CHAPTER - II

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

2.1 Abstract

The reaction of benzoyl chloride with potassium-O-alkyl xanthates afforded in good yields the corresponding O-alkyl-S-benzoyl xanthates. Similarly, ortho and para substituted benzoyl chloride with potassium-O-ethyl xanthate gave the corresponding chloro substituted benzoyl xanthates. On prolonged photolysis, O-alkyl-S-benzoyl xanthates gave benzoyl disulphide whereas sunlight photolysis of O-ethyl-S-aroyl xanthates gave in each case different products. However, thermal decomposition of O-alkyl-S-benzoyl xanthates gave benzoyl disulphide, corresponding ester and carbon disulphide. The reactions of a few aroyl xanthates with aromatic amines have also been studied.

2.2 Results and Discussion

Acyl and aroyl xanthates are relatively unstable compounds and not much information is available concerning their preparation and properties. Willcox[1] had reported the formation of O-ethyl-S-acetyl xanthate which readily decomposes to give ethyl acetate and carbon disulphide. A similar observation had been made by Richter[2] concerning the reaction between benzoyl chloride and potassium-O-ethyl xanthate to give

O-ethyl-S-benzoyl xanthate which decomposes at 40° to produce ethyl benzoate and carbon disulphide. Both the acetyl and benzoyl xanthates were isolated by removal of solvent in vacuum.

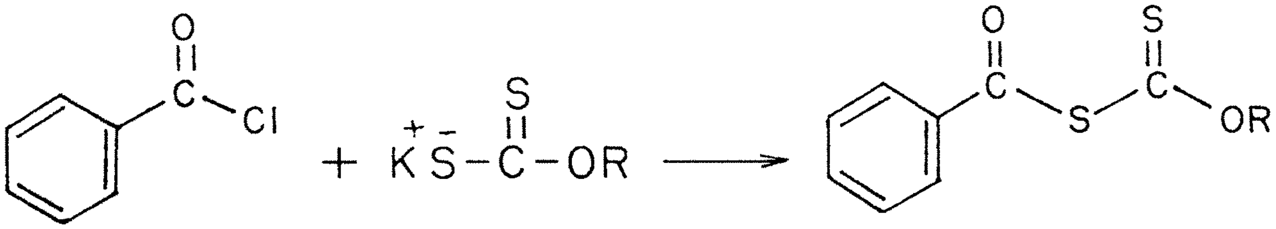
Bulmer and Mann[3] have reported the formation of several aroyl xanthates by the treatment of p-substituted benzoyl chlorides with potassium-O-ethyl xanthate. In a detailed study, Barton et al.[4] have shown that several acyl and aroyl xanthates can be conveniently prepared by the treatment of the corresponding acid chloride with potassium-O-ethyl xanthate, in a suitable solvent such as acetone, around-30°. Reactions at higher temperature produce thioanhydride. For example, at low temperature palmitoyl chloride gave the expected xanthate but at 0° only the thioanhydride could be isolated.[4]

In the present investigation, we have examined the reaction of several potassium-O-alkyl xanthates with aroyl chlorides, with a view to studying the nature of the products formed in these reactions. Thus, for example, reaction of benzoyl chloride (1) with potassium-O-ethyl xanthate (2a) in acetone solution around 0^{o} gave golden yellow liquid product (yield 70%) which was chracterised as O-ethyl-S-benzoyl xanthate (3a). Similarly, benzoyl chloride when treated with different potassium-O-alkyl xanthates gave O-alkyl-S-benzoyl xanthates (3a-d) in good yield (Scheme 1).

The structural assignment of 3a-d were consistent with the spectral data. The IR spectrum of these aroyl xanthates showed prominant bands at 1700 and 1270 cm^{-1}, due to the presence of C=O and C=S groups respectively. The NMR spectrum of 3c (Fig. 1) shows a multiplet at 7.4 ppm (5H) due to aromatic protons, a septet a 5.2 ppm (1H) due to -OCH protons and a doublet at 1.3 ppm (6H) due to gem methyl protons. The UV spectrum of 3a-d showed a low intensity absorption bands around 410 nm. Further evidence in support of the structure 3c for the xanthate was deduced from its conversion to benzaldehyde on treatment with Raney Nickel.

In continuation of this work, we have prepared a few substituted benzoyl xanthates. For example, o-chloro benzoyl chloride (4) reacted with potassium-O-ethyl xanthate (2a) around $0^{o}C$ to give O-ethyl-S-

SCHEME-1

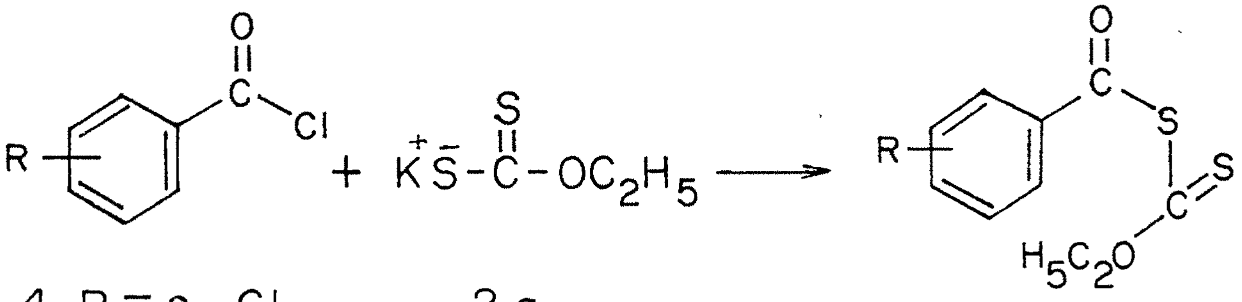


1

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

3 a-d

SCHEME-2

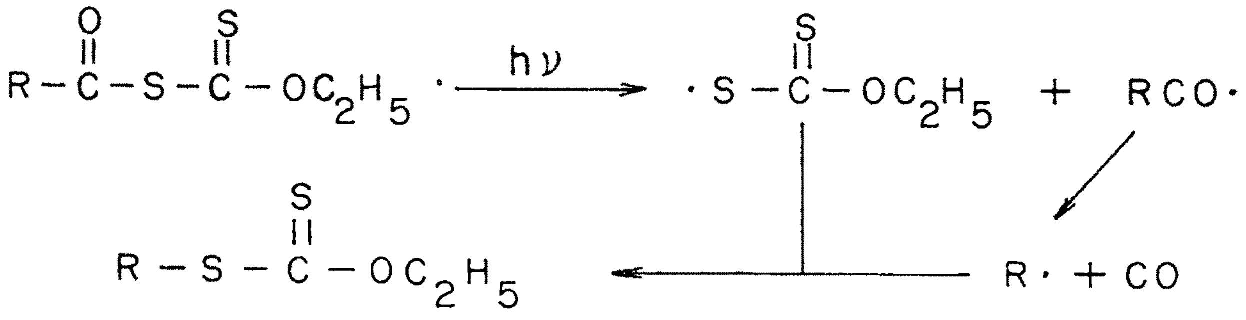


4, R = o-Cl
6, R = p-Cl

2 a

5, R = o-Cl
7, R = p-Cl

SCHEME-3



$$R-\overset{O}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{h\nu} \cdot S-\overset{S}{\overset{\|}{C}}-OC_2H_5 + RCO\cdot$$

$$RCO\cdot \rightarrow R\cdot + CO$$

$$R-S-\overset{S}{\overset{\|}{C}}-OC_2H_5$$

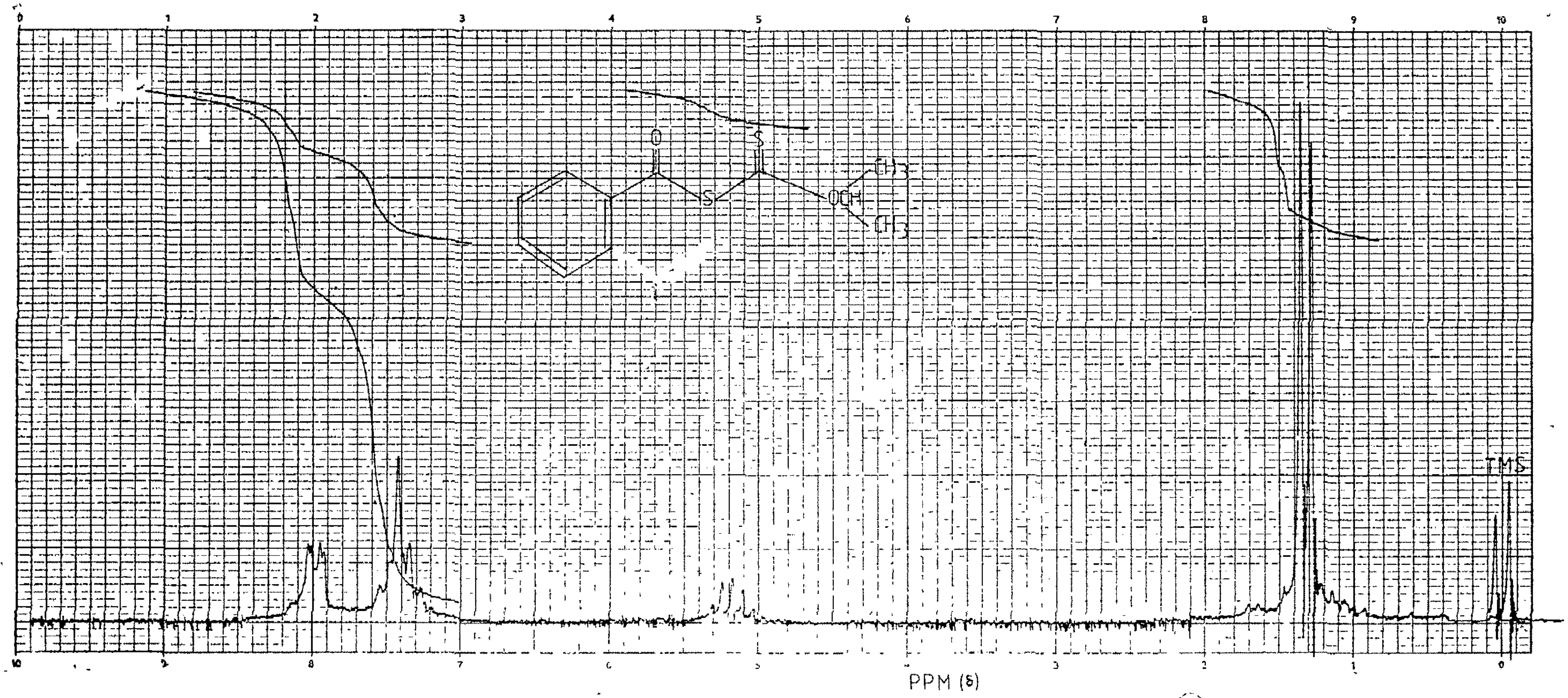


Fig. 1 NMR Spectrum (90 mcs) of O-isopropyl-S-benzoyl xanthate (3c)

o-chlorobenzoyl xanthate (5) in 83% yield. Similarly, O-ethyl-S-p-chlorobenzoyl xanthate (7) was obtained in good yield by the reaction of p-chlorobenzoyl chloride (6) with potassium-O-ethyl xanthate (2a) around 0^{o} (Scheme 2).

The structural assignment of substituted benzoyl xanthates (5 and 7) were characterised by a weak absorption band around 390 nm. The IR spectrum of O-ethyl-S-p-chlorobenzoyl xanthate (7) showed an absorption at 1700 cm^{-1} which is assigned to C=O stretching frequency whereas the strong absorption at 1200 cm^{-1} could be attributed to the C=S frequency. An intense absorption at 1030 cm^{-1} was ascribed to C-O frequency.[5]

The object of the present investigation was to study the photochemical transformation of these aroyl xanthates. Barton and co-workers[4] have shown that photolysis of acyl xanthates in solution leads to a C-S bond fission giving rise to acyl and xanthate radicals. The acyl radical subsequently decarbonylates and the residual radical combines with the xanthate radical giving rise to O-ethyl-S-alkyl xanthate as shown in Scheme 3.

Thus, for example, irradiation of O-ethyl-S-phenylacetyl xanthate in benzene solution under reflux resulted in O-ethyl-S-benzyl xanthate. A similar type of fragmentation has been reported in the photolysis of several acyl xanthates,[6] phthaloyl dixanthates[7,8] phthaloic bis dithiocarbamic-anhydrides,[8] O-alkyl-S-phthalyl xanthates[9] and dithiocarbamoyl phthalides.[9]

Barton et al.[4] have also shown that O-ethyl-S-benzoyl and O-ethyl-S-p-chlorobenzoyl xanthates were resistant to phtolysis in boiling benzene or toluene. This is due to the stability of ArCO radical, formed during the photolysis. Praefcke, Klaus and Beelitz, Klaus[10] have reported the formation of various products through α-splitting of either CO-S or CS-S bond in o-substituted benzoyl xanthates. For example, Irradiation of O-ethyl-S-o-chlorobenzoyl xanthate in benzene solution gave ethyl xanthic acid disulphide, o-chloro benzaldehyde and o-chlorobenzoyl disulphide.[10]

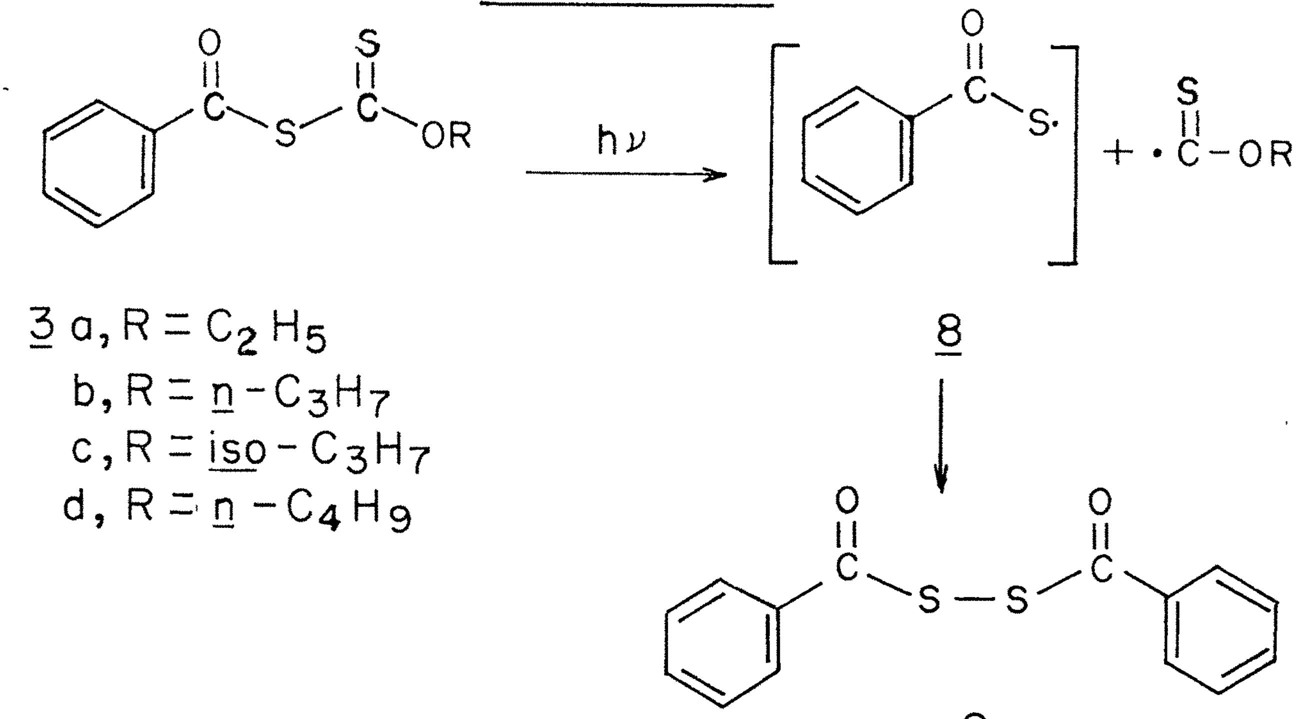
During the present investigation, we have carried out the photolysis of a few benzoyl xanthates (3a-d) in dry benzene for a period of 60-70 hrs.

with a mercury lamp in a pyrex flask which gave a gummy solid from which only benzoyl disulphide (9) could be isolated. A solution of the xanthate (3a-d) subjected to similar conditions in the absence of light did not show any appreciable change. A probable mechanism consistent with the formation of this product is shown in Scheme 4.

The free radical pathway involving a C(S)-S bond fission resulting in the thiobenzoate radical (8) and subsequent dimerisation explains the formation of benzoyl disulphide[10] (9). Disulphide (9) thus formed has been reported to be resistant to photolysis.[11] Earlier workers have reported the formation of free radicals due to the C(O)-S bond fission.[4,6] Our attempts to isolate benzil and dithiooxalic acid dialkyl esters from the reaction mixture were not successful, which indicates that the aroyl radical formed during the photolysis does not dimerise.[10]

With a view to study the effect of sunlight irradiation without solvent, we have carried out the photolysis of a few aroyl xanthates (3a, 5 and 7). For example, O-ethyl-S-benzoyl xanthate (3a), on

SCHEME - 4

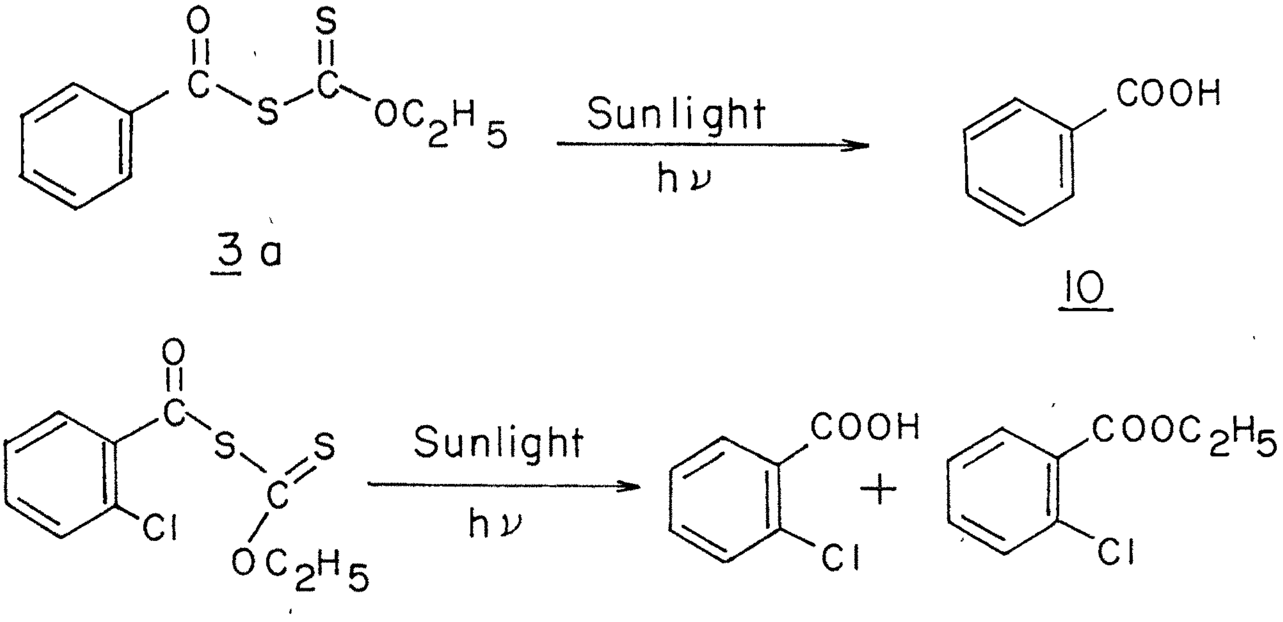


3 a, R = C_2H_5
b, R = n - C_3H_7
c, R = iso - C_3H_7
d, R = n - C_4H_9

8

9

SCHEME - 5



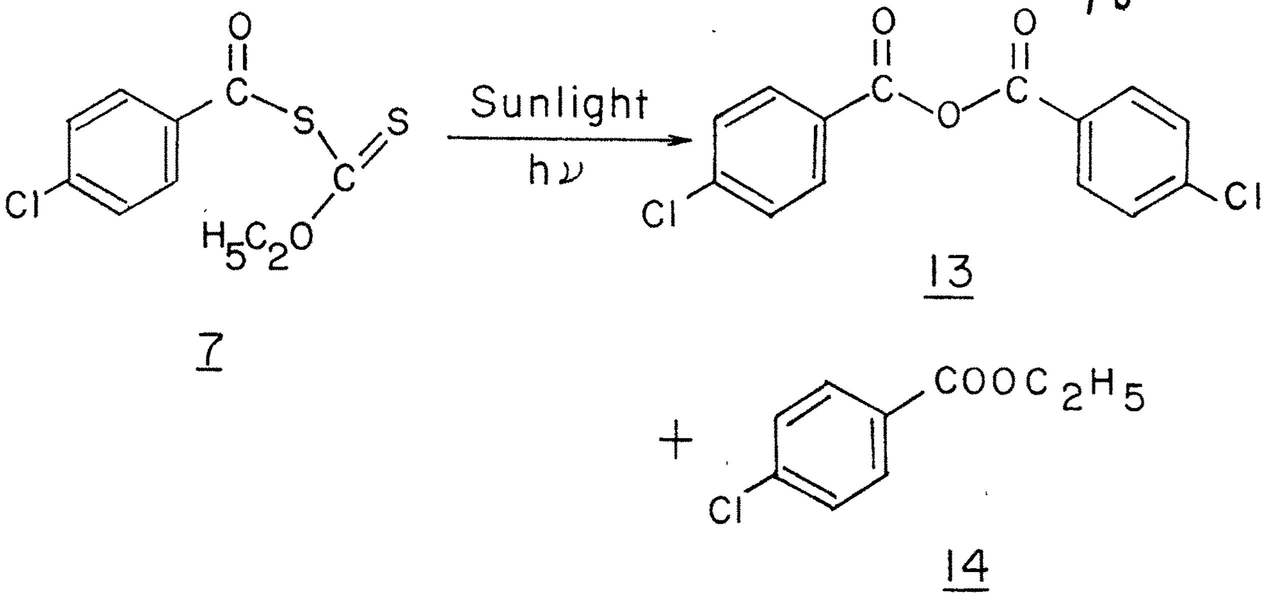
3 a

10

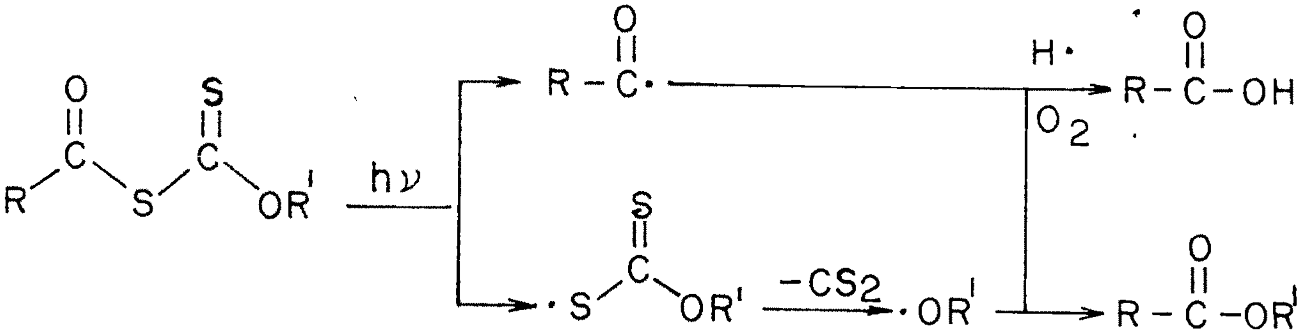
5

11

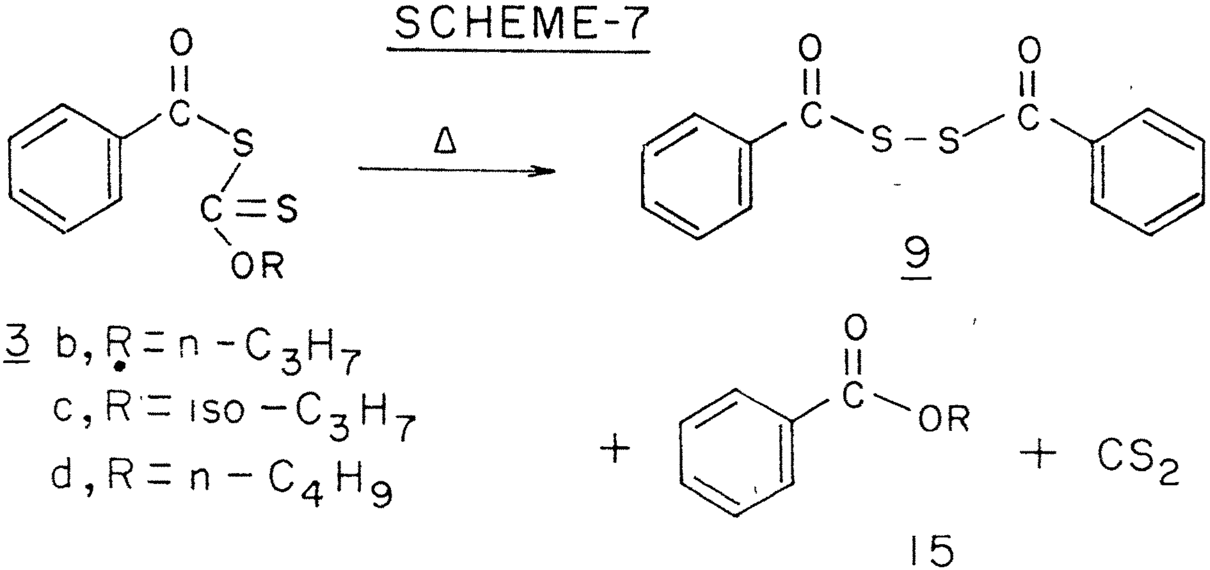
12



SCHEME -6



SCHEME-7



3 b, R = n − C_3H_7
c, R = iso − C_3H_7
d, R = n − C_4H_9

+ CS_2

irradiation for 145 hrs with bright day sunlight gave a gummy semisolid, from which only benzoic acid (10) could be isolated. Similarly, O-ethyl-S-o-chlorobenzoyl xanthate (5), on irradiation for 60 hrs with sunlight resulted in o-chloro benzoic acid (11) and ethyl-o-chlorobenzoate (12). Whereas o-ethyl-S-p-chlorobenzoyl xanthate (7) when irradiated in the crystalline state for 84 hrs gave p-chlorobenzoic anhydride (13) and ethyl-p-chlorobenzoate (14) (Scheme 5).

The plausible mechanism for the formation of these products is shown in Scheme 6.

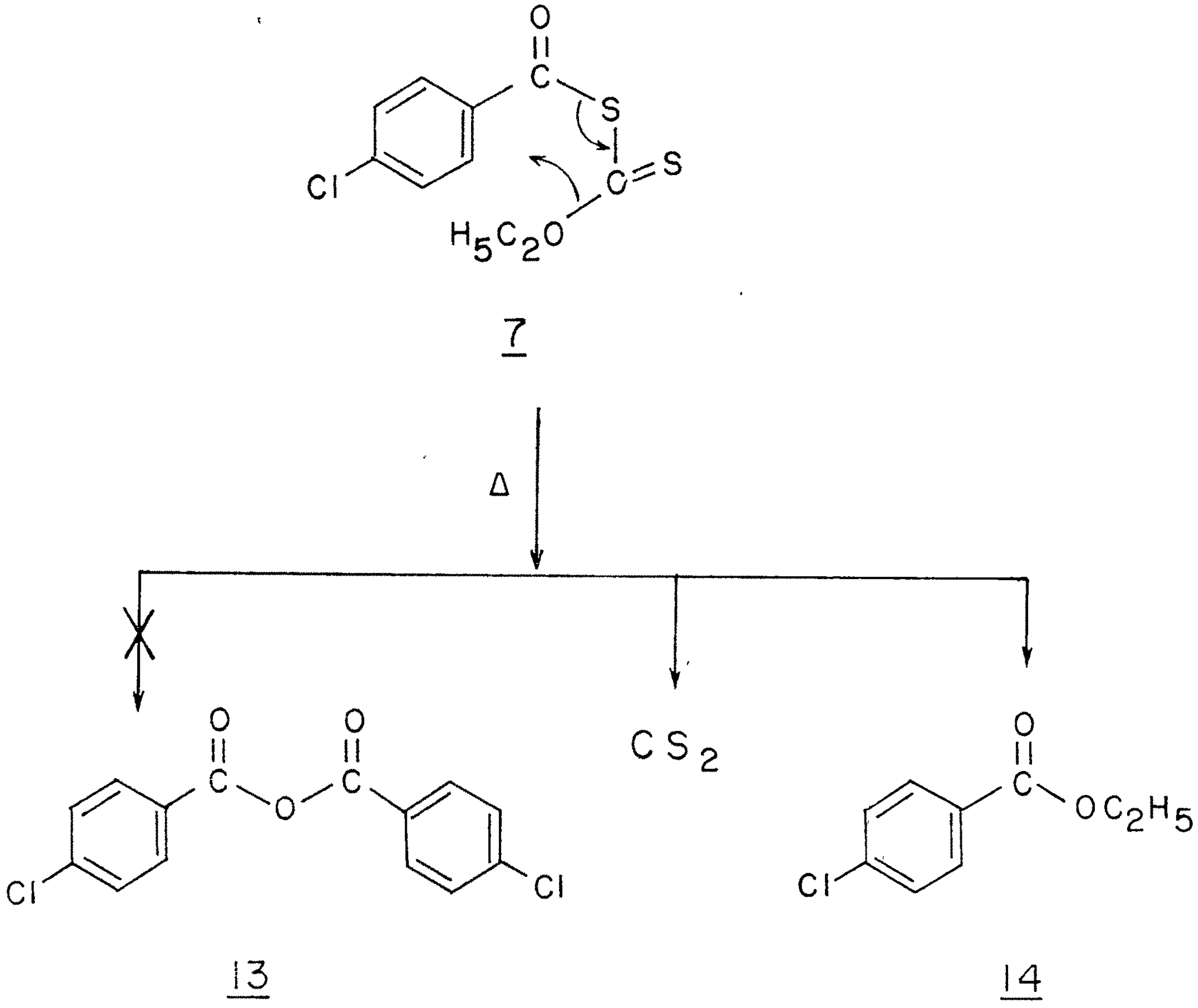
In order to ascertain truely the photolytic nature of these fragmentations of 3a, 5 and 7, they were subjected to similar conditions of temperature in the same interval of time for reference. No appreciable change was observed in these reference samples.

In continuation of our work, we have studied the thermal decomposition of a few aroyl xanthates. The thermal decomposition of aroyl xanthates have been reported to be much more complex.[3,4] Thus, for example, thermal decomposition of O-ethyl-S-benzoyl xanthate at 18 mm has been reported to give a mixture of benzoyl disulphide, ethyl benzoate, ethyl thiobenzoate, ethyl dithiobenzoate and tetraphenylthiophenenonasulphide.[3] Barton et al. have reported the thermal decomposition of acyl xanthates around 200° to give esters and carbon disulphide.[4] A four membered cyclic transition state has been suggested for such decomposition.[4,12,13] Pyrolysis of the xanthate 3b-d around 250° for 15 min gave benzoyl disulphide, corresponding esters and carbon disulphide as shown in Scheme 7.

Pyrolysis of O-ethyl-S-p-chlorobenzoyl xanthate (7) around 190° resulted in the formation of ethyl-p-chlorobenzoate (14) and carbon disulphide and not p-chlorobenzoic anhydride (13) as reported by earlier workers.[3] A four membered cyclic transition state[4,12,13] is consistent with the formation of these products (Scheme 8).

In continuation of this work, we have investigated the reactions of a few aroyl xanthates with aromatic amines. For example, o-ethyl-S-benzoyl

SCHEME-8



7

13

14

xanthate (3a) when treated with aniline in ether solution gave benzanilide (16). Similarly, xanthate 3a when treated with o-phenylenediamine resulted in dibenzoyl-o-phenylene diamine (17).

Similarly, O-Ethyl-S-o-chlorobenzoyl xanthate (5) and O-ethyl-S-p-chlorobenzoyl xanthate (7) were treated with different aromatic amines which resulted in the formation of corresponding benzoyl derivatives as reported for aroyl dithiocarbamic anhydrides.[14] (Scheme 9).

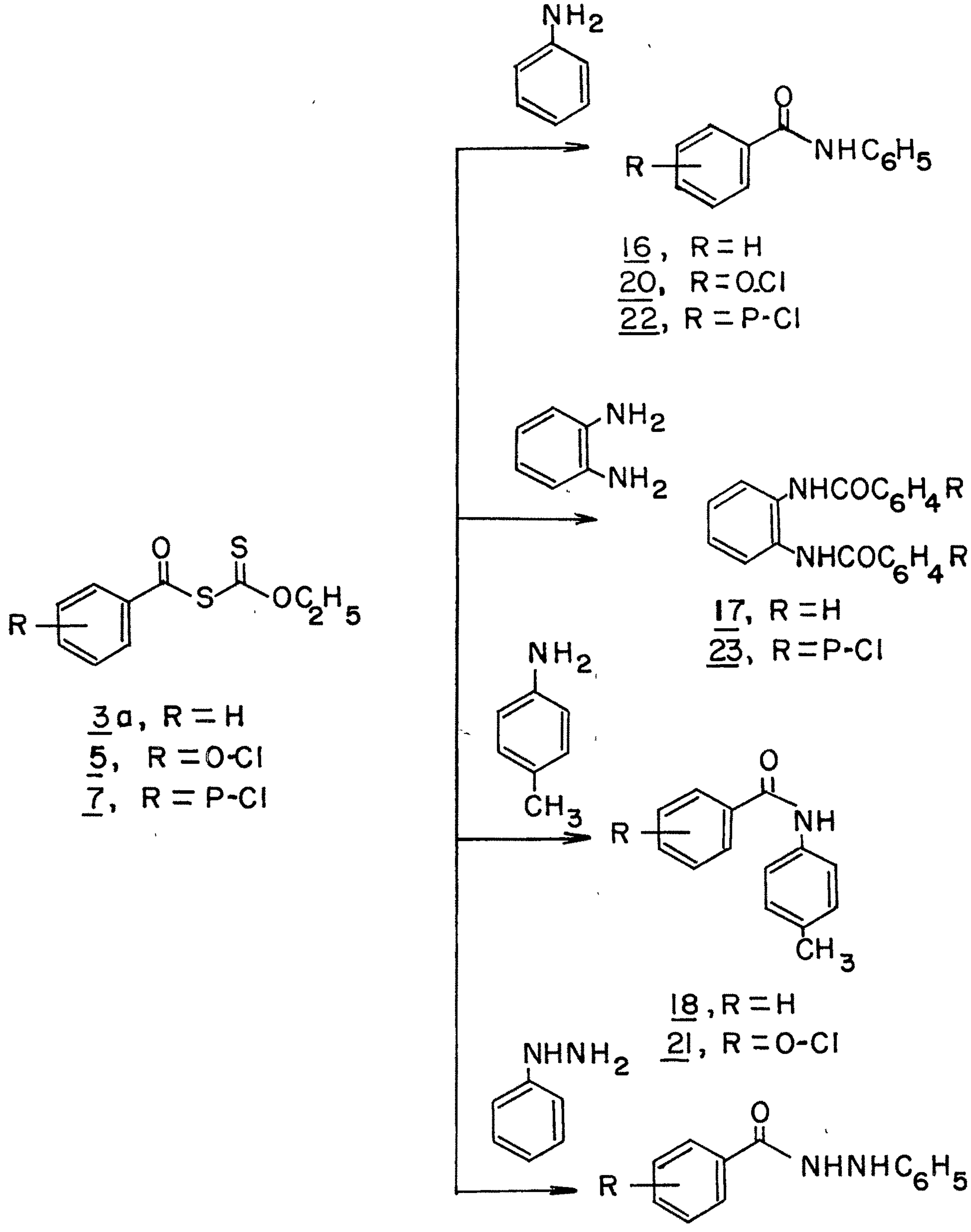
2.3 Experimental

IR spectrum were determined on a Beckman IR-20 Infrared Spectrophotometer and UV Spectra were determined on a specord UV VIS Spectrophotometer. NMR traces were recorded on a Perkin Elmer R-32 NMR Spectrometer using tetramethylsilane as internal standard. Irradiation was carried out in pyrex flasks with 100 w mercury lamp, under dry oxygen-free nitrogen.

Starting materials

Potassium-O-ethyl xanthate, m.p. 225°, potassium-O-

SCHEME-9



16, R = H
20, R = O.Cl
22, R = P-Cl

17, R = H
23, R = P-Cl

3a, R = H
5, R = O-Cl
7, R = P-Cl

18, R = H
21, R = O-Cl

19, R = H
24, R = P-Cl

n-propyl xanthate, m.p. 230°, potassium-O-isopropyl xanthate, m.p. 274° potassium-O-n-butyl xanthate, m.p. 258° were prepared by reported procedure.[15] Benzoyl chloride was supplied by E. Merck (India) Ltd., Bombay. Substituted benzoyl chloride were prepared by usual procedure.[16]

O-Ethyl-S-benzoyl xanthate (3a)

To a solution of 1 (1.4 g, 0.01 mole) in acetone (25 ml), maintained around 0° was added potassium-O-ethyl xanthate (1.6 g, 0.01 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 a 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 gave 1.6 g (70%) of the xanthate 3a as a yellow liquid. $\lambda_{max}^{Benzene}$ 395 nm (ϵ, 128).

Photolysis of O-Ethyl-S-benzoyl xanthate (3a)

A solution of 3a (1 g, 0.004 mole) in benzene

(AR ; 50 ml) was irradiated for 60 hr with mercury lamp in a pyrex flask. Removal of the solvent gave a product which on recrystallisation from a mixture (1:1) of methylene chloride and petroleum ether (b.p. 40-60°) gave 60 mg (10%) of benzoyl disulphide (9) m.p. 130° (mmp).[17]

A solution of the xanthate 3a subjected to similar conditions in the absence of light did not show any appreciable change.

Anal : Calcd for $C_{14}H_{10}O_2S_2$: C, 61.31 ; H, 3.65

Found : C, 61.62 ; H, 4.06

IR Spectrum (Nujol) ν max : 2980, 1705, 1690 (benzoyl group), 1600, 1585, 1450, 1385, 1210, 1180, 890, 775, 675 and 640 cm^{-1}.

Sunlight Photolysis of O-ethyl-S-benzoyl xanthate (3a)

The xanthate 3a (2.3 g, 0.01 mole) was taken in a petry dish with cover and was subjected to bright day sun light for 145 hrs.

Trituration of the resulting gummy mass with petroleum ether (40-60°) gave a white solid (0.31 g) which was identified as benzoic acid m.p. 119° (mmp). Similar photolysis experiment was carried out with the sample wrapped in a black paper in the identical condition for reference. No appreciable change was observed in the reference sample.

Reaction of O-Ethyl-S-benzoyl xanthate (3a) with aniline

To a solution of 3a (2.3 g, 0.01 mole) in diethyl ether (50 ml) maintained around 0° was added aniline (0.9 g, 0.01 mole) drop wise, over a period of 30 minutes. The precipitated product on recrystallisation from ethyl alcohol gave 1.0 g (50%) benzanilide (16) m.p. 162° (mmp).

Reaction of O-ethyl-S-benzoyl xanthate (3a) with o-phenylenediamine

To a solution of 3a (2.3 g, 0.01 mole) in diethyl ether (10 ml) maintained around 0° was added a solution of o-phenylene diamine (0.54 g, 0.005 mole) in ether (25 ml) drop wise over a period of 15 min. with constant stirring. The precipitated product on recrystallisation from ethanol gave 0.75 g (47%) of dibenzoyl-o-phenylene diamine (17) m.p. 300° (mmp).

Reaction of O-Ethyl-S-benzoyl xanthate (3a) with p-toluidine

To a solution of 3a (2.3 g, 0.01 mole) in diethyl ether (15 ml) maintained around 0° was added a solution of p-toluidine (1.1 g, 0.01 mole) in ether (20 ml) drop wise over a period of 30 minutes. The precipitated product on recrystallisation from ethyl alcohol gave 1.1 g (50%) benztoluidide (18) m.p. 159° (mmp).

Reaction of O-ethyl-S-benzoyl xanthate (3a) with phenyl hydrazine

To a solution of 3a (2.3 g, 0.01 mole) in diethyl ether (50 ml) maintained around 0° was added phenyl hydrazine (1.1 g, 0.01 mole) drop wise, over a period of 1 hr with constant stirring. The precipitated product on recrystallisation from ethyl alcohol gave 1.3 g (60%) N-phenylaminobenzamide (19) m.p. 168-70° (Lit. m.p. 168°).[14]

Anal : Calcd for $C_{13}H_{12}ON_2$: C, 73.58 ; H, 5.66

Found : C, 74.15 ; H, 5.86

O-n-propyl-S-benzoyl xanthate (3b)

To a solution of **1** (1.4 g, 0.01 mole) in acetone (20 ml), maintained around 0° was added potassium-O-n-propyl xanthate (1.7 g, 0.01 mole) in small portions, over a period of 30 min. with constant stirring. Work-up of the mixture in the usual manner gave 2.3 g (94%) of the xanthate **3b** as a yellow liquid, n_D^{25} 1.6010. Satisfactory analytical data for this xanthate **3b** were not secured due to unstability. Purity of compound was checked on TLC (Silica gel) using methylene chloride and petroleum ether (1:1) as eluent.

IR Spectrum (Liq. film) : ν max : 1700 (C=O) and 1270 cm^{-1} (C=S).

UV Spectrum : (Ethanol) λ max : 215 (ϵ, 13, 740) ; 245 (ϵ, 19, 200) ; 280 (ϵ, 10, 260) and 410 nm (ϵ, 76).

Photolysis of O-n-propyl-S-benzoyl xanthate (3b)

A solution of **3b** (1 g, 0.004 mole) in benzene (AR, 35 ml) was irradiated for 70 hr with mercury lamp in a pyrex flask. Removal of the solvent and work-up in usual manner gave 75 mg (13%) of benzoyl disulphide (**9**) m.p. 129° (mmp).[17]

Thermal Decomposition of O-n-propyl-S-benzoyl xanthate (3b)

The xanthate 3b (3.5 g, 0.014 mole) was heated under a continuous stream of nitrogen in an oil bath maintained at 250° for 15 minutes. The gaseous product was bubbled through a solution of piperidine (5 ml) in methylene chloride (50 ml). Removal of solvent gave 1.3 g piperidiniumcyclopentamethylene dithiocarbamate m.p. 169° (Lit. m.p. 169°)[9] corresponding to 36% yield of carbon disulphide.

The pyrolysed residue was triturated with petroleum ether (b.p. 40-60°) to give 0.21 g (11%) of benzoyl disulphide (9), m.p. 129° (mmp).[17] The residual mass was hydrolysed with 10% aq. KOH to give 0.28 g of benzoic acid m.p. 119° (mmp) corresponding to 16% yield of n-propyl benzoate (15b).

Reaction of O-n-propyl-S-benzoyl xanthate (3b) with phenyl hydrazine

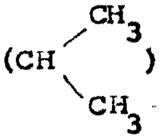
To a solution of 3b (1.9 g, 0.0095 mole) in diethyl ether (30 ml) maintained around 0° was added phenyl hydrazine (1.0 g, 0.0095 mole) drop wise, over a period of 1 hr with constant stirring. The precipitated product on recrystallisation from ethyl alcohol gave 1.2 g (58%) N-phenylamino benzamide (19) m.p. 168-70° (mmp).[14]

O-isopropyl-S-benzoyl xanthate (3c)

To a solution of 1 (1.4 g, 0.01 mole) in acetone (25 ml), maintained around 0° was added potassium-O-isopropyl xanthate (1.7 g, 0.01 mole) in small portions, over a period of 30 min. with constant stirring. Work-up of the mixture in the usual manner gave 1.2 g (52%) of the xanthate 3c as a yellow liquid, n_D^{25} 1.5010.

Anal : Calcd for $C_{11}H_{12}O_2S_2$; C, 55.00 ; H, 5.00

Found : C, 55.58 ; H, 5.27



IR Spectrum (Liq. film) νmax : 1700 (C=O), 1380 $\left(CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$ and 1270 cm^{-1} (C=S).

UV Spectrum (ethanol) : λmax 215 (ϵ, 9000), 245 (ϵ, 12,800), 290 (ϵ, 5,650) and 410 nm (ϵ, 39).

NMR Spectrum (CCl_4) : δ 7.4 ppm (5H, Aromatic), δ 5.2 ppm (1H) and δ 1.3 ppm (6H).

Treatment of O-isopropyl-S-benzoyl xanthate (3c) with Raney Nickel

A mixture of 3c (1 g, 0.004 mole) with Raney Nickel (6 g) in acetone (50 ml) was refluxed for 5 hr. Removal of the unchanged nickel and the solvent gave 300 mg (67%) of benzaldehyde which did not show depression in the mixture melting point with its phenylhydrazine derivative (m.p. 158°).

Photolysis of O-isopropyl-S-benzoyl xanthate (3c)

A solution of 3c (1 g, 0.004 mole) in benzene (AR ; 35 ml) was irradiated for 65 hr with mercury lamp in a pyrex flask. Removal of the solvent and work-up in usual manner gave 115 mg (20%) of benzoyl disulphide (9) m.p. 129° (mmp).[17]

Thermal Decomposition of O-isopropyl-S-benzoyl xanthate (3c)

The xanthate 3c (3.1 g, 0.013 mole) was heated under a continuous stream of nitrogen gas in an oil bath maintained at 250° for 15 minutes.

The gaseous product was bubbled through a solution of piperidine (5 ml) in methylene chloride (50 ml).

Removal of solvent gave 1.0 g piperidiniumcyclopentamethylenedithiocarbamate m.p. 169° (Lit. m.p. 169°)[9] corresponding to 34% yield of carbon disulphide.

The pyrolysed residue was worked up as in the previous case which gave 0.43 g (14%) of benzoyl disulphide (9), m.p. 129° (mmp)[17] and 0.36 g of benzoic acid m.p. 119° (mmp) corresponding to 17% yield of isopropyl benzoate (15c).

O-n-butyl-S-benzoyl xanthate (3d)

To a solution of 1 (1.4 g, 0.01 mole) in acetone (20 ml), maintained around 0° was added potassium-O-n-butyl xanthate (1.9 g, 0.01 mole) in small portions over a period of 30 min. with constant stirring. Work-up of the mixture in the usual manner gave 1.4 g (56%) of the xanthate 3d as a yellow liquid, n_D^{25} 1.5940.

Satisfactory analytical data for this xanthate 3d were not secured due to unstability. Purity of the xanthate was checked on TLC (Silica gel) using methylene chloride and petroleum ether (1:1) as eluent.

IR Spectrum (Liq. film) ν max : 1700 (C=O) and 1270 cm^{-1} (C=S).

UV Spectrum (Ethanol) λ_{max} ; 215 (ϵ, 12,192), 250 (ϵ, 14, 859), 285 (ϵ, 12, 192) and 410 nm (ϵ, 99).

Photolysis of O-n-butyl-S-benzoyl xanthate (3d)

A solution of **3d** (2.0 g, 0.008 mole) in benzene (AR ; 50 ml) was irradiated for 60 hr with mercury lamp in a pyrex flask. Removal of the solvent and work-up in usual manner gave 205 mg (19%) of benzoyl disulphide (**9**) m.p. 129° (mmp).[17]

Thermal Decomposition of O-n-butyl-S-benzoyl xanthate (3d)

The xanthate **3d** (3.6 g, 0.014 mole) was heated under a continuous stream of nitrogen gas in an oil bath maintained at 250° for 15 minutes.

The gaseous product was bubbled through a solution of piperidine (5 ml) in methylene chloride (50 ml). Removal of solvent gave 1.98 g piperidiniumcyclopentamethylenedithiocarbamate m.p. 169° (Lit. m.p. 169°)[9] corresponding to 57% yield of carbon disulphide. The pyrolysed residue was worked-up as in the previous case gave 0.21 g (11%) of benzoyl disulphide (9), m.p. 129° (mmp)[17] and 0.40 g of benzoic acid m.p. 119° (mmp) corresponding to 23% yield of n-butyl benzoate (15d).

Photolysis of Benzoyl disulphide (9)

A solution of 9 (0.500 g, 0.0018 mole) in benzene (AR ; 35 ml) was irradiated for 89 hrs. with a mercury lamp in a pyrex flask. Removal of solvent and work-up in usual manner gave 350 mg (70%) of starting material (9) m.p. 129-32° (mmp).[17]

O-ethyl-S-o-chlorobenzoyl xanthate (5)

Potassium-O-ethyl xanthate (8.0 g, 0.05 mole) dissolved in dry acetone (100 ml) was added dropwise with constant stirring to a solution of o-chlorobenzoyl chloride (8.8 g, 0.05 mole) in dry acetone (100 ml) around 0°C. Stirring was continued for additional fifteen minutes at the same temperature. Work-up of the mixture in the usual manner gave 10.8 g (83%) of the xanthate 5 as a golden yellow liquid λ max (Benzene) 400 nm (ϵ, 163).

The reaction of 2a with 4 at room temperature gave a red liquid ($\lambda_{max}^{benzene}$ 490 nm) and not the xanthate (5).

Sunlight photolysis of O-ethyl-S-o-chlorobenzoyl xanthate (5)

The xanthate 5 (5.2 g, 0.02 mole) was taken in a petry dish with cover and was subjected to bright day sunlight for 60 hrs.

Work-up of the residual mass as in the previous case gave 200 mg of o-chlorobenzoic acid m.p. 139-40° (mmp). Removal of petroleum ether gave a liquid product 2.0 g which on distillation was identified as ethyl ester of o-chlorobenzoic acid (12) b.p. 241-2° (Lit. b.p. 243°).

This ester was refluxed with 2N sodium hydroxide solution and subsequent acidification gave o-chlorobenzoic acid m.p. 139-40° (mmp). No appreciable change was observed in the blank experiment.

Reaction of O-ethyl-S-o-chlorobenzoyl xanthate (5) with aniline

To a solution of 5 (0.65 g, 0.0025 mole) in diethyl ether (40 ml) maintained around 0° was added aniline (0.23 g, 0.0025 mole) drop wise, over a period of 30 minutes. The precipitated product on recrystallisation from petroleum ether gave 0.30 g (48%) o-chlorobenzanilide (20) m.p. 118° (mmp).

Reaction of O-ethyl-S-o-chlorobenzoyl xanthate (5) with p-toluidine

To a solution of 5 (0.65 g, 0.0025 mole) in diethyl ether (15 ml) maintained around 0° was added a solution of p-toluidine (0.27 g, 0.0025 mole) in ether (20 ml) drop wise over a period of 30 minutes. The precipitated product on recrystallisation from ethyl alcohol gave 0.35 g (56%) o-chlorobenztoluidide (21) m.p. 131° (mmp).

O-ethyl-S-p-chlorobenzoyl xanthate (7)

To a solution of 6 (1.8 g, 0.01 mole) in acetone (40 ml) maintained around 0° was added potassium-O-ethyl xanthate (1.6 g, 0.01 mole) in small portions over a period of 30 min. with constant stirring. Work-up of the mixture in usual manner gave 1.5 g (59%) of the xanthate 7 as a yellow solid. m.p. 66-68° (Lit. m.p. 68°).[3]

IR Spectrum (Nujol) : ν_{max} 1700 (C=O), 1200 (C=S) and 1030 cm^{-1} (C=O).

UV Spectrum (Benzene) λ max : 204 (ϵ, 20, 900), 217 (ϵ, 13, 400), 262 (ϵ, 16, 110), 278 (ϵ, 14, 600) and 385 nm (ϵ, 128).

Sunlight photolysis of O-ethyl-S-p-chlorobenzoyl xanthate (7)

The xanthate 7 (3.6 g, 0.014 mole) was spread in a petridish with cover and was subjected to bright day sunlight for 84 hours.

Work-up of the residual mass as in the previous case gave 0.63 g of p-chlorobenzoic anhydride (13) m.p. 190-91° (mmp). Removal of petroleum ether gave a liquid (1.0 g) which on distillation was identified as ethyl ester of p-chloro benzoic acid (14) b.p. 237-8° (Lit. b.p. 238°). This ester was refluxed with 2N sodium hydroxide solution and subsequent acidification gave p-chloro benzoic acid m.p. 238° (mmp). No appreciable change was observed in blank experiment.

Thermal Decomposition of O-ethyl-S-p-chlorobenzoyl xanthate (7)

The xanthate 7 (2.6 g, 0.01 mole) was taken in two necked pear shape flask and heated in an oil bath maintained at 190-200° for 65 minutes. The evolved gases were passed through a solution of piperidine (4.3 g, 0.05 mole) in diethyl ether (100 ml). The ether solution gave 5.5 g (31%) of piperidiniumcyclopentamethylenedithiocarbamate m.p. 168° (Lit. m.p. 169°).[9]

The pyrolysed residue on distillation gave ethyl p-chlorobenzoate (14) (1 g, 50%) b.p. 238° which on refluxing with 20 ml NaOH solution (20%) and subsequent acidification gave p-chlorobenzoic acid m.p. 239° (mmp).

Reaction of O-ethyl-S-p-chlorobenzoyl xanthate (7) with aniline

To a solution of 7 (0.65 g, 0.0025 mole) in diethyl ether (40 ml) maintained around 0° was added aniline (0.23 g, 0.0025 mole) drop wise, over a period of 30 minutes. The precipitated product on recrystallisation from ethyl alcohol gave 0.28 g (45%) of p-chlorobenzanilide (22) m.p. 194° (mmp).

Reaction of O-ethyl-S-p-chlorobenzoyl xanthate (7) with o-phenylenediamine

To a solution of 7 (0.52 g, 0.002 mole) in diethyl ether (20 ml) maintained at room temperature was added a solution of o-phenylene diamine (0.1 g, 0.001 mole) in ether (20 ml) drop wise over a period of 15 minutes with constant stirring. The precipitated product on recrystallisation from ethanol gave 0.19 g (48%) of di-p-chlorobenzoyl-o-phenylenediamine (23) m.p. 245-46°.

Reaction of O-ethyl-S-p-chlorobenzoyl xanthate (7) with phenyl hydrazine

To a solution of 7 (0.65 g, 0.0025 mole) in diethyl ether (40 ml) maintained at room temperature was added phenyl hydrazine (0.25 g, 0.0025 mole) with constant stirring for a period of 30 min. The precipitated product on recrystallisation from methanol gave 0.27 g (44%) N-phenylamino-p-chlorobenzamide (24) m.p. 187°.

Anal : Calcd for $C_{13}H_{11}ON_2Cl$; C, 63.20 ; H, 4.46

Found : C, 63.01 ; H, 4.49.

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