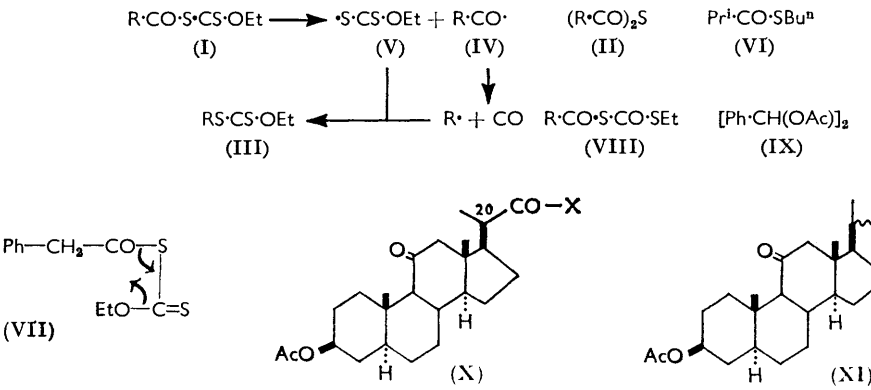
369. *Photochemical Transformations. Part XIII.* A New Method for the Production of Acyl Radicals.*

By D. H. R. Barton, M. V. George, and M. Tomoeda.

An efficient method for the synthesis of *S*-acylxanthates has been developed. Xanthate derivatives of alkane- and arylalkane-carboxylic acids are smoothly converted into acyl and xanthate radicals on photolysis in inert media by means of mercury-arc or tungsten lamps. At the appropriate temperatures the acyl radicals produced are decarbonylated to alkyl or arylalkyl radicals. In general, these combine with the xanthate radicals produced initially to furnish *S*-alkyl or *S*-arylalkyl xanthates which on hydrolysis afford thiols. A new method for decarboxylating acids is thus provided. Primary acyl radicals are sufficiently stable for one to expect that they may, in principle, combine in pairs to furnish α-diketones: one example of such a reaction is given for illustration.

The starting point of the work described in the present paper was a conviction that *S*-acyl xanthates (I) might show interesting photochemical behaviour. We reasoned that the xanthate residue, which shows pronounced ultraviolet absorption, might serve as probe for energy absorption, leading eventually to bond fission. In the case of acyl xanthates the expected fragments would be acyl and xanthate radicals.

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. We first developed a general procedure for acyl xanthate synthesis. Treatment of acid chlorides in acetone solution at −35°



with sodium *O*-ethyl xanthate gives *S*-acyl xanthates in high yield. Reaction at higher temperatures (0° or room temperature) produces thioanhydrides (II). For example, at low temperatures palmitoyl chloride gave the xanthate (I; R = $C_{15}H_{31}$), but at 0° only the thioanhydride (II; R = $C_{15}H_{31}$) could be isolated. The acyl xanthates obtained in this way are sufficiently stable to be distilled in small batches. Good analytical data have been secured on almost all those reported here and several have been obtained in nicely crystalline form.

Alkane- and arylalkane-carbonyl xanthates are smoothly decomposed by light from either a tungsten lamp or a mercury-arc lamp. The acyl xanthates have an absorption band at about 400 mμ which disappears during the photochemical reaction. In addition,

* Part XII, *J.*, 1962, 622.

[1] Bulmer and Mann, *J.*, 1945, 677.

the infrared carbonyl band of the acyl xanthate also disappears, as does the pronounced yellow colour. The course of the reaction can, therefore, be followed easily.

Irradiation of *O*-ethyl *S*-phenylacetyl xanthate in benzene solution under reflux gave in high yield *S*-benzyl *O*-ethyl xanthate [3] (III; R = Ph·CH_2). The reaction proceeded about six times faster when a mercury-arc rather than a tungsten lamp was used. A study of the process in various solvents under reflux (see Table) showed that the reaction was faster in higher-boiling solvents. Thus, in refluxing toluene (110°) only two hours were required, whereas in ether (36°) seven hours were needed to complete the reaction. All the experiments recorded in the Table refer to irradiation with mercury-arc lamp under standard conditions defined in the Experimental section. Yields were conveniently determined by alkaline hydrolysis. The percentage of toluene-α-thiol indicates the success of the desired reaction whilst the percentage of phenylacetic acid shows either that the reaction was not complete or that thermal acyl xanthate decomposition occurred in the sense discussed below. The poor yield, but rapid decomposition, of the acyl xanthate in ethanol is due to alcoholysis. Clearly the reaction should be carried out in a non-hydroxylic, neutral solvent.

Irradiation of *O*-ethyl *S*-phenylacetyl xanthate in various solvents.

Solvent	Approx. reflux temp.	Reaction time (hr.)	Products (after alkaline hydrolysis) Ph·CH_2·SH	Ph·CH_2·CO_2H
Et_2O	36°	7	97	Trace
C_4H_8O	65	5	96	Trace
CCl_4	77	6	75	11
EtOH	79	1	33	55
C_6H_6	80	4	82	4
Dioxan	102	3	96	Trace
Toluene	110	2	91	Trace

This, and the photochemical reactions of other acyl xanthates described in the sequel, are best explained by photochemical cleavage of the molecule into acyl radicals (IV) and xanthate radicals (V). Decarbonylation of (in the present case) the phenylacetyl radical to a benzyl radical and carbon monoxide would be unexceptional.[4] Combination of the benzyl and the xanthate radical (V) would then furnish the observed *S*-benzyl *O*-ethyl xanthate (III; R = Ph·CH_2). The latter compound is stable to the irradiation conditions (Pyrex flask) used in the present experiments, as are thioesters. For example, *S*-n-butyl thioisobutyrate (VI), synthesised for the purpose, was stable to irradiation in a Pyrex flask. We reasoned, therefore, that if toluene-α-thiol (2 mol.) were added to a solution of the acyl xanthate (I; R = Ph·CH_2) (1 mol.) undergoing photolysis, it should capture the phenylacetyl radical as benzyl thiophenylacetate which would be stable to further irradiation. In the event the percentage of phenylacetic acid obtained on alkaline hydrolysis of the product rose from 4% to 74%.

In all photochemical reactions described in the present paper the appropriate blank thermal experiment was carried out to ensure that a true photochemical reaction was under investigation. In addition, the pyrolysis of a typical acyl xanthate was studied. Heating *O*-ethyl *S*-phenylacetyl xanthate (I; R = Ph·CH_2) at 200° for 1·5 hours (complete decomposition) gave ethyl phenylacetate and carbon disulphide as main products. The reaction may proceed as indicated in (VII) through a four-centre type transition state.[4] The absence of any detectable amount of carbonyl sulphide in the pyrolysate suggests that the acyl xanthate (I; R = Ph·CH_2) does not rearrange to a dithiocarbonate (VIII; R = Ph·CH_2) before decomposition.[5] The thermal decomposition of aroyl

[2] See Willcox, *J. Amer. Chem. Soc.*, 1906, **28**, 1031.
[3] Djerassi, Gorman, Markley, and Oldenbury, *J. Amer. Chem. Soc.*, 1955, **77**, 568.
[4] Walling, " Free Radicals in Solution," J. Wiley and Sons, Inc., New York, 1957, p. 386.
[5] Cf. Taguchi and Nakao, *Tetrahedron*, 1962, **18**, 245, and references there cited. We thank Professor T. Taguchi for his kindness in providing a copy of this paper before its publication.

xanthates [1] appears to be a much more complex process. It is clear, however, that the pyrolytic and photolytic reactions of acyl xanthates lead to quite different products.

Irradiation of *O*-ethyl *S*-isobutyryl (I; R = Pr^i) and *S*-pivaloyl (I; R = Bu^t) xanthate in benzene proceeded smoothly, to give *O*-ethyl *S*-isopropyl (III; R = Pr^i) and -t-butyl xanthate (III; R = Bu^t). These compounds were characterised by alkaline hydrolysis to the corresponding thiols. The results obtained were independent of the light source (tungsten or mercury-arc lamps) used.

Somewhat different results were obtained in the photolysis of *O*-ethyl *S*-n-valeryl xanthate (I; R = Bu^n). In benzene solution, under a tungsten lamp, the rate of photochemical decomposition was slow and after 24 hours alkaline hydrolysis of the product gave 86% of n-valeric acid and only 8% of butane-1-thiol. We presumed that this apparent failure of the reaction was due to the stability of the primary n-valeryl radical in boiling benzene rather than to a change in the strength of the acyl–xanthate bond in the starting material. Relative stabilisation of the acyl radical would be expected in a primary radical [4,6] and it would favour the reverse of the primary dissociation [(IV + (V) ⟶ (I)]. If this is true then an increase in the temperature of the photolysis would increase the rate of decomposition of the n-valeryl radical into n-butyl radical and carbon monoxide.[6] In the event, a change to refluxing toluene and 48 hours' irradiation produced, after alkaline hydrolysis of the product, 43% of butane-1-thiol. Irradiation for 36 hours in benzene with a mercury-arc lamp also gave a reasonable yield of *O*-ethyl *S*-n-butyl xanthate (III; R = Bu^n), as judged by hydrolysis to the thiol (68%). Primary thiols can, therefore, be prepared from primary aliphatic acids by this method, but the process is slower than with the branched analogues.

Acetylmandelic acid gave a crystalline *O*-ethyl xanthate (I; R = Ph·CH·OAc) which photolysed smoothly. Hydrobenzoin diacetate (IX) (21%) was isolated from the product by direct crystallisation. The residue gave benzaldehyde (26%), isolated as the 2,4-dinitrophenylhydrazone, on acid hydrolysis. These results indicate that the radical R can, if it is specially stabilised, dimerise to R_2. The expected product, R·CH(OAc)·S·CS·OEt, was presumably also formed, as the origin of the benzaldehyde. We argued that dimerisation of the radical ·CHPh·OAc might be suppressed by addition of toluene-α-thiol, giving an improved yield of the aldehyde precursor Ph·CH(OAc)·S·CH_2Ph. In fact, the yield of benzaldehyde, after hydrolysis, was increased to 39%.

S-Benzoyl and *S*-*p*-chlorobenzoyl *O*-ethyl xanthate, prepared earlier by Bulmer and Mann,[1] were resistant to photolysis in boiling benzene or toluene. Alkaline hydrolysis of the product gave back a high yield of the aromatic acid. These results are understood as indicative of the stability of the Ar·CO· radical.

If the photolysis of acyl xanthates has been correctly interpreted above, then R· radicals, formed from R·CO· radicals as indicated, should give xanthates of type (I) with loss of stereochemistry at the α-carbon (in R·CO). This was confirmed in the following way. 3β-Acetoxy-11-oxo-5α-bisnorcholanoyl chloride (X; X = Cl) was converted into the *O*-ethyl xanthate (X; X = S·CS·OEt) and photolysed in benzene. Two *S*-(3β-acetoxy-11-oxo-5α-pregnan-20-yl) *O*-ethyl xanthates (XI; X = S·CS·OEt) resulted. These compounds must be 20α- and 20β-isomers, because both gave 3β-acetoxy-5α-pregnan-11-one (XI; X = H) on desulphurisation by Raney nickel. Preparation of an authentic specimen of the last compound is described in the Experimental section.

Since primary alkanecarbonyl radicals are stable near room temperature (see above) it should be possible to use them to synthetic advantage. For example, if the acyloin reaction is considered to involve intermediate α-diketones formed by the pairing of two acyl radicals,[4] then reactions of this type should now be possible photochemically. In agreement, glutaric acid gave a crystalline bisxanthate derivative which on photolysis in refluxing benzene afforded cyclopentane-1,2-dione (31%), isolated as the bis-2,4-dinitrophenylhydrazone. Increasing the dilution and reducing the temperature to 40°

[6] Cramer, *J. Amer. Chem. Soc.*, 1957, **79**, 6215.

increased the yield to 55%. Further investigation of this and of other synthetic reactions of photochemically generated acyl radicals is in hand.

Experimental

M. p.s were taken on the Kofler block. Ultraviolet absorption spectra were determined for ethanol solutions by using the Unicam S.P. 700 spectrophotometer. Infrared spectra were taken on the Infracord spectrometer (model 137) and refer to liquid films unless specified to the contrary. $[\alpha]_D$ are for $CHCl_3$ solutions. Unless specified to the contrary, " AnalaR " grade acetone (dried over K_2CO_3), methylene dichloride (dried over $CaCl_2$), and benzene and toluene dried by distillation over sodium, were used. Irradiation was carried out in Pyrex flasks with a 150-w tungsten lamp or a 125-w mercury lamp, under dry oxygen-free nitrogen. Iodometric analysis of mercaptans was carried out as described by Kolthoff and Belcher.[7]

O-Ethyl S-Palmitoyl Xanthate (I; R = $C_{15}H_{31}$). Sodium *O*-ethyl xanthate (320 mg.) was added in small portions to palmitoyl chloride (610 mg.) in methylene dichloride (10 ml.) and acetone (10 ml.) at −30° with stirring, which was continued for 30 min. more before the solution was allowed to warm to room temperature and washed with aqueous sodium hydrogen carbonate, then with water, and dried (Na_2SO_4). The solvent was removed *in vacuo* at room temperature. Crystallisation of the residue (736 mg.) from methanol at 0—20° gave *O-ethyl S-palmitoyl xanthate* as pale yellow needles, m. p. 28—30°, $\lambda_{max.}$ 203, 227, 275, and 392 mμ (ε 8200, 8500, 10,400 and 52, respectively), $\nu_{max.}$ 1727 (C=O) cm.$^{-1}$ (Found: S, 17·8. $C_{19}H_{36}O_2S_2$ requires S, 17·5%).

Repetition of the experiment at 0° instead of −30° gave, after chromatography over alumina (Grade 3), elution with light petroleum (b. p. 40—60°), and crystallisation from the same solvent, *palmitic thioanhydride* (II; R = $C_{15}H_{31}$), m. p. 72—74°, $\lambda_{max.}$ 214 and 242 mμ (ε 1300 and 4100, respectively), $\nu_{max.}$ (in CCl_4) at 1761 and 1706 (thioanhydride) cm.$^{-1}$ (Found: C, 75·15; H, 12·25; S, 6·6. $C_{32}H_{62}O_2S$ requires C, 75·25; H, 12·25; S, 6·3%).

O-Ethyl S-Phenylacetyl Xanthate (I; R = Ph·CH_2). Sodium *O*-ethyl xanthate (10·8 g.) in acetone (175 ml.) was added to phenylacetyl chloride (11·6 g.) in acetone (200 ml.) at −35° during 30 min. with stirring. After 1 hr. at this temperature the mixture was allowed to warm to room temperature. The solvent was removed *in vacuo*, water (50 ml.) added to the residue, and the product extracted into methylene dichloride. The extract was washed with aqueous sodium carbonate (1%), then with water, and dried (Na_2SO_4). Removal of the solvent *in vacuo* gave *O-ethyl S-phenylacetyl xanthate* (17·8 g.) as an orange-yellow liquid. Rapid distillation gave the pure xanthate (97%), b. p. 100—105°/6·5 × 10^{-2} mm., n_D^{25} 1·5971, $\lambda_{max.}$ 207, 226, 278, 300, and 396 mμ (ε 17,000, 9500, 8600, 6800, and 54, respectively), $\nu_{max.}$ 1725 (C=O) cm.$^{-1}$ (Found: C, 55·2; H, 5·25; S, 26·75. $C_{11}H_{12}O_2S_2$ requires C, 55·0; H, 5·05; S, 26·7%). Rapid distillation in small batches is essential in the purification of this, and other, acyl xanthates. When distilled at a higher pressure (b. p. 125—135°/0·5 mm.) the yield was reduced (86%) and from the residue, after treatment with activated charcoal and crystallisation from light petroleum (b. p. 60—80°), there was isolated *phenylacetic thioanhydride* (II; R = Ph·CH_2), m. p. 70·5—71·5°, $\lambda_{max.}$ 208, 244, and 402 (ε 21,200, 5600, and 26 respectively), $\nu_{max.}$ 1750 and 1700 (CO·S·CO) cm.$^{-1}$ (Found: C, 70·9; H, 5·45; S, 11·7. $C_{16}H_{14}O_2S$ requires C, 71·1; H, 5·2; S, 11·85%).

Irradiation of O-*Ethyl* S-*Phenylacetyl Xanthate* (I; R = Ph·CH_2).—(*a*) *In benzene with a tungsten lamp.* The xanthate (2·403 g.) in benzene (250 ml.) was irradiated under reflux for 24 hr. (fading of yellow colour). Removal of the solvent *in vacuo* gave *S*-benzyl *O*-ethyl xanthate (III; R = Ph·CH_2) (1·85 g.), b. p. 95—97°/0·1 mm., n_D^{25} 1·6000, $\lambda_{max.}$ 207, 226, 279, and 353 mμ (ε 16,500, 10,500, 10,900, and 63 respectively) (Found: C, 56·3; H, 6·15; S, 30·3. Calc. for $C_{10}H_{12}OS_2$: C, 56·55; H, 5·7; S, 30·2%). The compound was identified by these constants, by infrared comparison with an authentic specimen,[3] and by alkaline hydrolysis as follows. The irradiation product (2·11 g.) in N-sodium hydroxide in 1 : 9 aqueous ethanol (50 ml.) was heated under reflux under nitrogen for 1 hr. Removal of the solvent *in vacuo*, addition of water (25 ml.), cautious acidification by 2N-sulphuric acid, and extraction into methylene dichloride (100 ml.) gave a product containing traces of phenylacetic acid (7%; extracted with aqueous sodium hydrogen carbonate). Removal of the solvent *in vacuo* gave

[7] Kolthoff and Belcher, " Volumetric Analysis," Interscience Publ. Inc., New York, N.Y., 1957, Vol. III, p. 387.

toluene-α-thiol (1·00 g.), identified by iodometry, infrared spectrum, gas chromatography, and conversion into the 3,5-dinitrobenzoyl derivative (m. p. and mixed m. p.).

Irradiation as above for 5 hr. gave, after alkaline hydrolysis, toluene-α-thiol (22%) and phenylacetic acid (66%). After 12 hr. the results were thiol (31%) and acid (45%).

In a blank experiment the acyl xanthate (1·20 g.) in benzene (125 ml.) was refluxed under nitrogen for 24 hr. in the dark. Removal of the solvent *in vacuo* gave unchanged starting material (1·11 g.), identified by infrared spectrum and by alkaline hydrolysis to phenylacetic acid (99%).

(*b*) *In various solvents under reflux, with a mercury-arc lamp.* These experiments were carried out on the scale and under the conditions detailed above. The results have been given in the Theoretical section. The course of each reaction was followed by the change in ultraviolet spectrum.

(*c*) *In benzene in the presence of toluene-α-thiol.* The irradiation was carried out as above with a mercury-arc lamp for 5 hr. (ultraviolet control) with addition of toluene-α-thiol (2·48 g.). The benzene solution was washed with 4N-sodium hydroxide (to remove unchanged thiol), then with water, and dried (Na_2SO_4). Removal of the solvent and hydrolysis as under (*a*) gave phenylacetic acid (74%).

Thermal Decomposition of O-*Ethyl* S-*Phenylacetyl Xanthate* (I; R = Ph·CH_2).—The acyl xanthate (2·40 g.) was heated at 200° for 1·5 hr. (no more carbon disulphide evolved) in a stream of nitrogen, the gases being passed into 10% ethanolic potassium hydroxide (20 ml.). The xanthate content of this solution was determined (63%) by Matuszak's method.[8] The residue (1·59 g.), which showed strong infrared absorption at 1725 (C=O) $cm.^{-1}$, was hydrolysed as above to phenylacetic acid (86%). The residue contained (before and after hydrolysis) traces only of mercaptan.

In a second experiment the gases evolved in the nitrogen stream were passed into ether (75 ml.) containing piperidine (2·13 g.). The precipitated 1-dithiocarboxy-derivative (78%) was identified by m. p., mixed m. p., and infrared spectrum. The residue (1·72 g.) from this pyrolysis was distilled, to give ethyl phenylacetate (68%), b. p. 46°/0·5 mm., identified by infrared comparison.

Irradiation of S-*Benzyl* O-*Ethyl Xanthate* (III; R = Ph·CH_2).—The xanthate (1·06 g.) in benzene (125 ml.) was irradiated with a mercury-arc lamp for 8 hr. under reflux. Removal of the solvent *in vacuo* gave unchanged starting material (1·04 g.), identified by infrared comparison.

Preparation and Irradiation of O-*Ethyl* S-*Isobutyryl Xanthate* (I; R = Pr^i).—Sodium ethyl xanthate (7·21 g.) in acetone (100 ml.) was added slowly (30 min.) with stirring to isobutyryl chloride (5·33 g.) in acetone (150 ml.) at −35° and kept at this temperature for 1 hr. before being allowed to warm to room temperature. Removal of the solvent *in vacuo* and working up as described above for the phenylacetyl analogue gave yellow O-*ethyl* S-*isobutyryl xanthate* (8·41 g.). This had (distilled in 1·0-g. portions) b. p. 60—63°/0·1 mm., n_D^{25} 1·5335, $\lambda_{max.}$ 207, 229, 275, and 397 mμ (ε 5200, 6250, 8550, and 47, respectively), $\nu_{max.}$ 1730 (C=O) $cm.^{-1}$ (Found: C, 43·9; H, 6·0; S, 32·85. $C_7H_{12}O_2S_2$ requires C, 43·7; H, 6·3; S, 33·35%). The following irradiation conditions were applied to this compound:

(*a*) The xanthate (4·27 g.) in benzene (375 ml.) was irradiated under reflux by a tungsten lamp for 24 hr. (fading of yellow colour). Removal of the solvent *in vacuo* gave essentially pure *O*-ethyl *S*-isopropyl xanthate (III; R = Pr^i) (3·99 g.). This was hydrolysed with aqueous ethanolic sodium hydroxide as in the examples above, to give propane-2-thiol (99%), identified by titration and by conversion into 2,4-dinitrophenyl isopropyl sulphide (m. p., mixed m. p., and infrared comparison). There was no residual isobutyric acid.

In a control run in the dark the product gave isobutyric acid (87%) on hydrolysis.

(*b*) The xanthate (2·89 g.) in benzene (250 ml.) was irradiated under reflux with a mercury-arc lamp for 2 hr. (fading of yellow colour). The product gave propane-2-thiol (99%) and no isobutyric acid on hydrolysis.

Preparation and Irradiation of O-*Ethyl* S-*Pivaloyl Xanthate* (I; R = Bu^t).—Sodium ethyl xanthate (7·21 g.) in acetone (100 ml.) was added during 30 min. with stirring to pivaloyl chloride [9] (6·03 g.) in acetone (150 ml.) at −35° and kept at this temperature for 1 hr. before

[8] Matuszak, *Ind. Eng. Chem., Analyt.*, 1932, **4**, 98.
[9] Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325.

being allowed to warm to room temperature. Working up as above gave the golden-yellow O-*ethyl* S-*pivaloyl xanthate* (10·3 g.). This had (distilled in 1·0-g. portions), b. p. 75°/0·1 mm., n_D^{25} 1·5250, $\lambda_{max.}$ 207, 232, 275, and 398 mμ (ε 4900, 6200, 8000, and 49 respectively), $\nu_{max.}$ 1720 (C=O) cm.$^{-1}$ (Found: C, 47·15; H, 6·95; S, 31·25. $C_8H_{14}O_2S_2$ requires C, 46·6; H, 6·85; S, 31·1%). The following irradiation conditions were applied to this compound.

(*a*) The xanthate (2·06 g.) in benzene (250 ml.) was irradiated under reflux with a tungsten lamp for 14 hr. (ultraviolet control). Removal of the solvent *in vacuo* afforded somewhat impure O-*ethyl* S-*t-butyl xanthate* (III; R = Bu^t) (1·62 g.). This (1·445 g.; 81%) had b. p. 68—70°/1·75 mm., n_D^{25} 1·5248, $\lambda_{max.}$ 208, 219, 285, and 360 mμ (ε 7600, 7200, 11,800, and 70 respectively) (Found: C, 47·4; H, 7·5; S, 36·1. $C_7H_{14}OS_2$ requires C, 47·15; H, 7·9; S, 35·95%).

In a second experiment the acyl xanthate (3·1 g.) in benzene (250 ml.) was irradiated as above for 24 hr. (ultraviolet control). Removal of the solvent *in vacuo* and hydrolysis of the product (2·27 g.) with 1 : 9 aqueous-ethanolic N-sodium hydroxide (25 ml.) gave 2-methylpropane-2-thiol (79%), characterised as its 2,4-dinitrophenyl derivative (m. p., mixed m. p., and infrared comparison).

In a control experiment the acyl xanthate (2·06 g.) in benzene (165 ml.) was refluxed for 24 hr. in the dark. Removal of the solvent *in vacuo* gave unchanged starting material (infrared spectrum). Alkaline hydrolysis as above gave pivalic acid (88%) and only traces of mercaptan (odour).

(*b*) The acyl xanthate (2·06 g.) in benzene (250 ml.) was irradiated under reflux with a mercury-arc lamp for 4 hr. (ultraviolet control). Removal of the solvent gave *O*-ethyl *S*-t-butyl xanthate (1·46 g.), b. p. 62—64°/1·5 mm. (1·24 g.). This was identical (infrared comparison) with the compound obtained in experiment (*a*) immediately above.

Preparation and Irradiation of O-*Ethyl* S-*n-Valeryl Xanthate* (I; R = Bu^n).—Sodium ethyl xanthate (10·1 g.) in acetone (100 ml.) was treated with n-valeryl chloride (8·44 g.) in acetone (150 ml.) as in the analogous examples, giving *O*-ethyl *S*-n-valeryl xanthate as an orange-yellow liquid (99%), b. p. 92—94°/1 mm. (93%), n_D^{25} 1·5158, $\lambda_{max.}$ 208, 228, 276, and 394 mμ (ε 6000, 6300, 8700, and 50 respectively), $\nu_{max.}$ 1730 (C=O) cm.$^{-1}$. Satisfactory analytical data were not secured for this compound. The following irradiation conditions were applied to this compound.

(*a*) The xanthate (3·1 g.) in benzene (250 ml.) was irradiated under reflux with a tungsten lamp for 24 hr. Alkaline hydrolysis as in examples detailed above afforded n-valeric acid (86%) and butane-1-thiol (8%; determined iodometrically). In a second run, when the irradiation was continued for 48 hr., alkaline hydrolysis gave valeric acid (83%) and the mercaptan (14%).

(*b*) The xanthate (2·06 g.) in benzene (250 ml.) was irradiated under reflux with a mercury-arc lamp for 36 hr. Alkaline hydrolysis gave n-valeric acid (30%) and the mercaptan (68%).

(*c*) The xanthate (3·1 g.) in toluene (250 ml.) was irradiated under reflux with a tungsten lamp for 48 hr. (fading of the yellow colour). The product (2·34 g.) was hydrolysed as in the examples above, to give n-valeric acid (22%; infrared comparison) and the mercaptan (43%). The latter was characterised as its 2,4-dinitrophenyl derivative (m. p., mixed m. p., and infrared comparison). In a second run irradiation for 24 hr. furnished n-valeric acid (30%) and the mercaptan (40%).

In a control experiment the xanthate (3·1 g.) in toluene (250 ml.) was refluxed in the dark for 24 hr. Hydrolysis of the product gave n-valeric acid (73%; infrared comparison) and the mercaptan (2%; iodometric determination).

Preparation and Irradiation of S-*Acetylmandeloyl* O-*Ethyl Xanthate* (I; R = Ph·CH·OAc).—Sodium *O*-ethyl xanthate (10·63 g.) in acetone (125 ml.) was added to acetylmandeloyl chloride (10·63 g.) in acetone (125 ml.) at −35° as in the examples above. Removal of the solvent gave S-*acetylmandeloyl* O-*ethyl xanthate* (14·45 g.). Crystallised from light petroleum (b. p. 40—60°) this formed golden-yellow prisms (83%), m. p. 40—41°, $\lambda_{max.}$ 205, 222, 272, and 382 mμ (ε 18,400, 9500, 6900, and 46, respectively) (Found: C, 52·5; H, 4·8; S, 20·8. $C_{13}H_{14}O_4S_2$ requires C, 52·3; H, 4·75; S, 21·5%). The following irradiation conditions were applied to this compound.

(*a*) The xanthate (2·98 g.) in benzene (250 ml.) was irradiated under reflux for 6 hr. (ultraviolet control). Removal of the solvent *in vacuo* gave a viscous liquid (2·67 g.) which, on crystallisation from light petroleum (b. p. 40—60°), gave hydrobenzoin diacetate (21%),

identified by m. p., mixed m. p., and infrared comparison (Found: C, 72·5; H, 6·0. Calc. for $C_{18}H_{18}O_4$: C, 72·45; H, 6·1%).

In a second run the xanthate (2·98 g.) in benzene (250 ml.) was irradiated for 18 hr. The product was taken up in ethanol (10 ml.), water (5 ml.), and concentrated sulphuric acid (1·0 ml.), refluxed for 30 min., and then treated with 2,4-dinitrophenylhydrazine (2·97 g.) in ethanol (30 ml.) and concentrated sulphuric acid (5 ml.). This procedure furnished benzaldehyde 2,4-dinitrophenylhydrazone (26%), identified by m. p., mixed m. p., and infrared comparison.

(*b*) The xanthate (2·98 g.) and toluene-α-thiol (3·73 g.) in benzene (250 ml.) were irradiated under reflux with a mercury-arc lamp for 6 hr. Treatment with 2,4-dinitrophenylhydrazine reagent as above gave benzaldehyde 2,4-dinitrophenylhydrazone (39%), identified as above.

*Preparation and Irradiation of Di-*O*-Ethyl* *SS*-Glutaryl Dixanthate.*—Sodium *O*-ethyl xanthate (7·21 g.) in acetone (75 ml.) was added to glutaryl chloride (4·23 g.) in acetone (75 ml.) at −35° as in the examples above. Crystallisation of the product from light petroleum (b. p. 40—60°) gave the *dixanthate* (84%), m. p. 59—60°, $\lambda_{max.}$ 204, 225, 272, and 385 mμ (ε 16,400, 13,600, 17,700, and 99, respectively) (Found: C, 38·95; H, 4·75; S, 38·25. $C_{11}H_{16}O_4S_4$ requires C, 38·8; H, 4·75; S, 37·65%). The following irradiation conditions were applied to this compound.

The xanthate (1·70 g.) in benzene (250 ml.) was irradiated under reflux with a mercury-arc lamp for 26 hr. (fading of the yellow colour). Treatment of the product in ethanol with 2,4-dinitrophenylhydrazine reagent gave cyclopentane-1,2-dione bis-2,4-dinitrophenylhydrazone (31%), identified by m. p., mixed m. p., and infrared comparison.[10]

In a second run the acyl xanthate (1·70 g.) in benzene (750 ml.) was irradiated at 40° (fan) for 24 hr. Treatment of the product with 2,4-dinitrophenylhydrazine reagent gave the same hydrazone (55%).

Preparation and Irradiation of S-*Benzoyl* O-*Ethyl Xanthate* (I; R = Ph). Sodium *O*-ethyl xanthate (10·8 g.) in acetone (125 ml.) was treated with benzoyl chloride (10·55 g.) in acetone (250 ml.) at −35° in the usual manner. The orange yellow *S*-benzoyl *O*-ethyl xanthate [1] (16·9 g.) had $\lambda_{max.}$ 206, 250, 283, and 402 mμ (ε 17,500, 14,300, 12,900, and 120, respectively), $\nu_{max.}$ 1680 (C=O) cm.$^{-1}$. The following irradiation conditions were applied to this compound.

(*a*) The xanthate (3·39 g.) in benzene (250 ml.) was irradiated under reflux for 24 hr. with a tungsten lamp. Removal of the solvent gave a viscous liquid (3·26 g.) showing a strong infrared band at 1685 (C=O) cm.$^{-1}$. Alkaline hydrolysis as in the examples above gave benzoic acid (90%), identified by m. p., mixed m. p., and infrared comparison.

(*b*) The xanthate (3·39 g.) in toluene (250 ml.) was irradiated under reflux with a tungsten lamp for 24 hr. The product (3·27 g.) showed a strong infrared band at 1695 (C=O) cm.$^{-1}$ and gave benzoic acid (88%) on alkaline hydrolysis.

Preparation and Irradiation of S-p-*Chlorobenzoyl* O-*Ethyl Xanthate* (I; R = *p*-Cl·C_6H_4).—Sodium *O*-ethyl xanthate (2·88 g.) in acetone (50 ml.) was added to *p*-chlorobenzoyl chloride (3·5 g.) in acetone (50 ml.) at −35° as in the examples above. Crystallisation of the product (6·03 g.) from light petroleum (b. p. 40—60°) gave *S-p*-chlorobenzoyl *O*-ethyl xanthate (85%), m. p. 65·5—66·5°, $\lambda_{max.}$ 204, 217, 262, 278, and 385 mμ (ε 21,000, 13,500, 16,200, 14,700, and 133, respectively).[1]

This xanthate (1·3 g.) in benzene (125 ml.) was irradiated under reflux for 20 hr. with a mercury-arc lamp. Alkaline hydrolysis of the product gave *p*-chlorobenzoic acid (68%), identified by m. p., mixed m. p., and infrared comparison.

Preparation and Irradiation of 3β-*Acetoxy*-11-*oxo*-5α-*bisnorcholanoyl* O-*Ethyl Xanthate* (X; X = ·S·CS·OEt).—Reaction of sodium *O*-ethyl xanthate (740 mg.) with 3-β-acetoxy-11-oxo-5α-bisnorcholanoyl chloride (2·0 g.) (prepared from the acid [11] with oxalyl chloride in the usual way) in acetone (100 ml.) in the usual way (see above). Crystallisation of the product from ether–light petroleum gave 3β-*acetoxy*-11-*oxo*-5α-*bisnorcholanoyl* O-*ethyl xanthate* (1·80 g.) as yellow prisms, m. p. 123—125°, $[\alpha]_D$ +56° (*c* 1·55), $\lambda_{max.}$ 204, 231, 277, and 398 mμ (ε 8300, 7600, 10,800, and 94, respectively) (Found: C, 63·5; H, 7·9; S, 12·75. $C_{27}H_{40}O_5S_2$ requires C, 63·75; H, 8·0; S, 12·6%).

[10] Ramirez and Bellet, *J. Amer. Chem. Soc.*, 1954, **76**, 491.

[11] Chamberlin, Ruyle, A. E. Erickson, Chemerda, Aliminosa, R. L. Erickson, Sita, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 2396; Cameron, Hunt, Oughton, Wilkinson, and Wilson, *J.*, 1953, 3864.

This xanthate (600 mg.) in benzene (36 ml.) was irradiated with a tungsten lamp at 40° (fan) for 30 min. (disappearance of the yellow colour). The process was repeated four times. The combined product (2·89 g.) was chromatographed over alumina (grade III; 145 g.). Fractionation with light petroleum (b. p. 40—60°)–benzene gave two isomeric *xanthates* (XI; X = S·CS·OEt). The more easily eluted *isomer*-I formed needles, m. p. 193—195°, $[\alpha]_D$ +54° (*c* 0·50), $\lambda_{max.}$ 203, 224, and 281 mμ (ε 7500, 7900, and 14,000, respectively), $\nu_{max.}$ (in Nujol) 1726 (OAc) and 1705 (11-ketone) cm.$^{-1}$ (Found: C, 65·0; H, 8·3; S, 13·45. $C_{26}H_{40}O_4S_2$ requires C, 65·0; H, 8·4; S, 13·3%). The less easily isolated *isomer*-II formed prisms or plates, m. p. 138—140°, $[\alpha]_D$ +69° (*c* 0·73), $\lambda_{max.}$ 205, 223, and 281 mμ (ε 7400, 8100, and 13,500, respectively), $\nu_{max.}$ (in Nujol) 1732 (OAc) and 1705 (11-ketone) cm.$^{-1}$ (Found: C, 65·3; H, 8·6; S, 12·65%). The isomers gave a m. p. depression on admixture.

Isomer-I (150 mg.) and Raney nickel (1·5 g.) in methanol (50 ml.) were refluxed for 4 hr. Crystallisation of the product from aqueous methanol gave 3β-acetoxy-5α-pregnan-11-one (see below) (94 mg.), identified by m. p., mixed m. p., $[\alpha]_D$, and infrared comparison.

Isomer-II (50 mg.) and Raney nickel (1 g.) in methanol (30 ml.) similarly afforded 3β-acetoxy-5α-pregnan-11-one, identified similarly.

Preparation of 3β-*Acetoxy*-5α-*pregnan*-11-*one* (XI; X = H) (*with* Dr. S. STERNHELL).—3β-Acetoxy-5α-pregnane-11,20-dione (from Glaxo Laboratories Ltd.) (465 mg.) was treated with ethane-1,2-dithiol (10 drops) and boron trifluoride (45% in ether; 15 drops) at room temperature for 5 min. (solidified after 1 min.) and poured into an excess of methanol. Crystallisation of the product from methylene dichloride–ethanol gave 3β-*acetoxy*-5α-*pregnane*-11,20-*dione* 20-(*ethylene dithioketal*) (300 mg.), m. p. 234—237°, $[\alpha]_D$ +22° (*c* 1·50), $\nu_{max.}$ (in Nujol) at 1725 (OAc) and 1695 (11-ketone) (Found: C, 66·05; H, 8·5; S, 14·1. $C_{25}H_{38}O_3S_2$ requires C, 66·65; H, 8·5; S, 14·2%).

This dithioketal (237 mg.) in ethanol (50 ml.) was refluxed with Raney nickel (activity W1; 2 g.) for 16 hr. Crystallisation of the product from aqueous methanol gave 3β-*acetoxy*-5α-*pregnan*-11-*one* (XI; X = H), m. p. 160—163°, $[\alpha]_D$ +40° (*c* 1·90), $\nu_{max.}$ (in Nujol) at 1731 (OAc) and 1705 (11-ketone) cm.$^{-1}$ (Found: C, 76·6; H, 10·3; Ac, 11·85. $C_{23}H_{36}O_3$ requires C, 76·6; H, 10·05; Ac, 11·95%).

Preparation and Irradiation of n-Butyl Thioisobutyrate (VI).—Butane-1-thiol (4·51 g.) and isobutyryl chloride (5·33 g.) in pyridine (8 g.) were heated on the steam-bath for 2 hr. Working up in the usual way gave *n-butyl thioisobutyrate* (VI) (83%), b. p. 58—59°/3·3 mm., $\lambda_{max.}$ 233 and 276 mμ (ε 4100 and 688, respectively), $\nu_{max.}$ 1680 (C=O) cm.$^{-1}$ (Found: C, 60·2; H, 10·15; S, 19·75. $C_8H_{16}OS$ requires C, 60·0; H, 10·05, S, 20·0%).

This thioester (1·60 g.) in diethyl ether (100 ml.) was irradiated under reflux with a mercury-arc lamp for 6 hr. Removal of the solvent gave unchanged starting material (97%), identified by infrared comparison. Essentially the same result was observed after irradiation in ethanol for 7 hr.

We thank the Department of Scientific and Industrial Research, the Government Grants Committee of the Royal Society, Imperial Chemical Industries Limited, and the Du Pont Company for financial assistance. One of us (M. V. G.) acknowledges a Postdoctorate Fellowship from B.P. Limited, another (M. T.) a similar Fellowship from the Research Institute for Medicine and Chemistry. Gifts of chemicals from Glaxo Laboratories Lmited are gratefully acknowledged. Professor B. C. L. Weedon (Queen Mary College, London) kindly provided a specimen of pure palmitic acid.

IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, November 30th,* 1961.]