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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF CARBOXYLIC DITHIOCARBAMIC ANHYDRIDES AND ACYL XANTHATES

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Abstract—The reaction of diphenylchloroacetyl chloride with different dithiocarbamates gave the corresponding dithiocarbamic anhydrides. Under analogous conditions, dithiocarbamyl phenylacetic acids and dithiocarbamyl acetic acids were formed from the reaction of dithiocarbamates with phenylchloroacetyl chloride and chloroacetyl chloride, respectively. O-Ethyl S-acyl xanthates were formed from the reaction of potassium O-ethyl xanthate with diphenylacetyl chloride, diphenylchloroacetyl chloride, cyclopentylphenylacetyl chloride and triphenylacetyl chloride. Photolysis of dithiocarbamic anhydrides gave a mixture of products consisting of 1,2-dichlorotetraphenylethane, carbon monoxide and the corresponding thiocarbamoyl sulfides. Acyl xanthates, on the other hand, gave carbon monoxide and the corresponding substituted ethane derivatives. When dithiocarbamic anhydrides were refluxed in hydroxylic solvents such as methanol, ethanol and n-propanol, the corresponding dithiocarbamyl acetates were formed. Thermal decomposition of acyl xanthates gave carbon disulfide and the corresponding esters.

Photochemical and thermal transformations of few carboxylic dithiocarbamic anhydrides have been reported by Tarbell *et al.*[1,2] who have observed that several products are formed in these reactions depending on the nature of the starting materials. Thus, the photolysis of benzoic pentamethylenedithiocarbamic anhydride, for example, gave rise to a mixture of products consisting of benzoyl piperidide, benzoic acid, benzoyl cyclopentamethylenethiocarbamoyl disulfide and cyclopentamethylenethiuram disulfide. The thermal decomposition of this substance, on the other hand, gave only benzoyl piperdide. Benzoic cyclotetramethylenedithiocarbamic anhydride, on photolysis gave rise to a mixture of N-benzoylpyrrolidine tetramethylenethiuram hexasulfide and benzoic acid. Under analogous conditions, benzoic oxydiethylenedithiocarbamic anhydride gave a mixture of N-benzoylmorpholine, morpholyl (13-S) polysulfide and benzoic acid. Photolysis of benzoic dimethyldithiocarbamic anhydride gave benzoic acid, sulfur, benzoyl dimethylthiocarbamoyl disulfide, bis - (tetramethylthiuram) - disulfide, and N,N'-dimethylbenzamide. It has been suggested that the photolysis of carboxylic dithiocarbamic anhydrides proceed through a free-radical pathway, involving the initial fragmentation of a C–S bond. A similar type of fragmentation has been reported in the photolysis of several acyl xanthates,[3] phthaloyl dixanthates,[4,5] phthaloic bisdithiocarbamic anhydride,[5] O-alkyl S-phthalyl xanthates,[6] and dithiocarbamoyl phthalides.[6]

The object of the present investigation was to examine both the photochemical and thermal transformations of a few dithiocarbamic anhydrides and 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. In this connection, we have studied the reactions of several acid chlorides such as diphenylchloroacetyl chloride, diphenylacetyl chloride, phenylchloroacetyl chloride and chloroacetyl chloride with different dithiocarbamates.

Treatment of an ether solution of diphenylchloroacetyl chloride (**1**) with dimethyldithiocarbamate (**2a**) gave rise to a 57% yield of diphenylchloracetyl dimethyldithiocarbamic anhydride (**3a**), m.p. 95°. The structure of **3a** has been arrived at on the basis of analytical results and spectral data. The IR spectrum of **3a** showed bands at 1685 and 1440 cm^{-1} due to the presence of C=O and C=S groups, respectively. The UV spectrum of **3a** showed a weak absorption band at 408 nm, characteristic of aroyl dithiocarbamic anhydrides.[2,5] The NMR spectrum of **3a** showed a multiplet centred around 7·22 ppm (10H) due to the aromatic protons and a singlet at 3·29 ppm (6H) due to the Me protons.

Similarly, the reactions of diphenylchloroacetyl chloride with diethyldithiocarbamate (**2b**), tetramethylenedithiocarbamate (**2c**), pentamethylenedithiocarbamate (**2d**) and oxydiethylenedithiocarbamate (**2e**) gave the corresponding dithiocarbamic anhydrides (**3b–e**) in yields ranging between 50–90% (Scheme 1).

In one of our attempts at crystallizing diphenylchloroacetyl dimethyldithiocarbamic anhydride (**3a**) from a solvent such as methanol, we had observed that this substance undergoes transformation to give a product, identified as methyl 2 - (N,N - dimethyldithiocarbamyl) - 2,2 - diphenylacetate (**5a**), m.p. 175–176°. The structure of this product has been established on the basis of analytical results and spectral data. The IR spectrum of **5a** showed an ester CO group at 1730 cm^{-1} and a C=S band at 1440 cm^{-1}. The NMR spectrum of **5a** was characterized by the presence of a multiplet centred around 7·11 ppm (10H) due to the aromatic protons. In addition, the spectrum showed two singlets at 3·65 (3H) and 3·28 ppm (3H), due to the ester OMe protons and the Me protons attached to the N atom, respectively.

Similarly, the treatment of other dialkyldithiocarbamic anhydrides (**3b–e**) with methanol gave the corresponding methyl 2 - (N,N - dialkyldithiocarbamyl) - 2,2 - diphenylacetates (**5d, g, j** and **m**) in yields ranging between 70 and 90%.

Treatment of **3a** with ethanol gave rise to a 83% yield of ethyl 2 - (N,N - dimethyldithiocarbamyl) - 2,2 -

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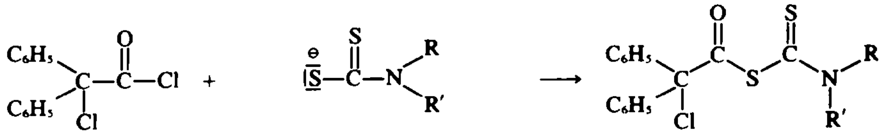


1

2a: R = R′ = CH_3
b: R = R′ = C_2H_5
c: R,R′ = $-(CH_2)_4-$
d: R,R′ = $-(CH_2)_5-$
e: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$

3a: R = R′ = CH_3
b: R = R′ = C_2H_5
c: R = R′ = $-(CH_2)_4-$
d: R,R′ = $-(CH_2)_5-$
e: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$

Scheme 1.

diphenylacetate (**5b**), whereas from the reaction of **3a** with n-propanol, a 66% yield of n-propyl 2 - (N,N - dimethyldithiocarbamyl) - 2,2 - diphenylacetate (**5c**) was obtained. Similarly, the reactions of other dialkyldithiocarbamic anhydrides (**3b–e**) with ethanol and n-propanol resulted in the formation of the corresponding ethyl 2 - (N,N - dialkyldithiocarbamyl) - 2,2 - diphenylacetates (**5e**, **h**, **k** and **n**) and n-propyl 2 - (N,N - dialkyldithiocarbamyl) - 2,2 - diphenylacetates (**5f**, **i**, **l** and **p**), respectively, in yields ranging between 50 and 85%.

Further confirmation of the structure of alkyl 2 - (N,N - dialkyldithiocarbamyl) - 2,2 - diphenylacetates (**5a–p**) was derived by the conversion of a representative substrate such as methyl 2 - (N,N - diethyldithiocarbamyl) - 2,2 - diphenyl-acetate (**5d**) to methyl diphenylacetate, on treatment with Raney-Nickel.

A probable route to the formation of alkyl 2 - (dialkyldithiocarbamyl) - 2,2 - diphenylacetates (**5**) from the corresponding dithiocarbamic anhydrides (**3**) is shown in Scheme 2. In this scheme, we assume that the displacement of the chloride ion is proceeding through an intramolecular process leading to the formation of a cyclic intermediate **4**, which undergoes further attack by the alcohol. It is also possible that the dithiocarbamic anhydride **3** undergoes initial solvolysis to give a carbonium ion intermediate which then goes through the cyclic intermediate **4** to the final product **5**.

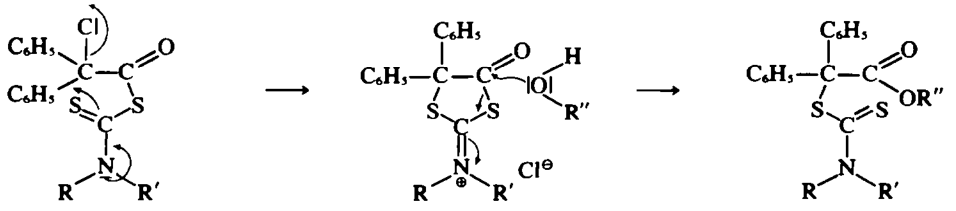
With a view to understanding the mechanism of the transformation of **3** to **5**, we have examined the kinetics of the reaction of a few dithiocarbamic anhydrides (**3a–e**) with methanol. The progress of the reaction, in each case was followed spectrophotometrically through the disappearance of the absorption max around 408 nm, due to the starting material. Table 1 summarizes the rate data for three different temperatures, 40°, 45° and 50°. These results indicate that the transformation of **3** to **5** obeys pseudo first order rate law.

The relatively low activation energies and large negative entropies should be in agreement with the suggested mechanism (Scheme 2).

In continuation of our studies, we have examined the reactions of α-chlorophenylacetyl dithiocarbamic anhydrides with different hydroxylic solvents to test the generality of such transformations. It might be mentioned in this connection that our attempts at preparing α-chlorophenylacetyl dimethyldithiocarbamic anhydride

Table 1. Kinetic data for the transformation of 3–5 in presence of methanol

Compound	Rate at 40° (sec^{-1})	Rate at 45° (sec^{-1})	Rate at 50° (sec^{-1})	Activation energy (kcal)	Entropy of activation (e.u.)
3a	$1{\cdot}32\times10^{-5}$	$2{\cdot}15\times10^{-5}$	$2{\cdot}46\times10^{-5}$	14·0	−36·3
3b	$5{\cdot}75\times10^{-5}$	$6{\cdot}3\times10^{-5}$	$10{\cdot}2\times10^{-5}$	12·2	−39·5
3c	$1{\cdot}53\times10^{-5}$	$2{\cdot}13\times10^{-5}$	$4{\cdot}13\times10^{-5}$	22·9	−8·0
3d	$2{\cdot}56\times10^{-5}$	$3{\cdot}4\times10^{-5}$	$6{\cdot}6\times10^{-5}$	19·6	−17·5
3e	$0{\cdot}38\times10^{-5}$	$1{\cdot}15\times10^{-5}$	$1{\cdot}6\times10^{-5}$	23·0	−9·0



3a: R = R′ = CH_3
b: R = R′ = C_2H_5
c: R,R′ = $-(CH_2)_4-$
d: R,R′ = $-(CH_2)_5-$
e: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$

4

a: R = R′ = CH_3, R″ = CH_3
b: R = R′ = CH_3, R″ = C_2H_5
c: R = R′ = CH_3, R″ = n-C_3H_7
d: R = R′ = C_2H_5, R″ = CH_3
e: R = R′ = C_2H_5, R″ = C_2H_5
f: R = R′ = C_2H_5, R″ = n-C_3H_7
g: R,R′ = $-(CH_2)_4-$, R″ = CH_3
h: R,R′ = $-(CH_2)_4-$, R″ = C_2H_5

5a–p

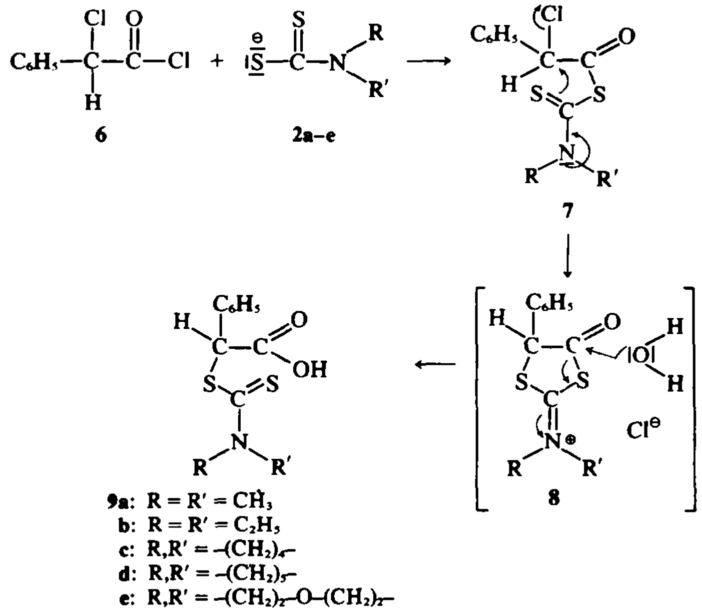
i: R,R′ = $-(CH_2)_4-$, R″ = n-C_3H_7
j: R,R′ = $-(CH_2)_5-$, R″ = CH_3
k: R,R′ = $-(CH_2)_5-$, R″ = C_2H_5
l: R,R′ = $-(CH_2)_5-$, R″ = n-C_3H_7
m: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$, R″ = CH_3
n: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$, R″ = C_2H_5
p: R,R′ = $-(CH_2)_2-O-(CH_2)_2-$, R″ = n-C_3H_7

Scheme 2.

(**7a**), employing the reaction of α-chlorophenylacetyl chloride (**6**) with **2a** in ether solution resulted in the formation of an yellow solution which showed an absorption max at 400 nm, presumably due to the formation of **7a**. However, the yellow colour of the solution rapidly faded and eventually yielded a colourless solution, which on work-up gave a 90% yield of a product, identified as 2 - (N,N - dimethyldithiocarbamyl) - 2 - phenylacetic acid (**9a**). The structure of **9a** was established on the basis of analytical results and spectral data. The IR spectrum of **9a** showed a C=O absorption band at 1700 cm^{-1}, indicative of a carboxylic acid. The UV spectrum was characterized by the presence of three absorption maxima at 250 nm (ε, 12,900), 278 (11,150) and 328 (70), respectively. The structure of **9a** was further confirmed by its conversion to phenylacetic acid, on treatment with Raney-Nickel.

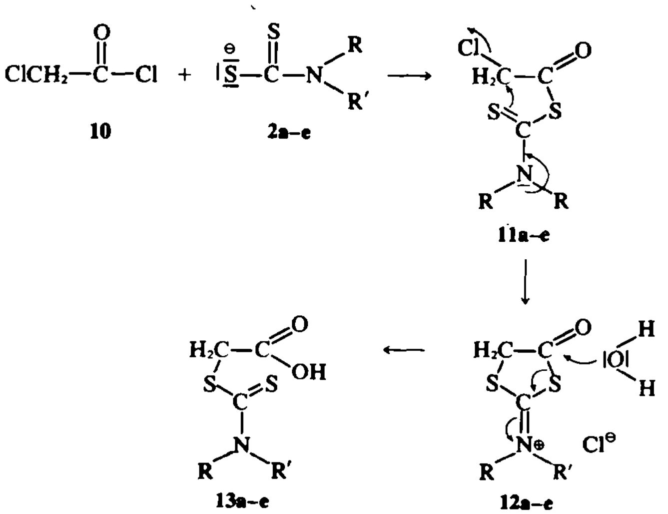
Similarly, the reaction of α-chlorophenylacetyl chloride (**6**) with **2b**, **2c**, **2d** and **2e** gave the corresponding dithiocarbamoyl phenylacetic acids, **9b–e** in yields ranging between 54 and 67% (Scheme 3).

In the reaction of chloroacetyl chloride (**10**) with dimethyldithiocarbamate (**2a**) also, the intermediate chloroacetyl dimethyldithiocarbamic anhydride (**11a**) could not be isolated as it underwent rapid transformation to a product identified as 2 - (N,N - dimethyldithiocarbamyl) - acetic acid (**13a**), m.p. 155–156° (Scheme 4). The initial formation of the intermediate **11a**, however, was established on the basis of the yellow colour of the reaction mixture, soon after mixing **10** and **2a**, which showed an



9a: R = R' = CH_3
b: R = R' = C_2H_5
c: R,R' = $-(CH_2)_4-$
d: R,R' = $-(CH_2)_5-$
e: R,R' = $-(CH_2)_2-O-(CH_2)_2-$

Scheme 3.



a: R = R' = CH_3
b: R = R' = C_2H_5
c: R,R' = $-(CH_2)_4-$
d: R,R' = $-(CH_2)_5-$
e: R,R' = $-(CH_2)_2-O-(CH_2)_2-$

Scheme 4.

absorption max at 400 nm, characteristic of dithiocarbamic anhydrides.[1,2,5] The reaction of chloroacetyl chloride with other dialkylthiocarbamates such as **2b**, **2c**, **2b** and **2e** gave the corresponding acetic acid derivatives, **13b–e**, in yields ranging betwee 47 and 67%.

It is interesting to note that the reaction of diphenylacetyl chloride (**14**) which does not contain an α-chlorosubstituent, with **2a** gave rise to a 50% yield of N,N - dimethyl - 2,2 - diphenylacetamide (**16a**) (Scheme 5) as the only isolable product. The formation of **16a** may be rationalized in terms of a facile decomposition of the initially formed diphenylacetyl dimethyldithiocarbamic anhydride (**15a**). Further conformation of the initial involvement of **15a** was derived from the presence of an absorption max around 400 nm in a fresh mixture of **2a** and **14**, in diethyl ether. The transformation of **15a** to **16a** may be going through a 4-membered cyclic transition state as shown in Scheme 5. Similarly, the reaction of **14** with diethyldithiocarbamate and pentamethylenedithiocarbamate gave **16b** and **16d** in 54 and 60% yields, respectively.

Our next objective was to study the photolysis of an α-chloroacetyl dialkyldithiocarbamic anhydride such as **3a**, to examine the nature of the products formed in these reactions. Photolysis of a benzene solution of **3a** resulted in the formation of a mixture of products consisting of 1,2 - dichlorotetraphenylethane (20%), carbon monoxide (54%) and diphenylchloromethyl dimethylthiocarbamoyl monosulfide (**21a**) (34%), m.p. 165° (Scheme 6). The structure of **21a** was confirmed on the basis of analytical results and spectral data. Further confirmation of the structure of **21a** was derived from its transformation to thiobenzophenone (**26**), on heating to its m.p. The formation of thiobenzophenone in this reaction may be rationalized in terms of 4-membered, cyclic transition state (**25**) as shown in Scheme 7. It might be mentioned in this connection that the thermal decompositions of **24c** and **24e** have also been reported to give rise to thiobenzophenone, presumably through a 6-membered transition state, as shown in Scheme 8.[7] Similarly, the thermal decompositions of **21b** and **21d** gave thiobenzophenone in each case.

The formation of products such as carbon monoxide, **20** and **21a** in the photolysis of **3a** can be rationalized in terms of the initial homolysis of **3a**, giving rise to the radical species **17** and **18**. The diphenylchloroacetyl radical (**17**) can then undergo very facile decarbonylation, resulting in the formation of diphenylchloromethyl radical (**19**). The radical **19** can then either dimerize to give dichlorotetraphenylethane (**20**) or combine with **18a** leading to the formation of **21a**.

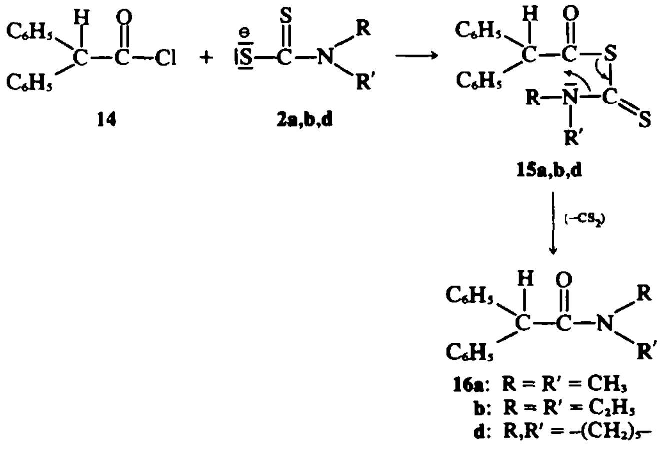
Similarly, the photolysis of **3b** and **3d** gave carbon monoxide, 1,2-dichlorotetraphenylethane and the corresponding monosulfides, **21b** and **21d**, respectively.

The photolysis of **3c**, on the other hand, gave rise to a mixture of products consisting of carbon monoxide, **20** and diphenylchloromethyl tetramethylenethiocarbamoyl disulfide (**24c**). The formation of **24c** may be explained in terms of the combination of the radical intermediate **22** with diphenylchloromethyl radical (**19**). The radical **22** may result from the reaction of the thiocarbamyl radical with itself, as shown in Scheme 6. It might be recalled in this connection that the formation of bis (tetramethylene)thiuram disulfide and bis(oxydiethylene)thiuram (13-S) polysulfide in the photolysis of benzoic tetramethylenedithiocarbamic anhydride and benzoic oxydiethylene dithiocarbamic anhydride, respectively have been explained by a mechanism involving the stepwise sulfur displacement on a growing thiocarbamyl polysulfide radical.[2] Similarly, the photolysis of **3e** gave carbon monoxide, **20** and **24e**.

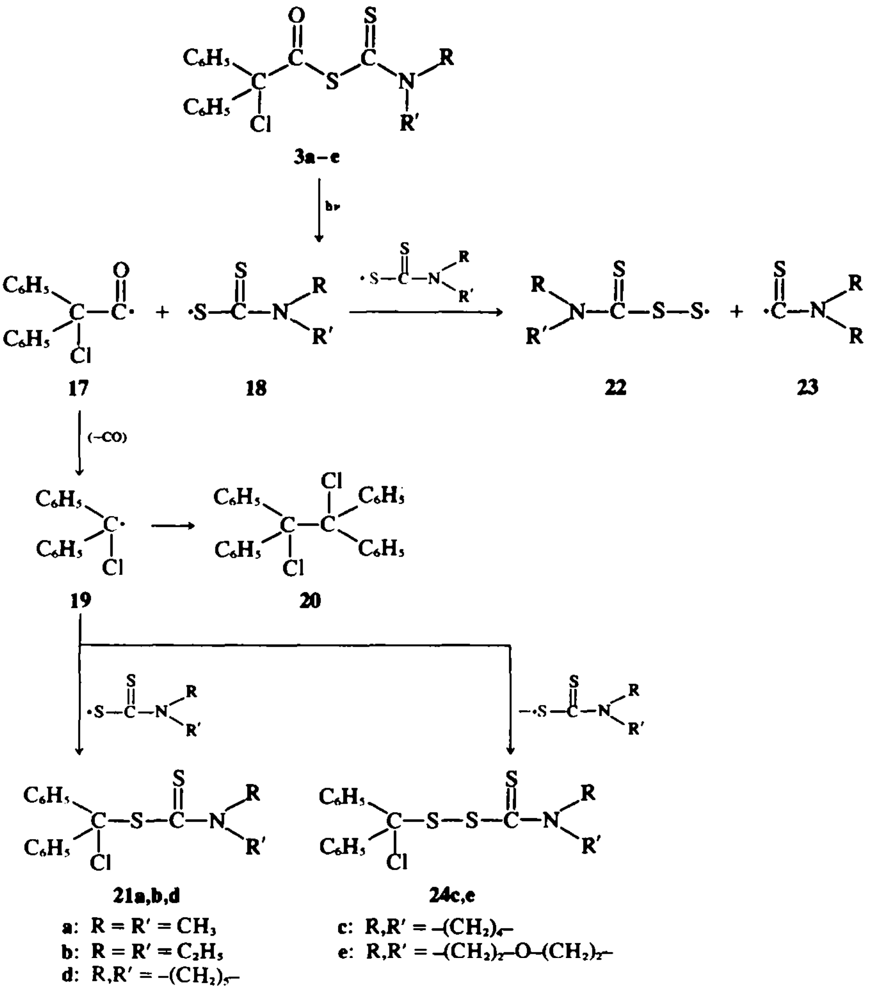
In continuation of our studies we have attempted the photolysis of methyl 2 - (N,N - dimethyldithiocarbamyl) - 2,2 - diphenylacetate (**5a**) in benzene solution. However, it was observed that even after 8 hr of irradiation, practically no change could be detected, indicating thereby that this compound does not undergo ready photolysis, unlike the carboxylic dithiocarbamic anhydrides.

Our next attempt was to study the reaction of different substituted acetyl chlorides with potassium O-ethyl xanthate and to study the photochemical transformations of the resulting acyl xanthates. These xanthates were prepared by a standard procedure,[3] involving the reaction of an acid chloride with potassium O-ethyl xanthate. Thus, in the reaction of diphenylacethyl chloride (**29a**) with potassium O-ethyl xanthate (**30**), a 64% yield of O-ethyl S-diphenylacetyl xanthate (**31a**) was obtained. The structure of **31a** was confirmed on the basis of analytical results and spectral data. The IR spectrum of **31a** showed strong absorption bands at 1736 $\mathrm{cm^{-1}}$ (C=O) and 1230 (C=S). The UV spectrum showed the presence of an absorption maximum at 398 nm (ε, 60), characteristic of acyl and aroyl xanthates.[3,4]

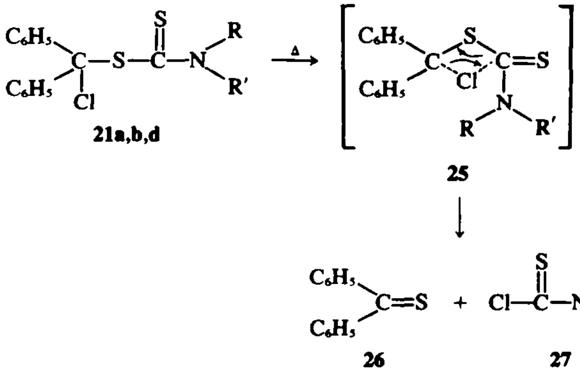
Similarly, the reaction of potassium O-ethyl xanthate with cyclopentylphenylacetyl chloride (**29b**),



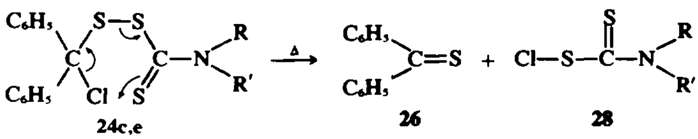
Scheme 5.



Scheme 6.



Scheme 7.



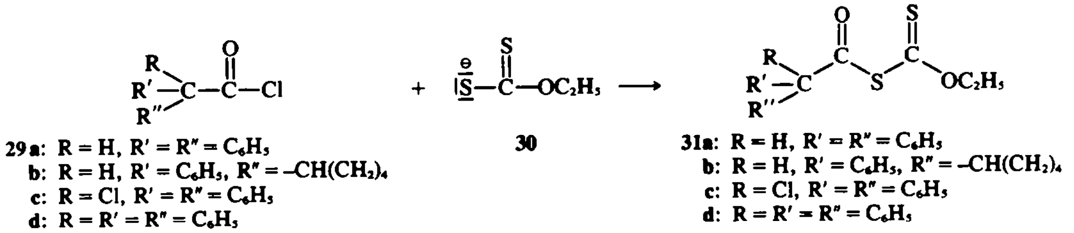
Scheme 8.

diphenylacetyl chloride (**29c**) and triphenylacetyl chloride (**29d**) gave the corresponding acetyl xanthates, **31b–d** in yields ranging between 65 and 70% (Scheme 9). The reaction of diphenoyl dichloride (**32**) with potassium O-ethyl xanthate, likewise, resulted in the formation of a 55% yield of di-O-ethyl S,S-diphenoyl dixanthate (**33**) (Scheme 10).

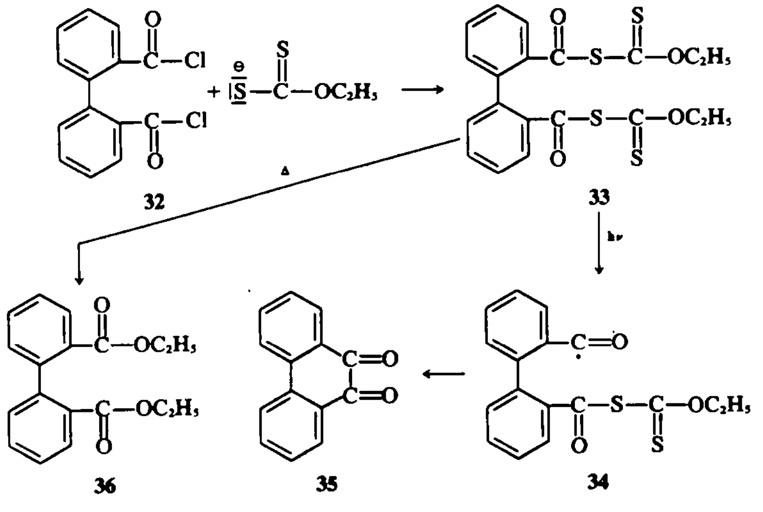
When the reaction of **29a** with potassium O-ethyl xanthate was carried out around room temperature, the product isolated was diphenylacetic thioanhydride and not the expected xanthate **31a**. A similar observation has been made in the attempted preparation of a few other acyl xanthates.[3,4]

Photolysis of O-ethyl S-diphenylacetyl xanthate (**31a**) in benzene solution resulted in the formation of a mixture of carbon monoxide and tetraphenylethane (**39a**). Similarly, the photolysis of the xanthates **31b** and **31c** gave carbon monoxide and the corresponding ethane derivatives, **39b** and **39c**, respectively. Photolysis of O-ethyl S-triphenylacetyl xanthate (**31d**), on the other hand, gave triphenylmethyl peroxide (**40**) and not the expected hexaphenylethane. The formation of these products can be explained in terms of an initial fission of the C–S bond to give the corresponding acyl radicals (**37**), which on decarbonylation give the corresponding substituted Me radicals (**38**). The decarbonylated radical (**38**) can undergo dimerization to give the corresponding ethane derivative (**39**). In the case of triphenylmethyl radical (**38d**), however, it has been observed that the combination with atmospheric oxygen to give triphenylmethyl peroxide (**40**) is the preferred mode as compared to the dimerization reaction (Scheme 11).

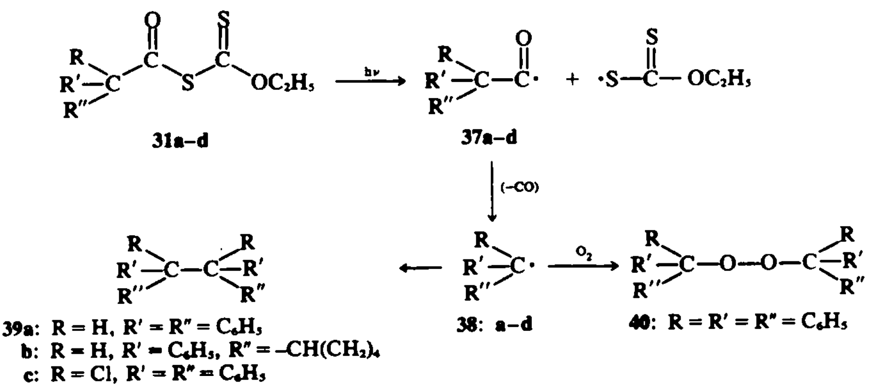
Photolysis of a benzene solution of di-O-ethyl S,S-diphenoyl dixanthate (**33**) gave a 33% yield of 9,10-



Scheme 9.



Scheme 10.



Scheme 11.

phenathraquinone (**35**). The formation of **35** may be rationalized through a cyclization of the radical species **34**, followed by the loss of a $CS_2OC_2H_5$ fragment (Scheme 10). A similar reaction has been observed in the formation of cyclopentane - 1,2 - dione from di-O-ethyl S,S-glutaryl dixanthate.[3]

Thermal reactions of acyl xanthates are reported to give esters and carbon disulfide.[3] For example, when O-ethyl S-diphenylacetyl xanthate (**31a**) was heated around 200°, both ethyl diphenylacetate (**41a**) and carbon disulfide were formed. A 4-membered, cyclic transition state has been suggested for such decompositions.[1,3] Similarly, the thermal decompositions of **31b** and **31c** gave the corresponding esters (**41b,c**) and carbon disulfide, as shown in Scheme 12. Di-O-ethyl S,S-diphenoyl dixanthate (**33**) also gave the ethyl ester of diphenic acid (**36**).

It is interesting to note that the thermal decomposition of triphenylacetylxanthate (**31d**) gave a mixture of carbon disulfide and triphenylthioacetic anhydride (**42**). No ethyl triphenylacetate was isolated from this reaction. The exact mechanism of the formation of **42** is not clear; however, it may proceed through a displacement reaction as shown in Scheme 13.

EXPERIMENTAL

All m.ps are uncorrected and were taken on a Melt-Temp, m.p. apparatus. IR spectra were recorded on a Perkin-Elmer, Model 137, Infracord spectrometer and UV spectra were determined on a Beckman DB Spectrometer. NMR traces were recorded on a Varian HR-100 spectrometer, using TMS as internal standard. All irradiation experiments were carried out using a Hanovia, medium pressure, mercury lamp (450 W).

Starting materials. Diphenylchloroacetyl chloride,[8] m.p. 50°, diphenylacetyl chloride,[9] m.p. 56°, phenylacetyl chloride,[10] b.p. 67° (0·8 mm), chloroacetyl chloride,[11] b.p. 180° (0·7 mm), cyclopentylphenylacetyl chloride,[12] b.p. 145° (12 mm), triphenylacetyl chloride,[13] m.p. 123° and diphenoyl dichloride,[14] m.p. 97° were prepared by standard procedures. Potassium O-ethyl xanthate,[15] m.p. 225–226° was prepared by a known procedure. Dimethyldithiocarbamate,[16] m.p. 136°, diethyldithiocarbamate,[17] m.p. 81°, tetramethylenedithiocarbamate,[2] m.p. 152°, pentamethylenedithiocarbamate,[2] m.p. 169–170° and oxydimethylenedithiocarbamate, m.p. 181–182° were prepared by reported procedures.

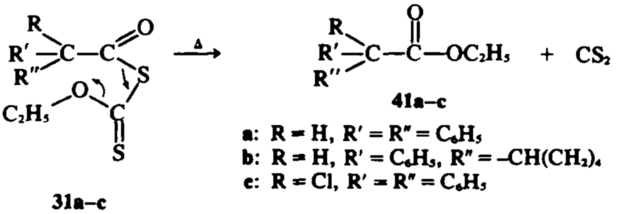
Diphenylchloroacetyl dialkyldithiocarbamic anhydrides (**3a–e**). In a representative run, an ether soln (25 ml) of **1** (4 g, 0·015 mol) was treated with **2a** (3 g, 0·018 mol) around 5°. The mixture was washed with excess of water to remove any unchanged **2a**. The ether layer was dried over Na_2SO_4 and removed the solvent under vacuum. The product was recrystallized from a mixture (1:1) of ether and light petroleum (b.p. 60–80°) to give a pure sample of **3a**, m.p. 95°. Details of yield, analytical results and spectral data of the different anhydrides (**3a–e**) are shown in Table 2.

Reaction of diphenylchloroacetyl dialkyldithiocarbamic anhydrides with alcohols. In a representative reaction, a MeOH soln (25 ml) of **3a** (1 g, 0·0028 mol) was refluxed for 45 min. Removal of the solvent under vacuum gave **5a**, which melted at 175–176°, after recrystallization from a mixture (1:1) of MeOH and methylene chloride. Table 3 summarizes the details of the yield, analytical results and spectral data of the different alkyl 2 - (N,N - dialkyldithiocarbamyl) - 2,2 - diphenylacetates.

Reaction of methyl 2 - (N,N - *Diethylthiocarbamyl*) - 2,2 - *diphenylacetate* (**5d**) *with Raney-Ni.* A mixture of **5d** (0·5 g, 0·0018 mol) and 2 g of Raney-Ni was refluxed in acetone (25 ml) for 4 hr. Removal of the unchanged Ni and the solvent gave 0·15 g (50%) of methyl diphenylacetate,[17] m.p. 59–60° (m. m.p.), after recrystallization from a mixture (1:1) of light petroleum (b.p. 60–80°) and methylene chloride.

Reaction of ethyl 2 - (N,N - *Diethyldithiocarbamyl*) - 2,2 - *diphenylacetate* (**5e**) *with Raney-Ni.* Treatment of a mixture of **5e** (0·5 g, 0·0012 mol) and Raney–Ni (2 g) in refluxing acetone (20 ml) for 5 hr and work-up as in the earlier case gave 0·21 g (66%) of ethyl diphenylacetate,[18] m.p. 56–57° (m. m.p.).

Kinetics of the transformations of carboxylic dithiocarbamic anhydrides (**3a–e**) *to methyl dithiocarbamyl diphenylacetates* (**5a–e**). The anhydrides **3a–e** employed for kinetic studies were recrystallized several times from a mixture (1:1) of methylene chloride and light petroleum (b.p. 60–80°). Kinetic measurements were made using approximately $8{\cdot}2 \times 10^{-3}$ M solns of **3a–e** in benzene. The progress of the reaction in each case was followed spectrophotometrically in a Beckmann DU, Model-2400 spectrophotometer. In a typical run, 2·5 ml of a standard soln of **3a** and 0·5 ml of MeOH were transferred to a Beckmann DU cell (1 cm), kept inside a variable temp. cell compartment, maintained at the required temp. After allowing few min. for equilibration, the progress of the reaction was followed by measuring the optical density of the band around 410 nm. All kinetic runs were made in

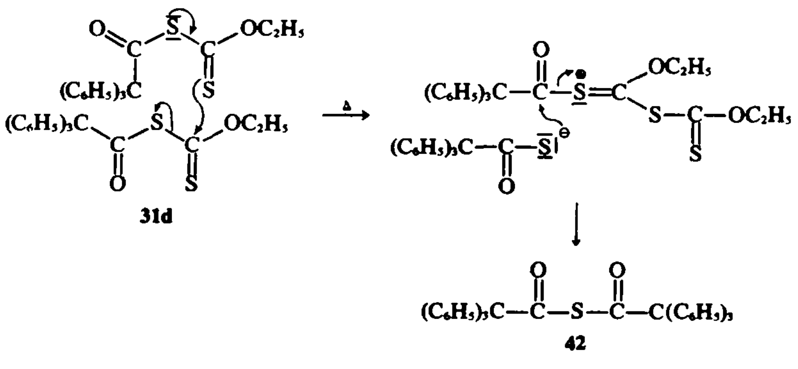


31a–c

41a–c

a: $R = H$, $R' = R'' = C_6H_5$
b: $R = H$, $R' = C_6H_5$, $R'' = -CH(CH_2)_4$
c: $R = Cl$, $R' = R'' = C_6H_5$

Scheme 12.



31d

42

Scheme 13.

Table 2. Diphenylchloroacetyl dialkyldithiocarbamic anhydrides

Compound	Yield (%)	M.p. (°C)	Molecular formula	Calc. (%)			Found, (%)			IR cm^{-1} C=O	(KBr) C=S	UV, λ_{max} nm (ϵ)
				C	H	N	C	H	N			
3a	57	95	$C_{17}H_{16}NOS_2Cl$	58·36	4·57	4·01	58·72	4·59	3·98	1685	1440	292(16,400), 408(150)
3b	92	119–120	$C_{19}H_{20}NOS_2Cl$	60·39	5·29	3·71	60·42	5·05	3·64	1675	1490	294(13,300), 400(80)
3c	71	140	$C_{19}H_{18}NOS_2Cl$	60·71	4·79	3·73	60·46	5·08	3·63	1680	1460	292(13,300), 392(110)
3d	90	122–123	$C_{20}H_{20}NOS_2Cl$	61·69	5·14	3·59	61·48	4·93	3·65	1684	1484	294(13,500), 404(150)
3e	58	114–115	$C_{19}H_{18}NO_2S_2Cl$	58·31	4·60	3·58	58·08	4·60	3·62	1686	1415	294(12,700), 410(140)

duplicate and the rates were evaluated graphically from a plot of concentration vs time. The rates were measured at three different temps and the values for activation energy and entropy were calculated as per a standard relationship.[19]

Photolysis of diphenylchloroacetyl dimethyldithiocarbamic anhydride (**3a**). A benzene soln (175 ml) of **3a** (2 g, 0·0057 mol) was irradiated at room temp. for 30 min. During photolysis, about 70 ml (54%) of CO was collected over KOH aq. The solid that separated out was filtered off to give 0·6 g (34%) of **21a**, m.p. 165°, after recrystallization from MeOH. (Found: C, 59·43; H, 5·20; N, 4·27. Calc. for $C_{16}H_{16}NS_2Cl$: C, 59·72; H, 4·97; N, 4·35%); IR spectrum (KBr) ν_{max}: 1480 cm^{-1} (C=S); UV spectrum (CH_3OH) λ_{max}: 240 nm (ϵ, 30,100).

Removal of the solvent under vacuum from the benzene-soluble fraction gave 0·22 g (24%) of **20**, m.p. 186° (lit.[20] m.p. 185°), on recrystallization from a mixture (1 : 1) of methylene chloride and acetone. (Found: C, 77·20; H, 5·05. Calc. for $C_{26}H_{20}Cl_2$: C, 77·41; H, 4·96%).

Thermal decomposition of diphenylchloromethyl dimethylthiocarbamoyl monosulfide (**21a**). The monosulfide **21a** (0·32 g, 0·001 mol) was heated to its m.p. (165°) and the whole mass became dark blue. The mixture was chromatographed over alumina. Elution with light petroleum (b.p. 60–80°) gave 0·15 g (75%) of **26** as a dark blue, viscous liquid, identified through a comparison of its IR spectrum with that of an authentic sample.[13]

On keeping **26** exposed to air for several hr resulted in its conversion to benzophenone, identified through its 2,4-dinitrophenylhydrazone, m.p. 239° (m.m.p.).

Photolysis of diphenylchloroacetyl diethyldithiocarbamic anhydride (**3b**). A benzene soln (175 ml) of **3b** (2·4 g, 0·0063 mol) was irradiated at room temp. for 30 min. During the photolysis, 120 ml (83%) of CO could be collected. Work-up of the photolyzed mixture in the usual manner gave 1·1 g (50%) of **21b**, m.p. 180°, after recrystallization from a mixture (1 : 1) of MeOH and benzene. (Found: C, 61·63; H, 5·78; N, 4·12. Calc. for $C_{18}H_{20}NS_2Cl$: C, 61·89; H, 5·73; N, 4·01%). IR spectrum (KBr) ν_{max}: 1490 cm^{-1} (C=S); UV spectrum (EtOH), λ_{max}: 242 nm (ϵ, 22, 100).

The benzene-soluble portion gave 0·28 g (23%) of 1,2-dichlorotetraphenylethane, m.p. 186° (m.m.p.).

The monosulfide **21b** (0·35 g, 0·001 mol) was heated to its m.p. and the blue colored mixture was chromatographed on alumina to give 0·14 g (70%) of thiobenzophenone, identified through its IR spectrum.

Photolysis of diphenylchloroacetyl tetramethylenedithiocarbamic anhydride (**3c**). Irradiation of a benzene soln (175 ml) of **3c** (2·4 g, 0·0064 mol) for 30 min gave 140 ml (94%) of CO. Work-up of the mixture in the usual manner gave 1 g (83%) of **24c**, m.p. 128°, on recrystallization from a mixture (1 : 1) of MeOH and benzene. (Found: C, 56·62; H, 4·65; N, 3·45. Calc. for $C_{18}H_{18}NS_3Cl$: C, 56·91; H, 4·74; N, 3·68%). IR spectrum (KBr) ν_{max}: 1490 cm^{-1} (C=S); UV spectrum (EtOH) λ_{max}: 242 nm (ϵ, 27,200).

The benzene-soluble fraction gave 0·4 g (33%) of 1,2-dichlorotetraphenylethane, m.p. 186° (m.m.p.).

Heating the disulfide **24c** (0·38 g, 0·001 mol) to its m.p. and chromatographing the mixture over alumina gave 0·12 g (60%) of thiobenzophenone, identified through its IR spectrum.

Photolysis of diphenylchloroacetyl pentamethylenedithiocarbamic anhydride (**3d**). A benzene soln of 1·5 g (0·0038 mol) of **3d** (in 175 ml) was irradiated for 30 min. During photolysis, 70 ml (87%) of CO was collected. Work-up of the photolysed mixture as in the earlier cases gave 0·55 g (42%) of **21d**, m.p. 180°, on recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°). (Found: C, 63·45; H, 5·65; N, 3·99. Calc. for $C_{19}H_{20}NS_2Cl$: C, 63·15; H, 5·53; N, 3·87%). IR spectrum (KBr) ν_{max}: 1480 cm^{-1} (C=S); UV spectrum (CH_2Cl_2) λ_{max}: 248 nm (ϵ, 3,250).

The benzene-soluble fraction gave 0·2 g (26%) of 1,2-dichlorotetraphenylethane, m.p. 186° (m.m.p.).

Heating the monosulfide **21d** (0·36 g, 0·001 mol) to its m.p. and chromatographing the mixture over alumina gave 0·16 g (80%) of thiobenzophenone, identified through its IR spectrum.

Photolysis of diphenylchloroacetyl oxydiethylenedithiocarbamic anhydride (**3e**). A benzene soln (175 ml) of **3e** (1·5 g, 0·0038 mol) was irradiated at room temp. for 30 min and the evolved gas (90 ml, 90%) was identified as CO. Work-up of the photolysed mixture gave 0·63 g (84%) of **24e**, m.p. 115°, on recrystallization from a mixture (1 : 1) of MeOH and benzene. (Found: C, 54·33; H, 4·83; N, 3·46. Calc. for $C_{18}H_{18}NOS_3Cl$: C, 54·61; H, 4·55; N, 3·78%). IR spectrum (KBr) ν_{max}: 1485 cm^{-1} (C=S); UV spectrum (EtOH), λ_{max}: 250 nm (ϵ, 23,000). The benzene-soluble fraction gave 0·2 g (26%) of 1,2-dichlorotetraphenylethane, m.p. 186° (m.m.p.).

Heating the disulfide **24e** (0·4 g, 0·001 mol) up to its m.p. for 15 min and work-up of the mixture by chromatographing over alumina gave 0·16 g (80%) of thiobenzophenone, identified through its IR spectrum.

Reaction of phenylchloroacetyl chloride with dialkyldithiocarbamates. In a representative run, an ether soln of phenylchloroacetyl chloride (3 g, 0·015 mol in 25 ml) was treated with dimethyldithiocarbamate (3 g, 0·018 mol) around 5°. The mixture was treated with water to remove any unchanged dimethyldithiocarbamate and the ether-layer was dried over Na_2SO_4. Removal of the solvent under vacuum gave a product which when recrystallized from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°) gave 3·5 g (90%) of **9a**, m.p. 179–180°. Details of analytical results and spectral data of the different phenylacetic acids **9a–e** are shown in Table 4.

Reaction of chloroacetyl chloride with dialkyldithiocarbamates. In a representative run, a soln of chloroacetyl chloride (2 g, 0·017 mol) in 30 ml of ether was treated with dimethyldithiocarbamate (3 g, 0·018 mol) around 5°. Removal of the solvent under vacuum and work-up of the mixture by treatment with water in the usual manner gave 1·5 g (50%) of **13a**, m.p. 155–156°, after recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°). (Found: C, 33·32; H, 5·32; N, 7·56. Calc. for $C_5H_9NO_2S_2$: C, 33·52; H, 5·02; N, 7·82%). IR spectrum (KBr), ν_{max}: 1690 cm^{-1} (C=O); UV spectrum (MeOH), λ_{max}: 250 nm (ϵ, 13,150), 276 (14,500) and 332(40).

Reaction of chloroacetyl chloride (3 g, 0·026 mol) with diethyldithiocarbamate (4 g, 0·03 mol) gave 3 g (54%) of **13b**, m.p. 90–91°, after recrystallization from methylene chloride. (Found: C, 40·64; H, 6·36; N, 6·65. Calc. for $C_7H_{13}NO_2S_2$: C, 40·58; H, 6·28; N, 6·76%). IR spectrum (KBr), ν_{max}: 1700 cm^{-1} (C=O); UV spectrum (MeOH), λ_{max}: 254 nm (ϵ, 13,400), 280 (16,250) and 336 (60).

Table 3. Alkyl 2-(N,N-Dialkyldithiocarbamyl)-2,2-diphenylacetates

Starting materials	Solvent	Product	Yield (%)	M.p. (°C)	Molecular formula	Calc. % C	Calc. % H	Calc. % N	Found, % C	Found, % H	Found, % N	IR cm^{-1} (KBr) C=O	UV, λ_{max} nm (ϵ)
3a	Methanol	**5a**	70	175–176	$C_{18}H_{19}NO_2S_2$	62·61	5·50	4·05	62·92	5·57	4·05	1730	285(14,700), 344(80)
3a	Ethanol	**5b**	83	145–146	$C_{19}H_{21}NO_2S_2$	63·51	5·85	3·90	63·21	6·01	4·00	1722	286(19,150) 344(120)
3a	n-Propanol	**5c**	66	130	$C_{20}H_{23}NO_2S_2$	64·34	6·16	3·75	64·23	6·26	3·70	1724	288(11,800), 344(90)
3b	Methanol	**5d**	90	140	$C_{20}H_{23}NO_2S_2$	64·34	6·16	3·75	64·34	6·46	4·01	1730	285(14,400), 344(120)
3b	Ethanol	**5e**	60	112	$C_{21}H_{25}NO_2S_2$	65·11	6·46	3·61	65·34	6·56	3·73	1717	286(15,500), 348(100)
3b	n-Propanol	**5f**	85	108	$C_{22}H_{27}NO_2S_2$	65·83	6·73	3·64	65·85	6·69	3·59	1724	286(10,300), 346(100)
3c	Methanol	**5g**	70	180	$C_{20}H_{21}NO_2S_2$	64·69	5·66	2·77	64·45	5·71	3·92	1730	286(14,550), 340(100)
3c	Ethanol	**5h**	70	155–156	$C_{21}H_{23}NO_2S_2$	65·46	5·93	3·63	65·39	6·05	3·92	1722	285(16,700), 340(110)
3c	n-Propanol	**5i**	85	153–154	$C_{22}H_{25}NO_2S_2$	66·16	6·27	3·50	65·89	6·13	3·59	1724	286(12,300), 342(90)
3d	Methanol	**5j**	83	176	$C_{21}H_{23}NO_2S_2$	65·45	5·92	3·63	65·33	6·05	3·54	1720	288(18,700), 340(120)
3d	n-Propanol	**5l**	83	128	$C_{23}H_{27}NO_2S_2$	66·82	6·53	3·38	66·72	6·36	3·44	1724	290(11,200), 348(110)
3e	Methanol	**5m**	66	190	$C_{20}H_{21}NO_3S_2$	62·01	5·42	3·62	62·32	5·62	3·92	1732	286(14,000), 352(130)
3e	Ethanol	**5n**	50	140	$C_{21}H_{23}NO_3S_2$	62·84	5·73	3·49	63·11	5·99	3·54	1722	290(14,400), 356(110)
3e	n-Propanol	**5p**	77	130–131	$C_{22}H_{25}NO_3S_2$	63·61	6·02	3·37	63·45	6·23	3·62	1724	290(11,900), 352(100)

NMR spectrum ($CDCl_3$), of **5a**: 7·11 ppm (10H, aromatic), 3·65 (3H, methoxyl), 3·28 (6H), methyl);
5b: 7·11 ppm (10H, aromatic), 4·11 (2H, methylene), 3·24 (6H, methyl), 1·23 (3H, methyl);
5c: 7·09 ppm (10H, aromatic), 4·05 (2H, methylene), 3·27 (6H, methyl), 1·68 (2H, methylene), 0·99 (3H, methyl);
5d: 7·41 (10H, aromatic), 3·77 (7H, methylene and methoxyl), 1·3 (6H, methyl);
5e: 7·45 (10H, aromatic), 4·34 (2H, methylene), 3·86 (4H, methylene), 1·29 (9H, methyl);
5f: 7·66 (10H, aromatic), 4·33 (2H, methylene), 4·0 (4H, methylene), 1·83 (2H, methylene), 1·33 (6H, methyl), 1·0 (3H, methyl).

Table 4. 2-(N,N-Dialkyldithiocarbamyl)-2-phenylacetic acids

Compound	Yield (%)	M.p. (°C)	Molecular formula	Calc. % C	Calc. % H	Calc. % N	Found, % C	Found, % H	Found, % N	IR cm^{-1} (KBr) C=O	UV, λ_{max}, nm (ϵ)
9a	90	179–180	$C_{11}H_{13}NO_2S_2$	51·76	5·09	5·49	51·94	4·81	5·47	1700	250(12,900), 278(11,150), 328(70)
9b	54	144–145	$C_{13}H_{17}NO_2S_2$	55·12	6·00	4·94	55·34	5·95	5·19	1725	258(15,350), 282(13,300), 332(90)
9c	67	154–155	$C_{13}H_{15}NO_2S_2$	55·51	5·33	4·98	55·81	5·40	4·77	1705	250(17,200), 276(15,000), 328(80)
9d*	64	154–155	$C_{14}H_{17}NO_2S_2$	56·94	5·76	4·74	57·21	5·97	4·61	1693	260(16,350), 282(14,400), 332(90)
9e†	58	158–159	$C_{13}H_{15}NO_3S_2$	52·52	5·05	4·71	52·28	5·15	4·44	1700	254(16,000), 280(15,900), 340(90).

*NMR spectrum of **9d** ($CDCl_3$): 8·67 ppm (1H, carboxylic), 7·41 ppm (5H, aromatic), 5·99 ppm (1H, tertiary), 4·02 ppm (4H, methylene) and 1·66 ppm (6H, methylene).

†NMR spectrum of **9e** ($CDCl_3$): 9·12 ppm (1H, carboxylic), 7·34 ppm (5H, aromatic), 5·83 ppm (1H, tertiary), 4·05 ppm (4H, methylene).

Under analogous conditions, the reaction of chloroacetyl chloride (5 g, 0·045 mol) with tetramethylenedithiocarbamate (10 g, 0·045 mol) gave 6 g (67%) of **13c**, m.p. 156–157°, after recrystallization from methylene chloride. (Found: C, 41·21; H, 5·58; N, 7·01. Calc. for $C_7H_{11}NO_2S_2$: C, 40·97; H, 5·36; N, 6·83%). IR spectrum (KBr) ν_{max}: 1695 cm^{-1} (C=O); UV spectrum (MeOH), λ_{max}: 250 nm (ϵ, 13,900), 274 (14,700) and 334 (60).

In the reaction of chloroacetyl chloride (4 g, 0·035 mol) with pentamethylenedithiocarbamate (9 g, 0·036 mol), a 55% yield (4·1 g) of **13d** was obtained, which on recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°), melted at 150°. (Found: C, 44·14; H, 5·99; N, 6·57. Calc. for $C_8H_{13}NO_2S_2$: C, 43·83; H, 5·93; N, 6·39%). IR spectrum (KBr) ν_{max}: 1695 (C=O); UV spectrum (MeOH), λ_{max}: 256 nm (ϵ, 12,550), 280 (15,650) and 338 (80).

Treatment of oxydiethylenedithiocarbamate (9 g, 0·036 mol) with chloroacetyl chloride (4 g, 0·035 mol) gave 3·6 g (47%) of **13e**, m.p. 174°, on recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°). (Found: C, 38·31; H, 4·85; N, 6·36. Calc. for $C_7H_{11}NO_3S_2$: C, 38·00; H, 4·97; N, 6·33%). IR spectrum (KBr), ν_{max}: 1690 cm^{-1} (C=O); UV spectrum (MeOH), λ_{max}: 258 nm (ϵ, 14,000), 282 (15,450) and 340 (70).

Reaction of diphenylacetyl chloride with dialkyldithiocarbamates. An ether soln (20 ml) of **14** (3 g, 0·013 mol) was treated with dimethyldithiocarbamate (2·5 g, 0·015 mol) around 5°. The mixture was treated with water to remove any unchanged dimethyldithiocarbamate and the ether layer was dried over Na_2SO_4. Removal of the solvent under vacuum gave 1·5 g (50%) of **16a**, m.p. 135° (lit.[21] m.p. 135°), after recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum. (Found: C, 80·25; H, 7·41; N, 5·90. Calc. for $C_{16}H_{17}NO$: C, 80·33; H, 7·11; N, 5·85%). IR spectrum (KBr) ν_{max}: 1622 cm^{-1} (C=O, amide); UV spectrum (CH_2Cl_2), λ_{max}: 260 nm (ϵ, 600).

In a repeat run, an ether soln of **14** (4 g, 0·017 mol) was treated with diethyldithiocarbamate (4 g, 0·018 mol) around 5°. Work-up of the mixture in the usual manner gave 2·5 g (54%) of **16b**, m.p. 62–63° (lit.[22] m.p. 63°). (Found: C, 81·11; H, 7·78; N, 5·32. Calc. for $C_{18}H_{21}NO$: C, 80·89; H, 7·86; N, 5·24%). IR spectrum (KBr) ν_{max}: 1625 cm^{-1} (C=O, amide); UV spectrum (CH_2Cl_2), λ_{max}: 262 nm (ϵ, 650).

Similarly, **14** (4 g, 0·017 mol) was treated with pentamethylenedithiocarbamate (5 g, 0·02 mol) in ether soln around 5°. Work-up of the mixture gave 3 g (60%) of **16d**, m.p. 120° (lit.[22] m.p. 120–121°), on recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°). (Found: C, 81·69; H, 7·44; N, 5·22. Calc. for $C_{19}H_{21}NO$: C, 81·41; H, 7·50; N, 5·00%). IR (spectrum (KBr), ν_{max}: 1635 cm^{-1} (C=O, amide); UV spectrum (CH_2Cl_2), λ_{max}: 260 nm (ϵ, 950).

O-Ethyl S-diphenylacetyl xanthate (**31a**). Potassium O-ethyl xanthate (13 g, 0·08 mol) was added to an acetone soln (50 ml) of diphenylacetyl chloride (16 g, 0·07 mol), over a period of 30 min. The soln was maintained around −30° during the addition. Removal of the solvent under vacuum gave a product which was washed with water to remove any unchanged xanthate. Extraction with methylene chloride and removal of the solvent under vacuum gave 14 g (64%) of **31a**, b.p. 165–167° (2 mm). (Found: C, 64·35; H, 5·00. Calc. for $C_{17}H_{16}O_2S_2$: C, 64·55; H, 5·06%). IR spectrum (CCl_4) ν_{max}: 1736 (C=O) and 1230 (C=S); UV spectrum (CH_2Cl_2), λ_{max}: 283 nm (ϵ, 15,950) and 398 (60).

In a repeat run, when the reaction of diphenylacetyl chloride (5 g, 0·02 mol) with potassium O-ethyl xanthate (4 g, 0·02 mol) was carried out in acetone around 0°, 3·4 g (75%) of diphenylthioacetic anhydride, m.p. 129–130° was obtained. (Found: C, 79·69; H, 5·28. Calc. for $C_{28}H_{22}O_2S$: C, 79·62; H, 5·21%). IR spectrum (CCl_4) ν_{max}: 1712 and 1776 cm^{-1} (thioanhydride C=O groups); UV spectrum (EtOH) λ_{max}: 256 (ϵ, 43,450).

Photolysis of O-ethyl S-diphenylacetyl xanthate (**31a**). A benzene soln (175 ml) of **31a** (2·7 g, 0·008 mol) was irradiated for 30 min around 5°. During the photolysis, about 180 ml (90%) of CO was collected. Removal of the solvent from the photolyzed mixture gave a product which on recrystallization from methylene chloride gave 1 g (70%) of **39a**, m.p. 219° (lit.[23] m.p. 214°). (Found: C, 93·27; H, 6·82. Calc. for $C_{26}H_{22}$: C, 93·40; H, 6·60%).

Thermal decomposition of O-ethyl S-diphenylacetyl xanthate. O-Ethyl S-diphenylacetyl xanthate (3·2 g, 0·01 mol) was heated around 210–220° for 30 min in a 10 ml pear shaped flask, provided with a N_2 inlet and water-cooled condenser. A continuous stream of N_2 was passed through the mixture and the gaseous products were trapped in a 10% soln of piperidine in ether. The gaseous product contained CS_2, as identified through its piperidinium salt (2·2 g, 88%), m.p. 168–170° (lit.[24] m.p. 168–170°).

The pyrolysed residue was distilled to give 1·2 g (50%) of ethyl diphenylacetate,[18] m.p. 56–57° (m.m.p.).

O-Ethyl S-cyclopentylphenylacetyl xanthate (**31b**). An acetone soln (50 ml) of **29b** (8 g, 0·036 mol) was treated with potassium O-ethyl xanthate (7·5 g, 0·04 mol) around −30° for 30 min. Work-up in the usual manner gave 8 g (72%) of **31b**, b.p. 121–122° (4 mm). (Found: C, 62·11; H, 6·24. Calc. for $C_{16}H_{20}O_2S_2$: C, 62·33; H, 6·49%). IR spectrum (CCl_4) ν_{max}: 1724 (C=O) and 1235 cm^{-1} (C=S). UV spectrum (CH_2Cl_2), λ_{max}: 282 nm (ϵ, 6,890) and 400 (50).

Photolysis of O-ethyl S-cyclopentylphenylacetyl xanthate (**31b**). A benzene soln (175 ml) of **31b** (2·6 g, 0·008 mol) was irradiated around 5° for 30 min. During photolysis, 45 ml (25%) of CO was collected. Work-up of the photolyzed mixture in the usual manner gave 0·5 g (40%) of **39b**, m.p. 138°, after recrystallization from methylene chloride. (Found: C, 90·26; H, 9·21. Calc. for $C_{24}H_{30}$: C, 90·56; H, 9·43%).

Thermal decomposition of O-ethyl S-cyclopentylphenyl xanthate. Heating 1·5 g (0·004 mol) of **31b** around 210° for 30 min resulted in the evolution of CS_2 gas which was identified through its piperidinium salt (0·45 g, 33%), m.p. 168–170° (m.m.p.).

The pyrolysed residue on distillation gave 0·7 g (63%) of ethyl cyclopentylphenylacetate, b.p. 170–173° (11 mm), identified by comparing its IR spectrum with that of an authentic sample.[25]

O-*Ethyl* S-*triphenylacetyl xanthate* (**31d**). An acetone soln (20 ml) of triphenylacetyl chloride (1·5 g, 0·004 mol) was treated with potassium O-ethyl xanthate (0·8 g, 0·005 mol) around −30° for 30 min. Work-up of the mixture in the usual manner gave 1·3 g (67%) of **31d**, m.p. 107–108°, after recrystallization from a mixture (1 : 1) of ether and light petroleum (b.p. 60–80°). (Found: C, 70·65; H, 4·84. Calc for $C_{23}H_{20}O_2S_2$: C, 70·40; H, 5·10%). IR spectrum (KBr) ν_{max}: 1720 (C=O) and 1250 cm^{-1} (C=S); UV spectrum (CH_2Cl_2) λ_{max}: 290 nm (ϵ, 10,500) and 400 (100).

Photolysis of O-*ethyl* S-*triphenylacetyl xanthate* (**31d**). A soln of **31d** (0·5 g, 0·0012 mol) in benzene (175 ml) was irradiated at room temp. for 15 min. Work-up of the photolysed mixture in the usual manner gave 0·11 g (33%) of **40d**,[26] m.p. 186–187° (m.m.p.).

Thermal decomposition of O-*ethyl* S-*triphenylacetyl xanthate.* Xanthate **31d** (0·4 g, 0·001 mol) was heated around 210–220° for 20 min and the evolved gas was identified as CS_2 through its piperidinium salt (0·04 g, 16%), m.p. 168–170° (m.m.p.).

The pyrolysed residue was triturated with a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°) to give 0·2 g (68%) of triphenylthioacetic anhydride, m.p. 204–205°, after recrystallisation from methylene chloride. (Found: C, 83·87; H, 4·97. Calc. for $C_{40}H_{30}O_2S$: C, 83·62; H, 5·22%). IR spectrum (KBr) ν_{max}: 1680 and 1740 cm^{-1} (thioanhydride C=O groups); UV spectrum (CH_2Cl_2), λ_{max}: 260 nm (ϵ, 10,950).

Di-O-*ethyl* S,S-*diphenoyl dixanthate* (33). To a soln of diphenoyl chloride (4·5 g, 0·16 mol) in ether (25 ml), maintained around 0° was added potassium O-ethyl xanthate (4·2 g, 0·032 mol) over a period of **30** min, with constant stirring. Work-up of the mixture in the usual manner gave 4 g (55%) of di-O-ethyl S,S-diphenoyl dixanthate, m.p. 60–61°, after recrystallization from a mixture (1 : 1) of methylene chloride and light petroleum (b.p. 60–80°). (Found: C, 53·53; H, 4·02. Calc. for $C_{20}H_{18}O_4S_4$: C, 53·33; H, 4·00%). IR spectrum (CCl_4) ν_{max}: 1709 (C=O) and 1042 cm^{-1} (C=S); UV spectrum ($CHCl_3$), λ_{max}: 290 nm (ϵ, 31,600) and 390 (220).

Photolysis of di-O-*ethyl S,S-diphenoyl dixanthate* (**33**). A benzene soln (175 ml) of **33** (1 g, 0·002 mol) was irradiated at room temp. for 30 min. Work-up of the photolysed mixture gave 0·15 g (33%) of **35**,[27] m.p. 208–209° (m.m.p.).

Thermal decomposition of di-O-*ethyl* S,S-*diphenoyl dixanthate* (**33**). Heating **33** (1 g, 0·002 mol) around 200° for 20 min resulted in the formation of CS_2 which was identified through its piperidinium salt (0·7 g, 66%), m.p. 168–170° (m.m.p.).

The pyrolysed residue, when chromatographed over alumina using light petroleum (b.p. 60–80°) gave 0·4 g (60%) of **36**, m.p. 42° (m.m.p.).

O-*Ethyl S-diphenylacetyl xanthate* (**31c**). To an acetone soln of diphenylchloroacetyl chloride (11 g, 0·04 mol) was added potassium O-ethyl xanthate (8 g, 0·04 mol) around −30°, over a period of 30 min. Work-up of the mixture gave 11 g (75%) of **31c**, b.p. 174–175° (3 mm). IR spectrum (CCl_4) ν_{max}: 1715 (C=O) and 1230 cm^{-1} (C=S); UV spectrum (CH_2Cl_2), λ_{max}: 294 nm (ϵ, 8,030) and 402 (60).

Photolysis of O-*ethyl* S-*diphenylchloroacetyl xanthate* (**31c**). A benzene soln (175 ml) of **31c** (2 g, 0·0057 mol) was irradiated around 5° for 30 min. During photolysis, 100 ml (75%) of CO was collected. Work-up of the photolysed mixture gave 0·4 g (36%) of 1,2-dichlorotetraphenylethane, m.p. 196° (m.m.p.).

Thermal decomposition of O-*ethyl* A-*diphenylchloroacetyl xanthate* (**31c**). Heating **31c** (1·75 g, 0·005 mol) around 220° for 30 min resulted in the formation of CS_2, identified through its piperidinium salt (1 g, 84%), m.p. 168–170° (m.m.p.).

The pyrolysed residue on distillation gave 1 g (73%) of ethyl diphenylchloroacetate,[28] m.p. 43–44° (m.m.p.).

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