CHAPTER - IV

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF O-ALKYL-S-PHTHALAYLGLYCYL XANTHATES

4.1 Abstract

The reaction of phthalylglycyl chloride with potassium-O-alkyl xanthates around 0° in ether solution gave the corresponding O-alkyl-S-phthalylglycyl xanthates. Similarly, O-alkyl-S-phthalylalanyl xanthates were prepared from the reaction of phthalylalanyl chloride with potassium-O-alkylxanthates. Irradiation of O-alkyl-S-phthalylglycyl xanthates for 1 hr resulted in the formation of N-phthalimido methylxanthates. However, O-alkyl-S-phthalylalanyl xanthates on irradiation gave a mixture of products consisting of xanthic acid disulphide, phthalyl alanine and thioanhydride of phthalylalanine. Thermal decomposition of O-alkyl-S-phthalylglycyl and S-phthalylalanyl xanthates gave the corresponding esters and carbon disulphide.

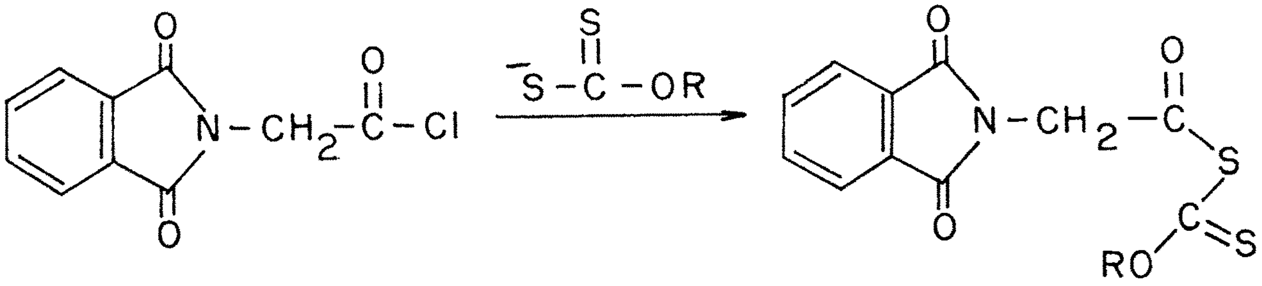
4.2 Results and Discussion

Few examples of acyl xanthates have been recorded in the literature. The most adequately described are several aroyl xanthates.[1] The xanthate derivatives of aliphatic acids are generally considered to be unstable.[2] It has been reported that phthalimides[3] and succinimides[4] with a sulfide function in their N-alkyl side chain undergo facile and regeoselective photocyclization to give azathiacyclols and pyrrolooxazolidines respectively. Keeping this view in mind, O-alkyl-S-phthalylglycyl and O-alkyl-S-phthalylalanyl xanthates were prepared.

Treatment of an ether solution of phthalyl glycyl chloride (1) with potassium-O-alkyl xanthates around 0° gave phthalylglycyl xanthates (2a-e) in good yields. (Scheme 1).

The structure of these xanthates 2a-e have been arrived at on the basis of analytical results and spectral data. The IR spectra of 2a-e showed absorption bands at 1720 and 1240 cm^{-1} due to presence of imide and thiocarbonyl groups respectively. The UV spectra of 2a-e showed absorption maximum at 395 nm, characteristic of aroyl xanthates.[2,5] The NMR spectrum (Fig. 1) of 2a showed a multiplet centred around 7.7 ppm (4H) due to aromatic protons, a singlet at 4.6 ppm (2H) due to methylene protons, a quartet at 4.7 ppm (2H) due to $-OCH_2$ protons and a triplet at 1.5 ppm (3H) due to methyl protons. Further evidence concerning the structure of 2a was derived from the conversion of this xanthate to phthalimidoacetaldehyde.

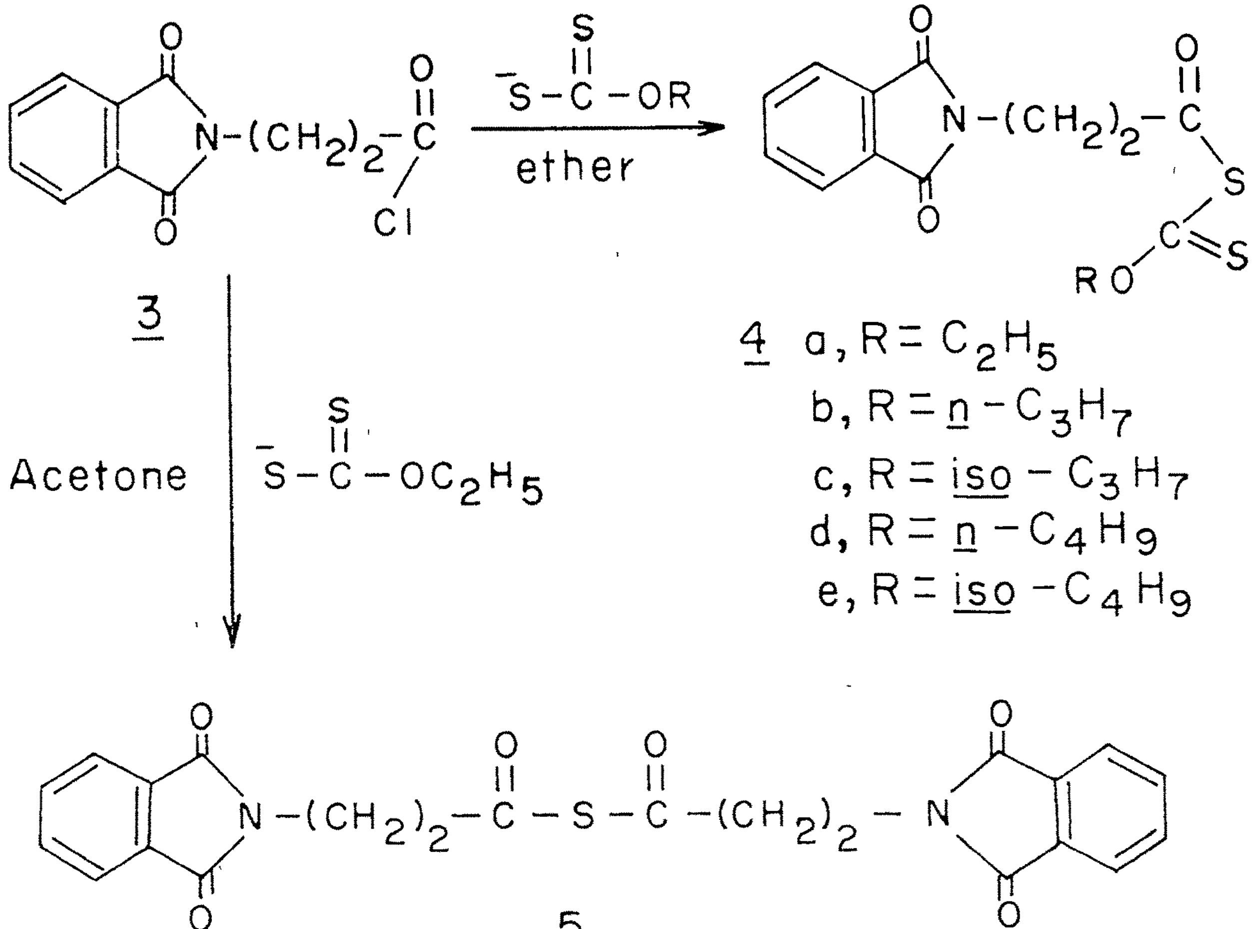
SCHEME-1



1

2 a, R = C_2H_5
b, R = n - C_3H_7
c, R = iso - C_3H_7
d, R = n - C_4H_9
e, R = iso - C_4H_9

SCHEME-2



3

4 a, R = C_2H_5
b, R = n - C_3H_7
c, R = iso - C_3H_7
d, R = n - C_4H_9
e, R = iso - C_4H_9

5

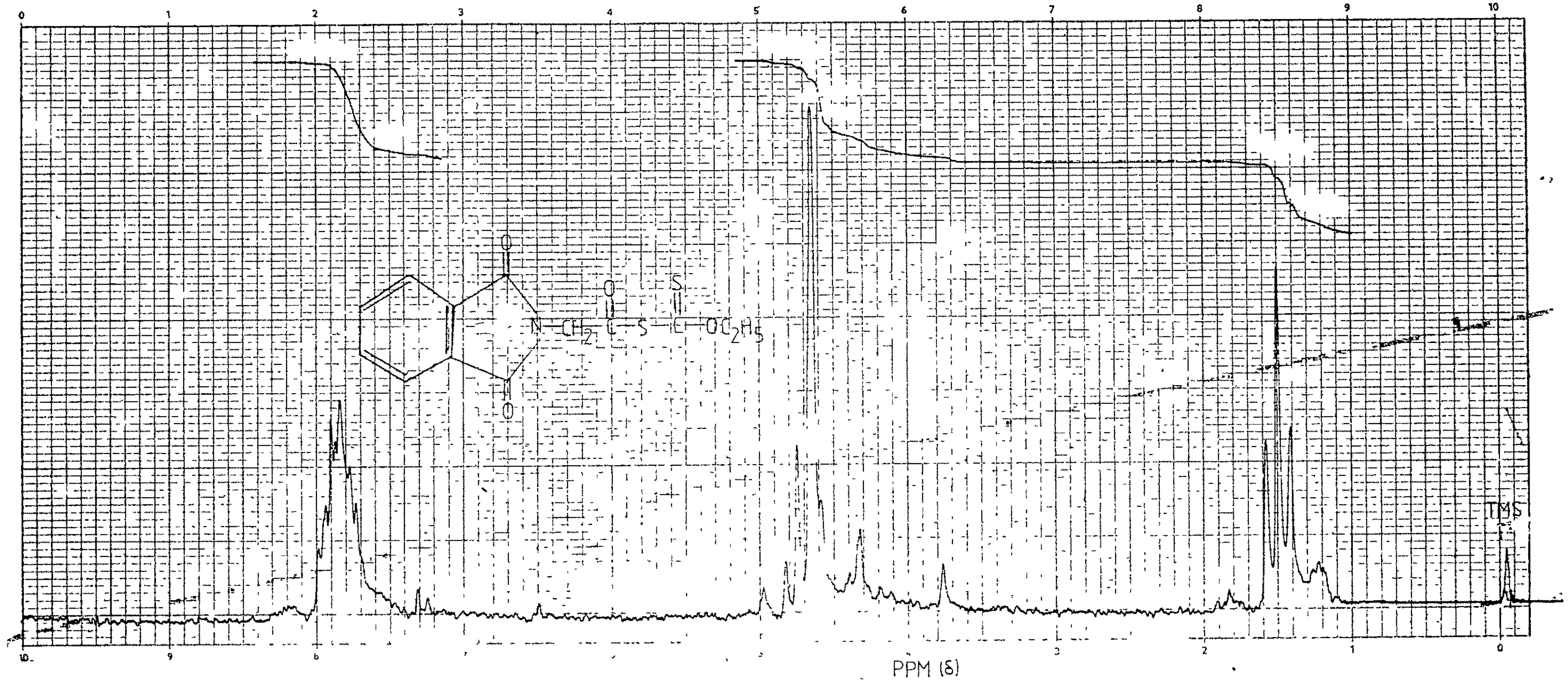


Fig. 1 NMR Spectrum (90 mcs) of O-ethyl-S-phthalylglycyl xanthate (2a)

Similarly, an ether solution of phthalylalanyl chloride (3) was treated with potassium-O-alkyl xanthates around 0° to give phthalylalanyl xanthate (4a-e) (Scheme 2).

The structure of these xanthates (4a-e) were confirmed on the basis of analytical and spectral data. The IR spectrum of 4c showed absorption bands at 1720, 1385, 1370 (doublet) and 1260 cm^{-1} due to presence of imide, isopropyl and thiocarbonyl groups respectively. The UV spectrum of 4c showed absorption maximum at 395 nm, characteristic of aroyl xanthates.[2,5] The NMR spectrum of 4c showed a multiplet centred around 7.7 ppm (4H) due to aromatic protons, two triplets at 4.0 and 3.1 ppm (4H) due to two methylene protons and a doublet at 1.5 ppm (6H) due to two methyl protons.

In a representative run, an acetone solution of phthalylalanyl chloride (3) was treated with potassium-O-ethyl xanthate around 0° gave in 38% yield of thioanhydride of phthalylalanine (5) m.p. 197° and not the expected xanthate 4a. A similar observation has been made in the attempted preparation of a few other acyl xanthates.[2,6,7]

It is reported that the photolysis of acyl xanthates[2,7] proceed through a free radical pathway involving the initial fragmentation of a CO-S bond, resulting in the formation of acyl and xanthate radicals which ultimately produce the corresponding alkyl xanthate.[2]

Singh and George[7] have reported that the photolysis of O-ethyl-S-diphenyl acetyl xanthate, gave rise to a mixture of carbon monoxide and 1,1,2,2-tetraphenyl ethane. Thermal decomposition of this substrate, on the other hand, gave ethyldiphenyl acetate and carbon disulphide. O-ethyl-S-triphenylacetyl xanthate, on photolysis gave triphenylmethyl peroxide. Thermal decomposition of this xanthate, on the other hand, gave a mixture of carbon disulphide and triphenyl thioacetic anhydride.

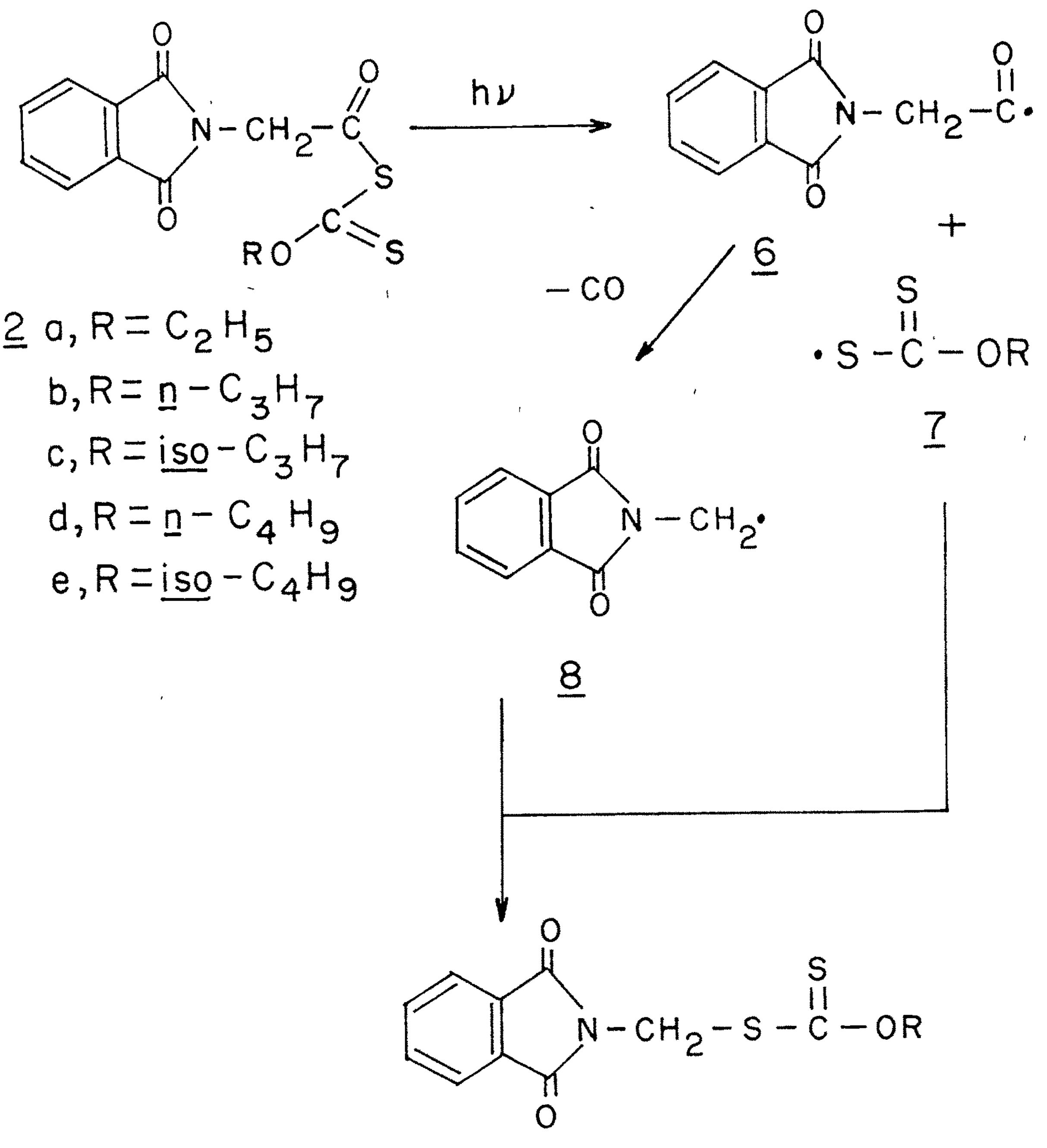
A similar type of fragmentation has been reported on the photolysis of several carboxylicdithiocarbamic anhydrides[8,9]; Benzoyl xanthates[5], phthaloyl dixanthates[6,10,11] and O-alkyl-S-phthalyl xanthates.[12] The project of the present investigation was to examine both the photochemical and thermal transformations of a few acyl xanthates with a view to studying the nature of the products formed in these reactions and also to examining the mode of these fragmentations.

Photolysis of these xanthates 2a-e in benzene solution resulted in the formation of N-phthalimido methyl xanthates (9). The formation of this product can be explained in terms of an initial fission of CO-S bond to give the corresponding acyl radical 6, which on decarbonylation gave N-phthalimidomethyl radical (8). The decarbonylated radical 8 can combine with the corresponding xanthate radical (7) to give the corresponding xanthates 9 as shown in Scheme 3.[2]

The identity of this product was confirmed on the basis of analytical results and spectral data. The IR spectrum of 9a showed absorption bands at 1720 and 1230 cm^{-1} due to presence of imide and thiocarbonyl groups. The UV spectrum of 9a showed an absorption maximum at 358 nm characteristic of alkyl xanthates.[2] Further evidence concerning the structure of 9a was derived from its conversion to methylphthalimide, on treatment with Raney nickel.

Our attempts to isolate cyclic product via intramolecular hydrogen abstraction was not successful as reported[13] for phthalimide system with a sulfur atom in N-alkyl side chain. In continuation of our work,[14] we have studied the photochemical reaction of

SCHEME-3



2 a, R = C_2H_5
b, R = n − C_3H_7
c, R = iso − C_3H_7
d, R = n − C_4H_9
e, R = iso − C_4H_9

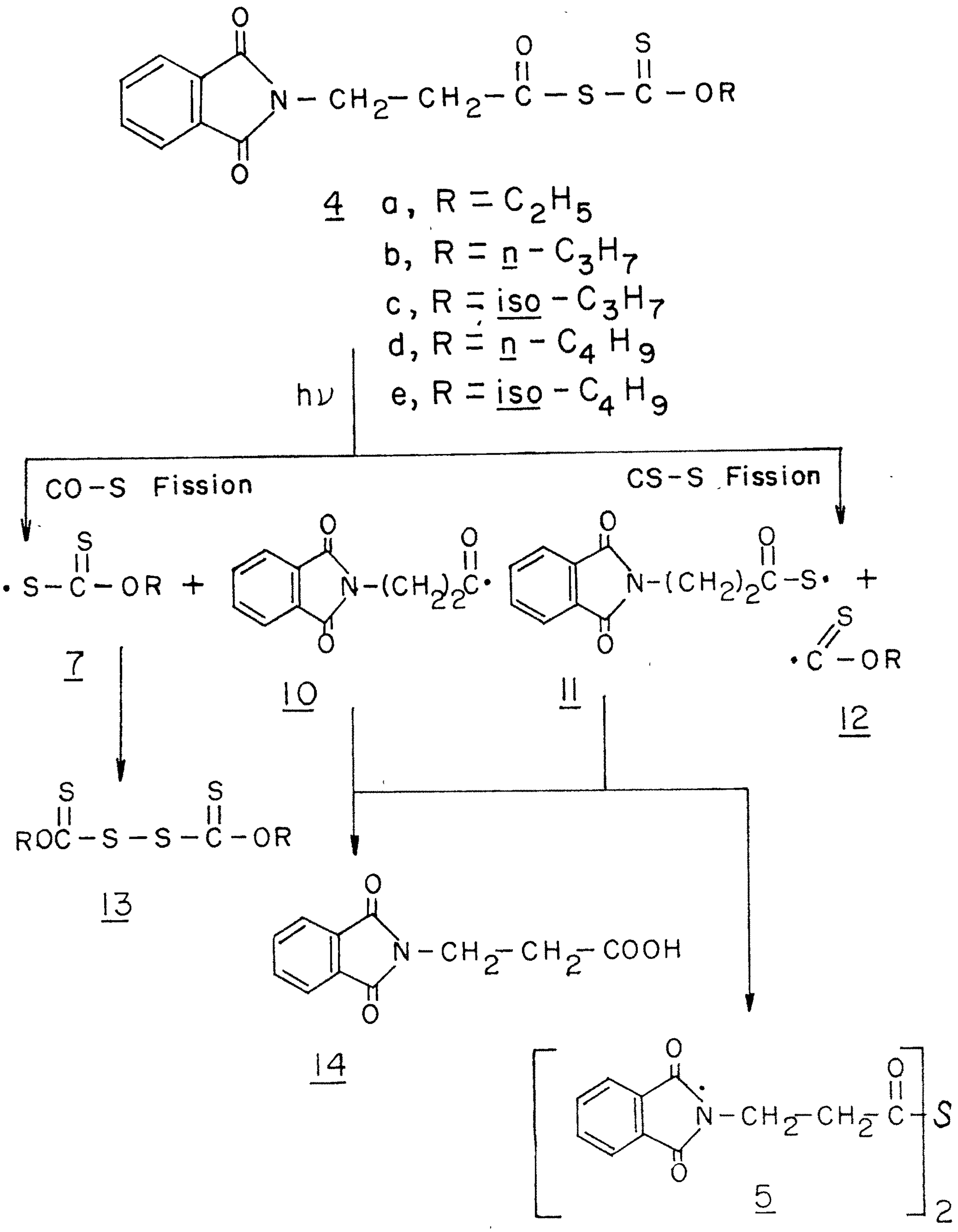
9 a, R = C_2H_5
b, R = n − C_3H_7
c, R = iso − C_3H_7
d, R = n − C_4H_9
e, R = iso − C_4H_9

extended side chain xanthate such as 4. Photolysis of these xanthates 4a-e in benzene solution for 1 hr with a high pressure mercury lamp (250 watt) resulted in various products which include xanthic acid disulphide (13), phthalylalanine (14) and the thioanhydride 5. A probable mechanism which explains the formation of these products involves the initial fragmentation of either CO-S or CS-S bond.[5,15] The fission of CO-S bond gave initially acyl radical 10 and xanthate radical 7. Another mode of fission results in radicals 11 and 12. The radical 11 can combine with the radical 10 to give thioanhydride 5 (Scheme 4).

The dimerisation of xanthate radical 7 gave xanthic acid disulphide[16] 13. The formation of phthalylalanine (14) can be explained through the formation of corresponding aldehyde.[15] The dimeric products of radicals 10 and 12 were not observed in the photolysis of these xanthates (4a-e).

In continuation of this work, photolysis of a few acyl xanthates 4a and 4d were carried out for 2.5 hr using a tungston lamp (200 watt). For example, photolysis of 4a and 4d in benzene solution gave

SCHEME-4


4 a, R = C2H5
b, R = n-C3H7
c, R = iso-C3H7
d, R = n-C4H9
e, R = iso-C4H9
hν
CO-S Fission
CS-S Fission
7
10
11
12
13
14
5

thioanhydride 5 and the corresponding esters 15 (Scheme 5).

The structure of these esters 15 were confirmed by mixture melting point and analytical data.

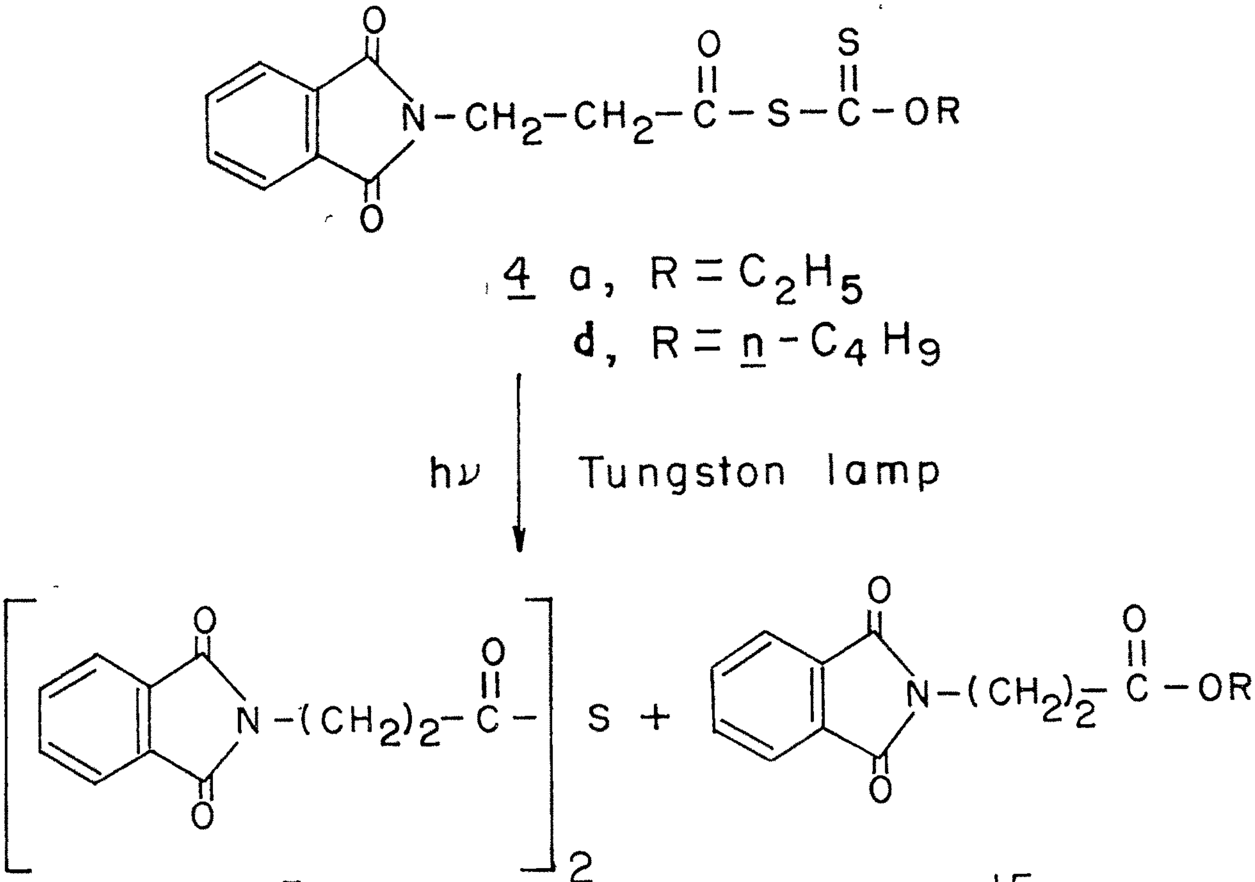
Thermal decomposition of acyl xanthates are reported to give esters and carbon disulphide.[2] For example, when phthalylglycyl xanthates (2a-e) were heated around 150-200° for 20-30 minutes, corresponding esters 16 and carbon disulphide were formed as shown in Scheme 6.

The structure of these esters 16 were confirmed by mixture melting point and analytical data. A four membered transition state has been suggested for such decomposition.[2,8] (Scheme 6).

Thermal decomposition of xanthates 4 around 150-60° for 15-20 minutes resulted in corresponding esters 15 and carbon disulphide (Scheme 7).

However, thermal decomposition of 4c resulted in the formation of thioanhydride 5 and the corresponding ester was not formed. A similar observation has been made by Singh and George[7] in the thermal decomposition of O-ethyl-S-triphenylacetyl xanthate. A probable

SCHEME - 5

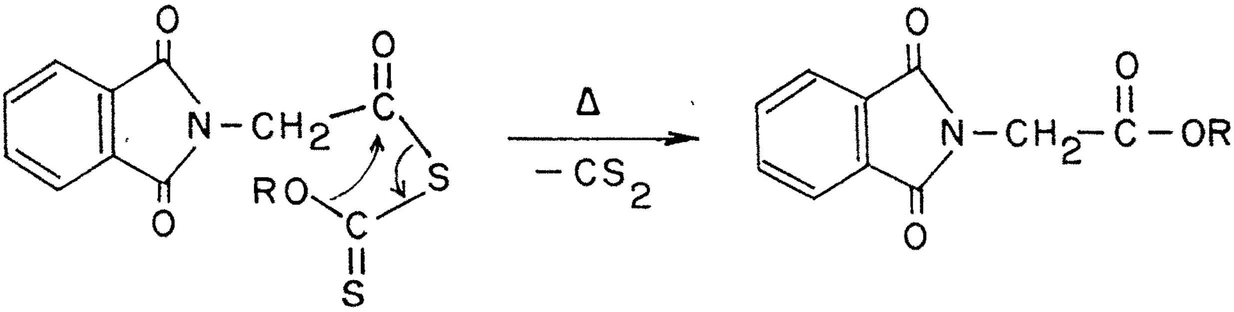


4 a, $R = C_2H_5$
d, $R = \underline{n}-C_4H_9$

5

15

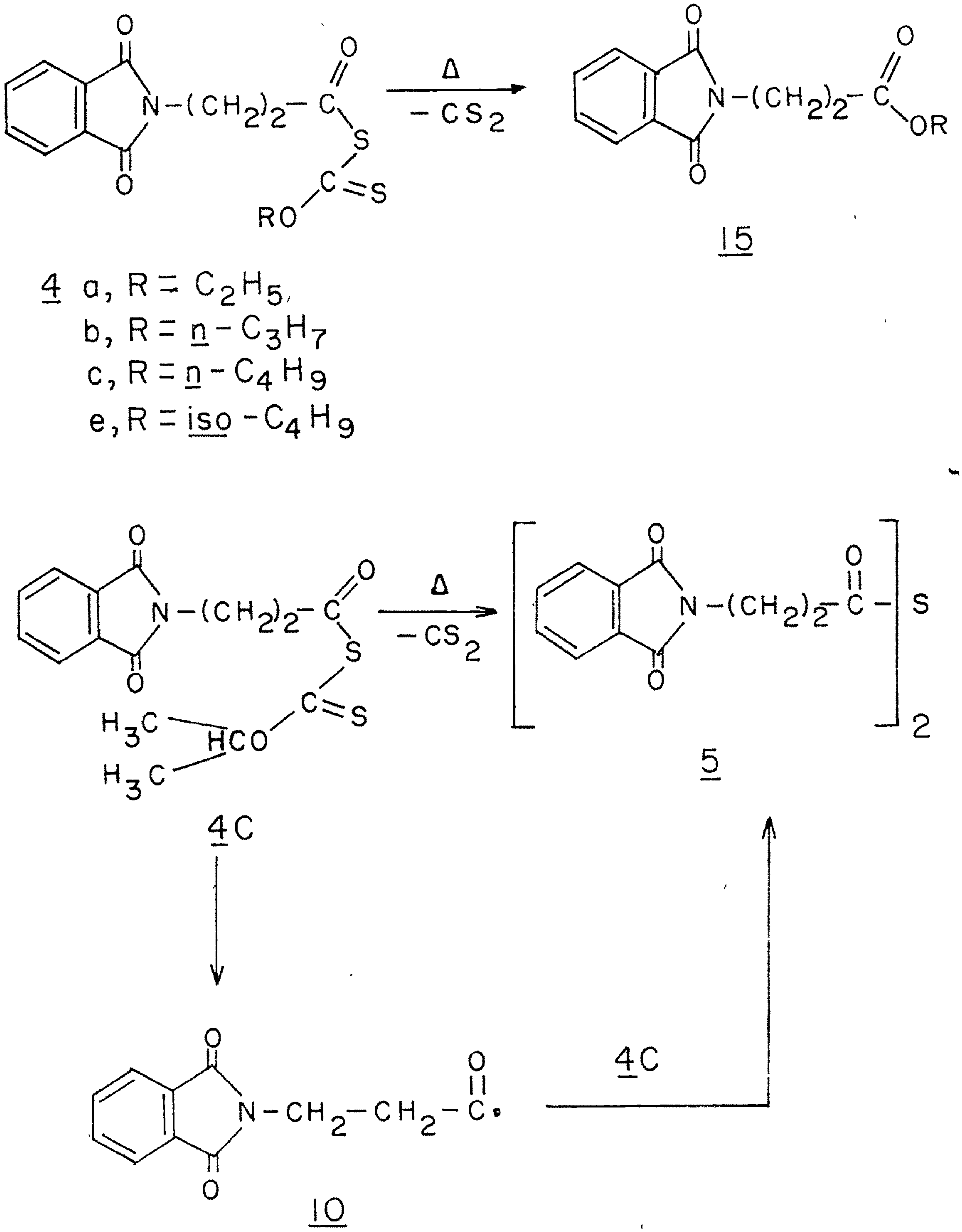
SCHEME - 6



2 a, $R = C_2H_5$
b, $R = \underline{n}-C_3H_7$
c, $R = \underline{iso}-C_3H_7$
d, $R = \underline{n}-C_4H_9$
e, $R = \underline{iso}-C_4H_9$

16

SCHEME - 7



4 a, R = C_2H_5
b, R = n - C_3H_7
c, R = n - C_4H_9
e, R = iso - C_4H_9

15

5

4C

10

mechanism for the formation of 5 in thermal decomposition of the xanthate 4c is shown in Scheme 7.

4.3 Experimental

IR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer and UV spectra on Specord UV-VIS Spectrophotometer. NMR traces were recorded on a Perkin Elmer R-32 NMR Spectrophotometer. Irradiations were carried out in Hanovia photochemical reaction assembly with a quartz immersion well and high pressure mercury lamps (125 and 250 watt), in oxygen free-nitrogen atmosphere.

Starting Materials

Phthalylglycyl chloride[17] and potassium-O-alkyl xanthates[18] were prepared as per reported procedures. Phthalylalanyl chloride[19] was prepared as per general procedure.

O-Ethyl-S-phthalylglycyl xanthate (2a)

To a solution of 1 (2.24 g, 0.01 mole) in ether (50 ml) was added potassium-O-ethyl xanthate (1.60 g, 0.01 mole) portionwise with constant stirring at 0° during 30 minutes and stirring continued for another 30 minutes at room temperature. Precipitated KCl was filtered and ether solution of the xanthate was washed with 1% aq. $NaHCO_3$. The ether extract was repeatedly washed with water, dried on Na_2SO_4 and solvent removed in vacuum to give 2.5 g (84%) of the xanthate 2a, m.p. 87° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{13}H_{11}O_4NS_2$: C, 50.48 ; H, 3.55

Found : C, 50.41 ; H, 3.64

IR Spectrum (Nujol) : ν max : 1720, 1410 and 1240 cm^{-1}.

UV Spectrum (Ethanol) : λ max : 288 (ϵ, 3224) and 394 nm (ϵ, 20).

NMR Spectrum (CCl_4) : δ 7.8 (multiplet, ArH), δ 4.8 (quartet, OCH_2), δ 4.6 (singlet, CH_2) and δ 1.5 ppm (triplet, CH_3).

Reduction of O-ethyl-S-phthalylglycyl xanthate (2a) with Raney-Nickel

To an acetone solution (100 ml) of the xanthate 2a (1 g, 0.003 mole) was added Raney-nickel (6 g) and the solution was refluxed for 4 hours. Filtration and evaporation of the solvent gave 0.48 g (79%) of phthalimidoacetaldehyde, m.p. 111° (phenyl hydrazine derivative, m.p. 163-65°).

Photolysis of O-ethyl-S-phthalylglycyl xanthate (2a)

A solution of 2a (1 g, 0.003 mole) in dry benzene (AR grade ; 450 ml) was irradiated for 1.5 hr with a high pressure mercury lamp (125 watt). Removal of the solvent gave a gummy solid which on treatment with petroleum ether furnished 0.50 g (56%) of O-ethyl-S-phthalimidomethyl xanthate (9a), m.p. 61-63° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{12}H_{11}O_3NS_2$: C, 51.20 ; H, 3.90

Found : C, 51.50, H, 4.30

IR spectrum (KBr) : ν max : 1720, 1410 and 1230 cm^{-1}

UV spectrum (ethanol) : λ max : 280 (ϵ, 16,240) and 358 nm (ϵ, 65).

Conversion of O-ethyl-S-phthalimidomethyl xanthate (9a) to methylphthalimide

A solution of 9a (0.3 g, 0.001 mole) in acetone (50 ml) was refluxed for 2.5 hours with Raney-nickel (4 g) and reaction mixture was worked-up as in previous case. It gave 0.09 g (53%) of methylphthalimide m.p. 133-34° (mmp).

Thermal decomposition of O-Ethyl-S-phthalylglycyl xanthate (2a)

O-Ethyl-S-phthalylglycyl xanthate (1 g, 0.003 mole) was heated under nitrogen atmosphere in an oil bath at 200° for 15-20 minutes. The gaseous product was trapped by passing through a piperidine solution (5 ml in 50 ml ether) which gave 0.70 g of piperidinium cyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 88% yield of carbon disulphide. The residual mass, on recrystallisation from ethanol gave 0.40 g (53%) ethyl ester of phthalylglycine (16a), m.p. 103° (mmp).

Anal : Calcd for $C_{12}H_{11}O_4N$: C, 60.80 ; H, 4.70

Found : C, 60.95 ; H, 5.10

O-n-propyl-S-phthalylglycyl xanthate (2b)

To a solution of 1 (2.24 g, 0.01 mole) in ether (50 ml) was added potassium-O-n-propyl xanthate (1.74 g, 0.01 mole) portionwise with continuous stirring. The ether solution of the xanthate was worked-up as in previous case and solvent removed in vacuum to give 2.5 g (79%) of the xanthate 2b, m.p. 76° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{14}H_{13}O_4NS_2$: C, 52.01 ; H, 4.02
Found : C, 52.42 ; H, 4.14

IR Spectrum (Nujol) : ν max ; 1720, 1410 and 1220 cm^{-1}
UV Spectrum (Ethanol) : λ max : 288 (ϵ, 3443) and 395 nm (ϵ, 18).

Reduction of O-n-propyl-S-phthalylglycyl xanthate (2b) with Raney-nickel

A solution of 2b (1 g, 0.003 mole) in acetone (100 ml) was refluxed for 4 hours with Raney-nickel (6 g) and reaction mixture was worked-up as in previous case. It gave 0.50 g (85%) of phthalimidoacetaldehyde m.p. 113° (phenyl hydrazine dervt. m.p. 163-65°).

Photolysis of O-n-propyl-S-phthalylglycyl xanthate (2b)

A solution of 2b (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr. with a high pressure meruury lamp. Removal of solvent and work-up in usual manner gave 0.35 g (38%) of the xanthate 9b, m.p. 61-63°.

Anal : Calcd for $C_{13}H_{13}O_3NS_2$: C, 52.80 ; H, 4.40
Found : C, 53.20 ; H, 4.70.

Thermal decomposition of O-n-propyl-S-phthalylglycyl xanthate (2b)

The xanthate 2b (1 g, 0.003 mole) was heated under N_2 atmosphere in an oil bath at 170° for 15-20 minutes. The gaseous products was trapped by passing through piperidine solution (5 ml in 50 ml ether) which gave 0.75 g of piperidinium cyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 98% yield of carbon disulphide. The residual mass, on recrystallisation from ethanol gave 0.40 g (52%) n-propyl ester of phthalylglycyne (16b), m.p. 82° (mmp).

Anal : Calcd for $C_{13}H_{13}O_4N$: C, 63.16 ; H, 5.26

Found : C, 62.74 ; H, 5.00

O-iso-Propyl-S-phthalylglycyl xanthate (2c)

To a solution of 1 (2.24 g, 0.01 mole) in ether (50 ml) was added potassium-O-isopropyl xanthate (1.74 g, 0.01 mole) portion wise with continuous stirring. The ether solution of the xanthate was worked-up as in previous case and solvent removed in vacuum to give 2.5 g (78%) of the xanthate 2c, m.p. 74-75° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{14}H_{13}O_4NS_2$: C, 52.01 ; H, 4.02
Found : C, 52.45 ; H, 4.07

UV Spectrum (Ethanol) : λ max : 290 (ϵ, 3691) and 393 nm (ϵ, 20).

Photolysis of O-isopropyl-S-phthalylglycyl xanthate (2c)

A solution of 2c (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr with a high pressure mercury lamp. Removal of solvent and work-up in usual manner gave 0.35 g (38%) of the xanthate 9c, m.p.78°.

Anal : Calcd for $C_{13}H_{13}O_3NS_2$: C, 52.80 ; H, 4.40
Found : C, 53.08 ; H, 4.61

UV Spectrum (Ethanol) : λ max : 282 (ϵ, 21, 948) and 360 nm (ϵ, 71).

Thermal decomposition of O-isopropyl-S-phthalylglycyl xanthate (2c)

The xanthate 2c (1 g, 0.003 mole) was heated under N_2 atmosphere in an oil bath at 150° for 30 minutes. The gaseous product was trapped by passing through piperidine solution (5 ml in 25 ml ether) which gave 0.70 g of piperidiniumcyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12]

corresponding to 92% yield of carbon disulphide. The residual mass, on recrystallisation from ethanol gave 0.45 g (59%) isopropyl ester of phthalylglycine (16c), m.p. 103-5° (mmp).

Anal : Calcd for $C_{13}H_{13}O_4N$: C, 63.16 ; H, 5.26

Found : C, 62.74 ; H, 5.07

O-n-Butyl-S-phthalylglycyl xanthate (2d)

To a solution of 1 (2.24 g, 0.01 mole) in ether (50 ml) was added potassium-O-n-butyl xanthate (1.88 g, 0.01 mole) portion wise with continuous stirring. The ether solution of the xanthate was worked-up as in previous case and solvent removed in vacuum to give 2.8 g (84%) of the xanthate 2d, m.p. 65° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{15}H_{15}O_4NS_2$: C, 53.42 ; H, 4.45

Found : C, 53.34 ; H, 4.50

IR Spectrum (Nujol) : ν max ; 1720, 1410 and 1240 cm^{-1}.

UV Spectrum (Ethanol) : λ max : 290 (ϵ, 3992) and 395 nm (ϵ, 17).

Photolysis of O-n-butyl-S-phthalylglycyl xanthate (2d)

A solution of 2d (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr with a high pressure mercury lamp. Removal of solvent and work-up in usual manner gave 0.45 g (49%) of the xanthate 9d, m.p. 69-71°.

Anal : Calcd for $C_{14}H_{15}O_3NS_2$: C, 54.30 ; H, 4.80

Found : C, 54.70 ; H, 5.10

UV Spectrum (Ethanol) : λ max : 280 (ϵ, 23, 752) and 356 nm (ϵ, 77).

Thermal decomposition of O-n-butyl-S-phthalylglycyl xanthate (2d)

The xanthate 2d (1 g, 0.003 mole) was heated under N_2 atmosphere in an oil bath at 150° for 30 min. The gaseous product was trapped by passing through piperidine solution (5 ml in 25 ml ether) which gave 0.55 g of piperidiniumcyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 75% yield of carbon disulphide. The residual mass, on recrystallisation from ethanol gave 0.40 g (52%) n-butyl ester of phthalylglycine (16 d), m.p. 59° (mmp).

Anal : Calcd for $C_{14}H_{15}O_4N$: C, 64.36 ; H, 5.74

Found : C, 64.23 ; H, 5.29

O-isobutyl-S-phthalylglycyl xanthate (2e)

To a solution of 1 (2.24 g, 0.01 mole) in ether (50 ml) was added potassium-O-isobutyl xanthate (1.88 g, 0.01 mole) portion wise with continuous stirring. The ether solution of the xanthate was worked up as in previous case and solvent removed in vacuum to give 2.1 g (65%) of the xanthate 2e, m.p. 63° after recrystallisation from petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{15}H_{15}O_4NS_2$: C, 53.42 ; H, 4.45

Found : C, 53.90 ; H, 4.80

UV Spectrum (Ethanol) : λmax : 290 (ϵ, 2,802) and 394 nm (ϵ, 18).

Photolysis of O-isobutyl-S-phthalylglycyl xanthate (2e)

A solution of 2e (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr with a high pressure mercury lamp. Removal of solvent and work-up in usual manner gave 0.40 g (44%) of the xanthate 9e m.p. 59-61°.

Anal : Calcd for $C_{14}H_{15}O_3NS_2$: C, 54.30 ; H, 4.80

Found : C, 53.90 ; H, 5.20

Thermal decomposition of O-isobutyl-S-phthalylglycyl xanthate (2e)

The xanthate 2e (1 g, 0.003 mole) was heated under N_2 atmosphere in an oil bath at 150° for 30 min. The gaseous product was trapped by passing through piperidine solution (5 ml in 25 ml ether) which gave 0.45 g of piperidiniumcyclopentamethylenedithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 62% yield of carbon disulphide. The residual mass, on recrystallization from ethanol gave 0.25 g (32%) isobutyl ester of phthalylglycine (16e) m.p. 63° (mmp)

Anal : Calcd for $C_{14}H_{15}O_4N$: C, 64.36 ; H, 5.74

Found : C, 64.71 ; H, 5.70

O-Ethyl-S-phthalylalanyl xanthate (4a)

To a solution of 3 (2.38 g, 0.01 mole) in ether (150 ml) was added potassium-O-ethyl xanthate (1.6 g, 0.01 mole) portion wise with constant stirring at 0° for 30 minutes. Precipitated KCl was filtered and ether solution of the xanthate was washed with 1% aq. $NaHCO_3$. The ether extract was repeatedly washed with water, dried on Na_2SO_4 and solvent removed in vacuum to give 2.4 g (75%) of the xanthate 4a, m.p. 60° after recrystallisation from a mixture (1:1) of ether petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{14}H_{13}O_4NS_2$: C, 52.01 ; H, 4.02

Found : C, 52.45 ; H, 3.71

UV Spectrum (Ethanol) : λmax : 278 (ϵ, 8,216) and 395 nm (ϵ, 70).

Reaction of phthalylalanyl chloride (3) with potassium -O-ethyl xanthate in acetone

To a solution of 3 (4.8 g, 0.02 mole) in acetone (100 ml) was added potassium-O-ethyl xanthate (3.2 g, 0.02 mole) portion wise with constant stirring at 0° for 30 minutes. Precipitated KCl was filtered and solvent removed in vacuum. The residual mass, on recrystallisation from benzene gave 1.7 g (38%) of thioanhydride 5 ; m.p. 197°.

Anal : Calcd for $C_{22}H_{16}O_6N_2S$: C, 60.55 ; H, 3.60

Found : C, 60.60 ; H, 3.60

Photolysis of O-ethyl-S-phthalylalanyl xanthate (4a) :

A solution of 4a (1 g, 0.003 mole) in dry benzene (AR grade ; 450 ml) was irradiated for 1 hr with a high pressure mercury lamp (250 watt). Removal of solvent gave a gummy solid which was extracted in petroleum ether (b.p. 40-60°). The petroleum ether extract gave 0.13 g (35%) of ethyl xanthic acid disulphide 13a, which was compared on TLC (Silicagel; eluent, pet. ether) with authentic sample.[16]

The insoluble residue was extracted in chloroform and washed with 1% aq. $NaHCO_3$. The aqueous layer on acidification with dil. HCl (1:1) gave 0.1 g (15%) of phthalylalanine (14), m.p. 150° (mmp). The chloroform layer was repeatedly washed with water, dried on Na_2SO_4 and solvent removed in vacuum to give 0.30 g (45%) of thioanhydride 5, m.p. 197°.

Photolysis of O-ethyl-S-phthalylalanyl xanthate (4a) using tungston lamp

A solution of 4a (1 g, 0.003 mole) in dry benzene (250 ml) was irradiated using tungston lamp (200 watt) for 2.5 hrs. Removal of solvent gave 0.30 g (45%) of thioanhydride 5, m.p. 197° and 0.08 g (10%) of ethyl ester of phthalylalanine (15a) m.p. 74° (mmp)

Anal : Calcd for $C_{13}H_{13}O_4N$: C, 63.16 ; H, 5.26

Found : C, 63.10 ; H, 5.00.

Thermal decomposition of O-ethyl-S-phthalylalanyl xanthate (4a)

The xanthate 4a (1 g, 0.003 mole) was heated under nitrogen atmosphere in an oil bath at 150° for 10-15 minutes. The gaseous products was trapped by passing through piperidine solution (3 ml in 50 ml ether) which gave 0.65 g of piperidiniumcyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 85% yield of carbon disulphide. The residual mass, on recrystallisation from petroleum ether (b.p. 40-60°) gave 0.35 g (46%) ethyl ester of phthalylalanine 15a, m.p. 74° (mmp).

O-n-Propyl-S-phthalylalanyl xanthate (4b)

To a solution of 3 (2.38 g, 0.01 mole) in ether (150 ml) was added potassium-O-n-propylxanthate (1.74 g, 0.01 mole) portion wise with continuous stirring. The ether solution of the xanthate was worked-up as in previous case and solvent removed in vacuum to give 1.8 g (53%) of the xanthate 4b, m.p. 78° after recrystallisation from a mixture (1:1) of ether-petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{15}H_{15}O_4NS_2$: C, 53.42 ; H, 4.45

Found : C, 53.88 ; H, 4.61.

UV Spectrum (Ethanol) : λ_{max} : 278 (ϵ, 8,432) and 397 nm (ϵ, 53).

Photolysis of O-n-propyl-S-phthalylalanyl xanthate (4b)

A solution of 4b (1 g, 0.0029 mole) in dry benzene (450 ml) was irradiated for 1 hr with a high pressure mercury lamp. Removal of solvent and work-up as in previous case gave 0.13 g (33%) of n-propyl xanthic acid disulphide 13b, which was compared on TLC (Silica gel ; eluent, petroleum ether) with authentic sample.[16]

The insoluble residue on work-up gave 0.07 g (11%) of phthalylalanine (14), m.p. 150° (mmp) and 0.15 g (23%) of thioanhydride 5, m.p. 197°.

Thermal decomposition of O-n-propyl-S-phthalylalanyl xanthate (4b)

The xanthate 4b (1 g, 0.003 mole) was heated under N_2 atmosphere in an oil bath at 150° for 15 minutes. The gaseous product was trapped by passing through piperidine solution (3 ml in 50 ml ether) which gave 0.35 g of piperidiniumcyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 48% yield of carbon disulphide. The residual mass, on recrystallisation from petroleum ether (b.p. 40-60°) gave 0.50 g (65%) n-propyl ester of phthalylalanine 15b, m.p. 66° (mmp).

Anal : Calcd for $C_{14}H_{15}O_4N$: C, 64.36 ; H, 5.74

Found : C, 64.78 ; H, 5.30

O-isopropyl-S-phthalylalanyl xanthate (4c)

To a solution of 3 (2.38 g, 0.01 mole) in ether (150 ml) was added potassium-O-isopropyl xanthate (1.74 g, 0.01 mole) portion wise with continuous stirring. The ether solution of the xanthate was worked up in usual manner. The solvent removed in vacuum to give 2.0 g (58%) of the xanthate 4c, m.p. 79° after recrystallisation from a mixture (1:1) of ether-petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{15}H_{15}O_4NS_2$: C, 53.42 ; H, 4.45

Found : C, 53.21 ; H, 4.63

IR Spectrum (Nujol) : νmax : 1720, 1410, 1385 and 1260 cm^{-1}.

UV Spectrum (Ethanol) : λmax : 278 (ϵ, 8,872) and 395 nm (ϵ, 73).

NMR Spectrum ($CDCl_3$) : δ 7.7 (multiplet, ArH), δ 4.0 (triplet, 2H), δ 3.1 (triplet, 2H) and δ 1.5 (doublet, 6H).

Photolysis of O-isopropyl-S-phthalylalanyl xanthate (4c)

A solution of 4c (1.5 g, 0.004 mole) in dry benzene (450 ml) was irradiated for 1 hr with a high pressure mercury lamp. Removal of solvent and work-up in usual manner gave 0.25 g (42%) of isopropyl xanthic acid disulphide 13c, m.p. 56° (mmp).[16]

The insoluble residue on work-up gave 0.11 g (11%) of phthalylalanine (14) m.p. 150° (mmp) and 0.20 g (21%) of thioanhydride 5, m.p. 197°.

Thermal decomposition of O-isopropyl-S-phthalyl alanyl xanthate (4c)

The xanthate 4c (1 g, 0.0029 mole) was heated under N_2 atmosphere in an oil-bath at 150° for 20 minutes. The gaseous product was trapped by passing through piperidine solution (3 ml in 50 ml ether) which gave 0.70 g of piperidinium cyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 95% yield of carbon disulphide. The residual mass, on recrystallisation from chloroform gave 0.5 g (77%) of thioanhydride 5, m.p. 197°.

O-n-Butyl-S-phthalylalanyl xanthate (4d)

To a solution of 3 (2.375 g, 0.01 mole) in ether (150 ml) was added potassium-O-n-butyl xanthate (1.88 g, 0.01 mole) portion wise with continuous stirring. Worked-up in usual manner, gave 1.8 g (53%) of the xanthate 4d, m.p. 58° after recrystallisation from a mixture (1:1) of ether-petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{16}H_{17}O_4NS_2$: C, 54.7 ; H, 4.8

Found : C, 54.29 ; H, 4.9

IR Spectrum (Nujol) : νmax : 1720, 1410 and 1270 cm^{-1}

UV Spectrum (C_2H_5OH) : λ max : 280 (ϵ, 35,101) and 397 nm (ϵ, 54)

NMR Spectrum ($CDCl_3$) : δ 7.7 (multiplet, ArH), δ 4.6 (triplet, $-OCH_2$), δ 4.0 (triplet, 2H), δ 3.1 (triplet, 2H), δ 1.8 (multiplet, 4H) and δ 1.0 (triplet, 3H).

Photolysis of O-n-butyl-S-phthalylalanyl xanthate (4d)

A solution of 4d (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr. Removal of solvent and work-up in usual manner gave 0.21 g (50%) of n-butyl xanthic acid disulphide 13d, which was compared on TLC (silica gel, eluent, pet. ether) with the authentic sample.[16]

The insoluble residue on work-up gave 0.2 g (33%) of phthalylalanine, m.p. 150° (mmp) and 0.2 g (32%) of thioanhydride 5, m.p. 197°.

Photolysis of O-n-butyl-S-phthalylalanyl xanthate (4d) using tungston lamp

A solution of 4d (1 g, 0.0028 mole) in dry benzene (250 ml) was irradiated using tungston lamp for 2.5 hr. Removal of solvent gave 0.20 g (32%) of thioanhydride 5, m.p. 197° and 0.1 g (13%) n-butyl ester of phthalylalanine (15d), m.p. 63° (mmp).

Anal : Calcd for $C_{15}H_{17}O_4N$: C, 65.45 ; H, 6.18

Found : C, 65.00 ; H, 5.71

Thermal decomposition of O-n-butyl-S-phthalylalanyl xanthate (4d)

The xanthate 4d (1.6 g, 0.005 mole) was heated under N_2 atmosphere in an oil bath at 160° for 15 minutes. The gaseous products was trapped by passing through piperidine solution (3 ml in 50 ml ether) which gave 0.70 g of piperidinium cyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 64% yield of carbon disulphide.

The residual mass, on recrystallisation from petroleum ether (b.p. 40-60°) gave 0.72 g (58%) of n-butyl ester of phthalylalanine (15d), m.p. 63° (mmp).

O-isobutyl-S-phthalylalanyl xanthate (4e)

To a solution of 3 (2.4g, 0.01 mole) in ether (150 ml) was added potassium-O-isobutyl xanthate (1.88 g, 0.01 mole) portion wise with continuous stirring. Worked-up in the usual manner gave 1.5 g (44%) of the xanthate 4e, m.p. 63° after recrystallisation from a mixture (1:1) of ether - petroleum ether (b.p. 40-60°).

Anal : Calcd for $C_{16}H_{17}O_4NS_2$: C, 54.70 ; H, 4.80

Found : C, 55.15, H, 4.50

UV Spectrum (Ethanol) : λ max : 280 (ϵ, 30, 120) and 395 nm (ϵ, 63).

Photolysis of O-isobutyl-S-phthalylalanyl xanthate (4e)

A solution of 4e (1 g, 0.003 mole) in dry benzene (450 ml) was irradiated for 1 hr. Removal of solvent and work-up in usual manner gave 0.19 g (45%) of isobutyl xanthicacid disulphide 13e, which was compared on TLC (Silica gel ; eluent, pet. ether) with authentic sample.[16]

The insoluble residue on work-up gave 0.15 g (25%) of phthalylalanine, m.p. 150° (mmp) and 0.18 g (29%) of thioanhydride 5, m.p. 197°.

Thermal decomposition of O-isobutyl-S-phthalylalanyl xanthate (4e)

The xanthate 4e (0.70g, 0.0019 mole) was heated under N_2 atmosphere in an oil bath at 150-60° for 15 minutes. The gaseous products was trapped by passing through piperidine solution (1 ml in 30 ml ether) which gave 0.28 g of piperidinium cyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[12] corresponding to 59% yield of carbon disulphide.

The residual mass, on recrystallisation from petroleum ether (b.p. 40-60°) gave 0.30 g (55%) of iso-butyl ester of phthalylalanine (15e), m.p. 60° (mmp).

Anal : Calcd for $C_{15}H_{17}O_4N$: C, 65.45 ; H, 6.18

Found : C, 65.82 ; H, 5.71.

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