. The mechanism involving a four membered cyclic transition state has been suggested for this reaction.[1] During the present investigation, we have examined the thermal decomposition of several unsymmetrical phthaloyl dixanthates with a view to studying the nature of the products formed in these reactions. Heating unsymmetrical di-O-isopropylphthaloyldixanthate (5a) to around 250° for about 30 minutes, for example, gave rise to a mixture of products which include trans-biphthalyl (20) (24%), thio-phthalic anhydride (7) (29%), O,S-diisopropylxanthate (21a) (16%) and carbonyl sulphide 22 (82%), identified through its piperidinium salt.[25] (Scheme 6).

Similarly, the thermal decomposition of unsymmetrical phthaloyl dixanthate 5c, gave rise to a mixture of trans-biphthalyl, thio-phthalic anhydride, carbonyl sulphide and the corresponding O,S-diisoamyl xanthate (21c). The formation of trans-biphthalyl (20) in the thermal decomposition of these dixanthates suggests that a minor mode of decomposition is through the carbene intermediate 13, which dimerises to give trans-biphthalyl. The exact nature of the pyrolytic decomposition of the unsymmetrical phthaloyl dixanthate is not very clearly understood. A probable mechanism which accounts for the formation of products such as carbonyl sulphide (22), thiophthalic anhydride (7) and O,S-dialkylxanthate 21, is one which involves a cyclic concerted process as shown in Scheme 6. The formation of thiophthalic anhydride may be through a rearrangement of the initially formed thionphthalic anhydride (6).[10]

In continuation of this work, we have carried out reaction of the dixanthate 5 with hydrazine hydrate and hydrogen peroxide. For example, ether solution of the dixanthate 5a when treated with hydrazine hydrate at room temperature, gave 60% yield of phthalaz-1,4-dione (23).[26] Reaction of phenyl hydrazine and hydrazine hydrate on C-S bond of carbonyl carbon are known in case of thiophthalic anhydride, substituted phthalides and 2-dithiobenzoyl.[26] Our next approach was to study the oxidation reaction of phthaloyl dixanthate such as 5. Dithiocarbamic acid esters[27] and xanthates[28] were reported to undergo oxidation reaction with hydrogen peroxide. It has been shown that  $O-\overset{O}{\overset{\|}{C}}-S-$ bond gets transformed into O-H in these oxidations.[28] The dixanthate **5a**, for example, in acetic acid when treated with hydrogen peroxide gave 60% yield of phthalic acid (**24**). A reference sample of **5a**, in acetic acid alone did not show any change in the same interval of time (Scheme 7).

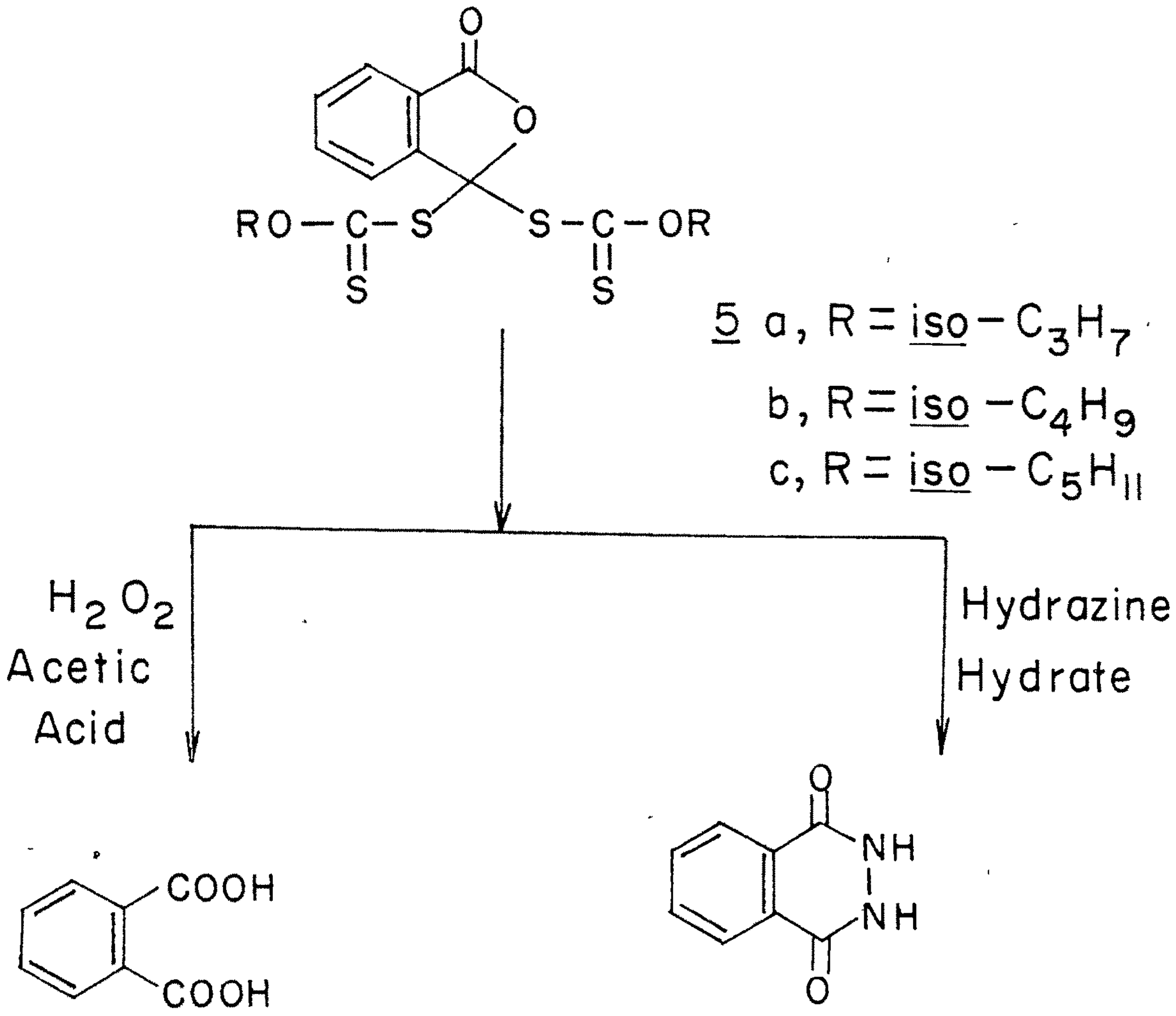
3.3 Experimental

IR spectra were recorded on a Beckman IR-20 Infrared Spectrophotometer and UV Spectra were recorded on Specord UV Spectrophotometer. NMR traces were recorded on a Perkin Elmer R-32 NMR Spectrometer using tetramethylsilane as internal standard. Irradiations were carried out in Hanovia photochemical reaction assembly with a quartz immersion well and medium pressure mercury lamp (100 watt), under dry oxygen free nitrogen.

Starting materials

Potassium-O-methylxanthate, m.p. 184° ; potassium O-isopropylxanthate, m.p. 274° ; potassium-O-isobutylxanthate, m.p. 258° and potassium-O-iso-amyl

SCHEME - 7



5 a, $R = \underline{iso}-C_3H_7$
b, $R = \underline{iso}-C_4H_9$
c, $R = \underline{iso}-C_5H_{11}$

24

23

xanthate, m.p. 265° were prepared by reported procedures.[29] Symmetrical phthaloyl dichloride, b.p. 131-135° (11 mm) was supplied by Fluka AG, Switzerland. 3-Chloro-3-(p-chlorophenyl)phthalide was prepared by known procedure.[30]

Unsymmetrical Di-O-isopropyl S,S-phthaloyl Dixanthate (5a) :

To a solution of 1 (2.03 g, 0.01 mole) in diethyl ether (30 ml), maintained around 0° was added potassium-O-isopropylxanthate (3.48 g, 0.02 mole) in small portions, over a period of 30 min. with constant stirring. Stirring was continued for additional 30 min. at room temperature. Filtration of precipitated potassium chloride and removal of the solvent under vacuum gave residue which was dissolved in methylene chloride (25 ml) and washed with 1% $NaHCO_3$ solution. The methylene chloride extract was repeatedly washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent in vacuum gave 1.65 g (42%) of the xanthate 5a, which melted at 105-7°, on recrystallisation from a mixture (1:1), of methylene chloride and petroleum ether (b.p. 40-60°).

Anal. Calcd for $C_{16}H_{18}O_4S_4$: C, 47.77 ; H, 4.47

Found : C, 47.41 ; H, 4.66

IR Spectrum (Nujol) : ν max : 1780 (γ-lactone), 1385 - 1370 (Isopropyl doublet) and 1260 cm^{-1} (C=S),

UV spectrum (CH_2Cl_2) λ max : 290 (ϵ, 56, 531) and 365 nm (ϵ, 127).

NMR Spectrum (CCl_4) : 7.7 ppm (4H, aromatic), 5.6 ppm (2H) and 1.4-1.0 ppm (Two doublets, 12H).

Treatment of Diisopropyl S,S-phthaloyl dixanthate (5a) with Raney-Nickel

A mixture of 5a (1 g, 0.0025 mole) with Raney-Nickel (6 g) in acetone (50 ml) was refluxed for 5 hrs. Removal of the unchanged nickel and the solvent gave 0.20 g (60%) of phthalide,[31] which melted at 75° (mmp), after recrystallisation from methylenechloride.

Reaction of Symmetrical Phthaloyldichloride (1) with excess of potassium-O-isopropylxanthate

Phthaloyl dichloride (2.03 g, 0.01 mole) was taken in acetone (50 ml) solution. To this potassium-O-isopropyl xanthate (6.96 g, 0.04 mole) was added below 0°, stirring was continued for 30 min. at 0° and additional 30 min. at room temperature. Evaporation of solvent after removal of unreacted potassium-O-isopropyl xanthate yielded 1 g (61%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 1.4 g (59%) of anhydrosulfide of isopropyl xanthic acid (8a) m.p. 52-54° (lit. m.p. 54°).[7]

Anal. Calcd for $C_8H_{14}O_2S_3$: C, 40.33 ; H, 5.80

Found : C, 39.44 ; H, 5.50

UV Spectrum (Ethanol) λ max : 222 (ϵ, 13,630), 258 (ϵ, 11, 150), 303 (ϵ, 15, 490), 357 (ϵ, 178) and 412 nm (ϵ, 161).

Reaction of unsymmetrical phthaloyldixanthate (5a) with potassium-O-isopropyl xanthate :

An acetone solution (40 ml) of 5a (2 g, 0.005 mole) was treated with potassium-O-isopropyl xanthate (0.87 g, 0.005 mole) at room temperature for 30 mins. Evaporation of solvent after removal of unreacted potassium-O-isopropyl xanthate yielded 0.40 g (49%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 0.90 g (76%) of anhydrosulphide of isopropylxanthic acid (8a) mp. 52-54° (Lit. m.p. 54°).[7]

Reaction of sym. phthaloyldichloride (1) with potassium-O-isopropyl xanthate

Phthaloyl dichloride (2.03 g, 0.01 mole) was taken in acetone (40 ml) solution. To this potassium-O-isopropyl xanthate (3.48 g, 0.02 mole) was added around 0°, stirring was continued for 30 min at 0° and additional 30 min at room temperature. Evaporation of solvent after filtration of precipitated potassium chloride gave residue which was dissolved in methylene chloride (30 ml) and washed with 1% $NaHCO_3$ solution. The methylene chloride extract after usual work up gave 0.75 g (46%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 0.54 g (14%) of the xanthate 5a, m.p. 105-7°.

Photolysis of Di-O-isopropyl S,S-Phthaloyl dixanthate (5a) :

A solution of 5a (1 g, 0.0025 mole) in dry benzene (A.R. ; 450 ml) was irradiated for 7 hr. Removal of the solvent gave a gummy solid which on treatment with petroleum ether resulted in 0.23 g (70%) of trans-biphthalyl (20), which melted over the range m.p. 350-52° (Lit. m.p. 352-54°)[18], on recrystallisation from acetic acid. A solution of the dixanthate 5a subjected to similar conditions in the absence of light did not show any appreciable change.

A solution of the dixanthate 5a (0.5 g, 0.0012 mole) in methanol (450 ml) was irradiated for 8.5 hr. work up as above gave 0.1 g (61%) of trans-biphthalyl (20) m.p. 351-53°.

Thermal Decomposition of Di-O-isopropyl S,S-phthaloyl dixanthate (5a)

The xanthate 5a (1 g, 0.0025 mole) was heated under a continuous stream of nitrogen in an oil bath maintained at 250° for 30 min. The gaseous product was bubbled through a solution of piperidine (5 ml) in methylene chloride (50 ml). Removal of the solvent gave 0.94 g of piperidinium-1-piperidine carbothiolate m.p. 112° (lit. m.p. 112°)[25] corresponding to 82% yield of carbonyl sulphide (22).

Treatment of pyrolysed mixture with methylene chloride gave 0.08 g (24%) of trans-biphthalyl, m.p. 350-52° (Lit. m.p. 352-54°)[18] on recrystallisation from acetic acid. Removal of the solvent from methylene chloride extract gave a mixture of products, which on treatment with petroleum ether (b.p. 40-60°) gave 0.12 g (29%) of thiophthalic anhydride, m.p. 110° (mmp).

The petroleum ether soluble fraction was chromatographed over Alumina, to give 0.07 g (16%) of o,s-diisopropyl xanthate (21a), identified on TLC (Silica gel) with the authentic sample using methylene chloride and petroleum ether (1:1) as eluent.

Reaction of Di-O-isopropyl S,S-phthaloyldixanthate (5a) with hydrazine hydrate

To a solution of the xanthate 5a (0.40 g, 0.001 mole) in ether (20 ml) was added hydrazine hydrate (0.1 g, 0.002 mole) drop wise with stirring for 15 minutes at room temperature. Precipitated product was filtered, dried and recrystallised from ethanol. It gave 0.1 g (60%) of phthalaz-1,4-dione (23), m.p. 315° (mmp).[26]

Reaction of Di-O-isopropyl S,S-phthaloyldixanthate (5a) with hydrogen peroxide

To a solution of the xanthate 5a (0.40 g, 0.001 mole) in glacial acetic acid (15 ml) was added hydrogen peroxide (2.5 ml, 30%) and the reaction mixture was kept for 8 days. Water was added to precipitate the product. It was filtered, dried and identified as phthalic acid (0.10 g, 60%) m.p. 205° (dec.).

A reference sample of 5a (0.40 g, 0.001 mole) in glacial acetic acid (15 ml) was kept for 8 days and worked up as above gave the original dixanthate 5a, m.p. 105-7°.

Unsymmetrical Di-O-isobutyl S,S-phthaloyldixanthate (5b)

Treatment of a solution of 1 (2.03 g, 0.01 mole) in diethyl ether (30 ml) with potassium-O-isobutyl xanthate (3.76 g, 0.02 mole) around 0° and work up of the mixture in the usual manner gave 1.85 g (43%) of di-O-isobutyl S,S-phthaloyldixanthate (5b), which melted at 72-74° on recrystallisation from a mixture (1:1) of methylene chloride and petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{18}H_{22}O_4S_4$: C, 50.23 ; H, 5.11

Found : C, 50.70 ; H, 5.47

IR Spectrum (Nujol) νmax : 1780 (γ-lactone), 1385 - 1370 $\left(\mathrm{CH}\begin{smallmatrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{smallmatrix}\right)$ and 1270 cm^{-1} (C=S).

UV Spectrum (CH_2Cl_2) λ max : 290 (ϵ, 32, 380) and 365 nm (ϵ, 106).

Reaction of symmetrical Phthaloyldichloride (1) with excess of potassium-O-isobutylxanthate

To a solution of 1 (2.03 g, 0.01 mole) in acetone (50 ml) was added potassium-O-isobutyl xanthate (7.52 g, 0.04 mole) around 0° and stirring continued as in previous case. Work-up of the mixture in the usual manner gave 1.20 g (75%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 1.13 g (42%) of anhydrosulfide of isobutylxanthic acid (8b),

n_D^{25} 1.5470

Anal : Calcd for $C_{10}H_{18}O_2S_3$: C, 45.11 ; H, 6.70

Found : C, 44.65 ; H, 6.97

UV Spectrum (Ethanol) λ max : 222 (ε, 12, 750), 250 (ε, 12, 750), 303 (ε, 16, 350), 357 (ε, 222) and 412 nm (ε, 176).

Reaction of unsymmetrical phthaloyldixanthate (5b) with potassium-O-isobutylxanthate

An acetone solution (40 ml) of 5b (2.15 g, 0.005 mole) was treated with potassium-O-isobutyl xanthate (0.94 g, 0.005 mole) at room temperature for 30 minutes. Work up of the mixture in the usual manner gave 0.45 g (56%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 1.0 g (75%) of anhydrosulfide of isobutyl xanthic acid (8b).

Reaction of Symmetrical phthaloyl dichloride (1) with potassium-O-isobutyl xanthate

Phthaloyl dichloride (2.03 g, 0.01 mole) was taken in acetone (40 ml) solution. To this potassium O-isobutyl xanthate (3.76 g, 0.02 mole) was added around 0° and stirring continued as in the previous case. Work up of the mixture in usual manner gave 0.80 g (50%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 0.75 g (17%) of the xanthate (5b, m.p. 72-74°.

Photolysis of Di-O-isobutyl S,S-phthaloyldixanthate (5b)

A solution of 5b (1 g, 0.0023 mole) in benzene (450 ml) was irradiated at room temperature for 7.5 hr. Removal of the solvent under vacuum gave a product which on recrystallisation from acetic acid gave 0.11 g (36%) of trans-biphthalyl (20), m.p. 352-54°.

Reaction of Di-O-isobutyl S,S-phthaloyldixanthate (5b) with hydrazine hydrate

To a solution of the xanthate 5b (1.29 g, 0.003 mole) in ether (40 ml) was added hydrazine hydrate (0.3 g, 0.006 mole) dropwise with 15 minutes stirring at room temperature. Work-up of the mixture in usual manner gave 0.13 g (25%) of phthalaz-1,4-dione (23) m.p. 315° (mmp).

Reaction of Di-O-isobutyl S,S-phthaloyldixanthate (5b) with hydrogen peroxide

To a solution of the xanthate 5b (0.3g, 0.0007 mole) in glacial acetic acid (10 ml) was added hydrogen peroxide (2 ml, 30%) and the reaction mixture was kept for 8 days. Water was added to precipitate the product. It was filtered, dried and identified as phthalic acid (0.07 g, 65%) m.p. 205° (dec.).

A reference sample of 5b (0.3 g, 0.0007 mole) in glacial acetic acid (10 ml) was kept for 8 days and worked up as above gave original dixanthate 5b, m.p. 74°.

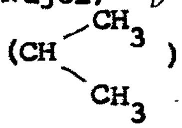
Unsymmetrical Di-O-isoamyl S,S-phthaloyldixanthate (5c)

Treatment of a solution of 1 (2.03 g, 0.01 mole) in ether (30 ml) with potassium-O-isoamylxanthate (4.04 g, 0.02 mole) around 0° and work-up of the mixture in the usual manner gave 1.82 g (40%) of the xanthate 5c, m.p. 87–89°, after recrystallisation from a mixture (1:1) of methylene chloride and petroleum ether (b.p. 40–60°).

Anal : Calcd for $C_{20}H_{26}O_4S_4$: C, 52.40 ; H, 5.70

Found : C, 52.34 ; H, 6.03

IR Spectrum (Nujol) ν max : 1780 (γ-lactone), 1385 – 1370



$(CH(CH_3)_2)$

and 1270 cm^{-1} (C=S).

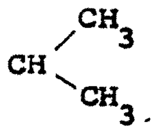
UV Spectrum (CH_2Cl_2) λ max : 290 (ϵ, 43, 620) and 365 nm (ϵ, 114).

Reaction of symmetrical phthaloyldichloride (1) with excess of potassium-O-isoamylxanthate

To a solution of 1 (2.03 g, 0.01 mole) in acetone (40 ml) was added potassium-O-isoamylxanthate (6.06 g, 0.03 mole) around 0° and stirring continued as in the previous case. Work up of the mixture in the usual manner gave 1.14 g (70%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 1.90 g (65%) of anhydrosulfide of isoamyl xanthic acid (8c), n_D^{25} 1.5440

Anal : Calcd for $C_{12}H_{22}O_2S_3$: C, 49.00 ; H, 7.40

Found : C, 49.80 ; H, 7.63

IR Spectrum (Liq. film) ν max : 1390 - 1270  $CH\langle^{CH_3}_{CH_3}$.
and 1230 cm^{-1} (C=S).

UV Spectrum (Ethanol) λ max : 220 (ϵ, 23, 001), 250 (ϵ, 22, 370), 298 (ϵ, 24, 920), 357 (ϵ, 371) and 412 nm (ϵ, 321).

Reaction of unsymmetrical phthaloyldixanthate (5c) with potassium-O-isoamylxanthate

An acetone solution (40 ml) of **5c** (2.29 g, 0.005 mole) was treated with potassium-O-isoamyl xanthate (1.0 g, 0.005 mole) at room temperature for 30 minutes. Work-up of the mixture in the usual manner gave 0.50 g (61%) thiophthalic anhydride (**7**)^{10} m.p. 110° (mmp) and 1.2 g (82%) of anhydrosulfide of isoamylxanthic acid (**8c**).

Reaction of symmetrical phthaloyl dichloride (1) with potassium-O-isoamylxanthate

Phthaloyl dichloride (2.03 g, 0.01 mole) was taken in acetone (40 ml) solution. To this potassium-O-isoamylxanthate (4.04 g, 0.02 mole) was added around 0° and stirring continued as in the previous case. Work-up of the mixture in the usual manner gave 0.87 g

(53%) thiophthalic anhydride (7)[10] m.p. 110° (mmp) and 0.70 g (15%) of the xanthate 5c, m.p. 87-89°.

Photolysis of Di-O-isoamyl S,S-phthaloyldixanthate (5c)

A solution of 5c (1 g, 0.002 mole) in benzene (450 ml) was irradiated at room temperature for 7 hrs. Removal of the solvent under vacuum gave a product which on recrystallisation from acetic acid gave 0.09g (31%) of trans-biphthalyl (20), m.p. 352-54°.

Thermal Decomposition of Di-O-isoamyl S,S-phthaloyl dixanthate (5c)

Dixanthate 5c (1 g, 0.002 mole) was heated around 250° for 30 minutes under a stream of nitrogen and the evolved gases were bubbled through a solution of piperidine (5 ml) in methylene chloride (50 ml). Removal of solvent gave 0.80 g of piperidinium-1-piperidine carbothiolate m.p. 112° (Lit. m.p. 112°)[25] corresponding to 80% yield of carbonyl sulphide (22).

Treatment of pyrolysed mixture with methylene chloride gave 0.02 g (7%) of trans-biphthalyl, m.p. 350-52° (Lit. m.p. 352-54°)[18] on recrystallisation from acetic acid. Removal of the solvent from methylene chloride extract gave a mixture of products, which on treatment with petroleum ether (b.p. 40-60°), gave 0.11 g (31%) of thiophthalic anhydride m.p. 110° (mmp).

The petroleum ether soluble fraction was chromatographed over Alumina, to give 0.08 g (16%) of O,S-diisoamylxanthate (21c), identified on TLC (silica gel) with the authentic sample using methylene chloride and petroleum ether (1:1) as eluent.

Reaction of Di-O-isoamyl S,S-phthaloyldixanthate (5c) with hydrazine hydrate

To a solution of the xanthate 5c (0.46 g, 0.001 mole) in ether (20 ml) was added hydrazine hydrate (0.1 g, 0.002 mole) dropwise with 15 minutes stirring at room temperature. Work-up of the mixture in usual manner gave 0.06 g (40%) of phthalaz-1,4-dione (23) m.p. 315° (mmp).

Reaction of Di-O-isoamyl S,S-phthaloyldixanthate (5c) with hydrogen peroxide

To a solution of the xanthate 5c (0.46 g, 0.001 mole) in glacial acetic acid (15 ml) was added hydrogen peroxide (2.5 ml, 30%) and the reaction mixture was kept for 8 days. Water was added to precipitate the product.

It was filtered, dried and identified as phthalic acid (0.09 g, 57%) m.p. 205° (dec.).

Reaction of 3-chloro-3-(p-chlorophenyl) phthalide (9) with potassium-O-methylxanthate

To a solution of 9 (5.37 g, 0.019 mole) in acetone (100 ml) was added potassium-O-methylxanthate (2.81 g, 0.019 mole) at room temperature. The mixture was refluxed for 30 minutes. Removal of solvent after filtration of precipitated potassium chloride gave sticky mass which was dissolved in minimum quantity of methylenechloride and chromatographed over Alumina (eluent, Benzene), to give 1.9 g (37%) of 3-methoxy-3-(p-chlorophenyl) phthalide (11) m.p. 109° (Lit. m.p. 109°).

Anal : Calcd for $C_{15}H_{11}O_3Cl$: C, 65.58 ; H, 4.00

Found : C, 65.43, ; H, 4.47

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