178. *The Chemistry of Xanthic Acid Derivatives. Part III. The Interaction of Carboxylic Acid Chlorides and Potassium Ethyl Xanthate.*

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The few *O*-ethyl-*S*-(carboxy)acyl-xanthates previously recorded have been isolated only as unstable liquids. It is now shown that *p*-nitrobenzoyl chloride reacts with potassium ethyl xanthate to form the crystalline *O-ethyl* S-p-*nitrobenzoyl xanthate*, $EtO{\cdot}CS{\cdot}S{\cdot}CO{\cdot}C_6H_4NO_2$, which can be recrystallised unchanged: the p-*chlorobenzoyl* analogue is similar. The thermal decomposition products of each have been investigated.

O-Ethyl *S*-benzoyl xanthate is, however, an unstable liquid which undergoes violent thermal decomposition affording initially dibenzoyl disulphide and ultimately a mixture of ethyl benzoate, thiobenzoate and dithiobenzoate, and 2 : 3 : 4 : 5-*tetraphenylthiophen nonasulphide*, the properties of which have been studied.

Xanthates thus obtained from carboxylic acid chlorides are, however, more stable that those from sulphonyl chlorides, which apparently undergo spontaneous decomposition on formation (see Part IV).

Very little knowledge is available concerning the interaction of metallic xanthates and carboxylic acid chlorides. Welde (*J. pr. chem.*, 1877, (2), **15**, 44) and Willcox (*J. Amer. Chem. Soc.*, 1906, **28**, 1031) showed that ethyl chloroformate reacted with potassium ethyl xanthate to form diethyl sulphurdicarbothionate, $(EtO{\cdot}CS{\cdot})_2S$; Wheeler and Dustin (*Amer. Chem. J.*, 1900, **24**, 443) found, however, that this interaction also furnished *O*-ethyl *S*-ethyl xanthate, *OO'*-diethyl thiocarbonate, diethyl carbonate, carbon disulphide and carbon dioxide. Willcox (*loc. cit.*) showed that phosgene also reacted with potassium xanthate to form diethyl sulphurdicarbothionate. Strictly speaking, however, these reactions are not those of true carboxylic acid chlorides of type, R·COCl.

Willcox found that potassium ethyl xanthate reacted with acetyl chloride dissolved in ice-cold ether to form the liquid *O*-ethyl *S*-acetyl xanthate, EtO·CS·S·COMe, which readily decomposed to ethyl acetate and carbon disulphide; when, however, the acetyl chloride was dissolved in only a small quantity of ether at room temperature, the chief product was diethyl sulphurdicarbothionate. Richter (*Ber.*, 1916, **49**, 1026), using chilled carbon disulphide as a solvent, also isolated the acetyl xanthate: he showed that benzoyl chloride reacted similarly to form the liquid *O*-ethyl *S*-benzoyl xanthate, EtO·CS·S·COPh, which decomposed at 40—45° to produce ethyl benzoate and carbon disulphide. Both the acetyl and the benzoyl xanthates were isolated only by the low temperature evaporation of their ethereal or carbon disulphide solutions: their instability precluded any form of purification.

We have investigated the reaction of potassium xanthate with benzoyl and certain *p*-substituted benzoyl chlorides. The latter, which give the simplest results, will be described first.

When dry powdered potassium ethyl xanthate and *p*-nitrobenzoyl chloride in equimolecular quantities were intimately mixed at room temperature, a reaction occurred with evolution of heat and the formation of O-*ethyl* S-p-*nitrobenzoyl xanthate* (I). This crystalline xanthate, m. p. 65°, has comparatively high stability:

$$EtO{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2 + CS_2 \longleftarrow \underset{\text{(I.)}}{EtO{\cdot}CS{\cdot}S{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2} \longrightarrow HO{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2 + CS_2 + C_2H_4$$

it could be freely recrystallised from boiling ligroin, and distilled with very slight decomposition at 120—123°/0·01 mm. When heated at 18 mm. it decomposed forming *p*-nitrobenzoic acid and ethyl *p*-nitrobenzoate. Although

the latter probably arises, accompanied by carbon disulphide, by simple decomposition of the xanthate, the mechanism by which the *p*-nitrobenzoic acid is formed remains uncertain; it is probable that the thermal disruption of the xanthate molecule is accompanied by partial dissociation of the ethoxy-group to a hydroxyl group and ethylene. The gaseous products of this decomposition at various temperatures warrant detailed investigation. When potassium xanthate was added to molten *p*-nitrobenzoyl chloride at 80°, ethyl *p*-nitrobenzoate and *p*-nitrobenzoic anhydride were formed. In view of the readiness with which this anhydride is formed from the free acid, there is little doubt that at this higher temperature the xanthate (I) was again formed, and then underwent the same thermal decomposition as before.

Potassium xanthate reacted similarly with cold *p*-chlorobenzoyl chloride, affording O-*ethyl* S-p-*chlorobenzoyl xanthate* (as I), yellow crystals, m. p. 69—69·5°, which also distilled unchanged at 122—125°/0·1 mm. This compound when heated at 19 mm. afforded however only *p*-chlorobenzoic anhydride, and no evidence of the formation of the ethyl ester could be obtained; it is probable that this anhydride also arose from the free acid and was not a direct product of the thermal decomposition.

We have confirmed Richter's observation that potassium xanthate reacts with an ice-cold solution of benzoyl chloride in carbon disulphide (or in ether) to form *O*-ethyl *S*-benzoyl xanthate, the identity of which we have confirmed by both analyses and molecular weight determinations. When this yellow liquid xanthate was heated at 18 mm. pressure, it underwent violent decomposition. By stopping the heating at this stage, we have isolated from the residue dibenzoyl disulphide, $(Ph{\cdot}CO{\cdot}S{\cdot})_2$. This compound has the same m. p. as that synthesised by Engelhardt, Latschinow and Malyschew (*Z. Chem.*, 1868, **4**, 358) by treating benzoyl chloride with sodium sulphide to form the salt, PhCO·SNa, and oxidising the latter with iodine; this synthesis, and the further evidence adduced by Busch and Stern (*Ber.*, 1896, **29**, 2150), place the structure of the disulphide beyond doubt. By continuing the heating after the above violent decomposition had subsided we obtained a crude distillate which on repeated fractionation ultimately afforded ethyl benzoate, ethyl thiobenzoate, ethyl dithiobenzoate and the crystalline 2 : 3 : 4 : 5-*tetraphenylthiophen nonasulphide*, $C_{28}H_{20}S_{10}$, (II), the structure of which is discussed below.

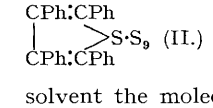
When potassium xanthate was added to one molecular proportion of chilled benzoyl chloride in the absence of a solvent much heat was evolved and the product, after removal of potassium chloride, afforded a yellowish-brown oil which apparently consisted mainly of the above xanthate, since, on heating as before, the same five products were obtained.

It is clear that the dibenzoyl disulphide must arise as an initial product of the decomposition of the xanthate :

$$2EtO{\cdot}CS{\cdot}S{\cdot}COPh = (PhCO{\cdot}S{\cdot})_2 + Et_2O + CS_2 + CO$$

The other initial product of this reaction would presumably be diethyl dithio-oxalate $(EtO{\cdot}CS{\cdot})_2$, which would decompose under the above conditions; the gaseous products thus formed are unknown, but may be those indicated in the above equation. The formation of ethyl benzoate and its mono- and di-thio-derivatives shows, however, that the xanthate can decompose by other routes, and it is significant that these esters are identical in type with those isolated by Wheeler and Dustin (*loc. cit.*) by the thermal decomposition of their chloroformate–xanthate condensation product. The vigour of the thermal decomposition of our benzoyl xanthate precluded accurate temperature control, and the products isolated must represent those formed over a wide range of temperature; there is little doubt therefore that the xanthate, in addition to decomposing to dibenzoyl disulphide as indicated above, also decomposes to ethyl benzoate and carbon disulphide (as Richter observed), to ethyl thiobenzoate and carbonyl sulphide, and to ethyl dithiobenzoate and carbon dioxide. It is not known whether our ethyl thiobenzoate has the structure PhCO·SEt or PhCS·OEt : these liquid isomerides have closely similar physical properties and are not readily identified.

The origin and properties of the compound $C_{28}H_{20}S_{10}$ (II), of m. p. 165·5—166°, are of great interest. The compound shows a normal molecular weight in boiling acetone, alcohol and benzene, from all of which solvents it can be recrystallised unchanged; it can also be distilled unchanged at reduced pressure, and it is unaffected by boiling aqueous potassium permanganate, by boiling alcoholic chloramine-T and by prolonged refluxing with methyl iodide. Its existence as a definite chemical compound cannot be doubted. On the other hand, it loses nine-tenths of its sulphur, with conversion to 2 : 3 : 4 : 5-tetraphenylthiophen (the " thionessal " of the earlier chemists) on treatment with a boiling acetone solution of potassium permanganate, or with cold concentrated aqueous ammonium sulphide, or by repeated crystallisation from ligroin. The fact that this transformation in ligroin is due to dissociation has been confirmed by experiments performed in pure 2 : 2 : 4-trimethyl-*n*-pentane : in this boiling solvent the molecular weight of the compound (II) indicates considerable dissociation, and again repeated recrystallisation furnishes the above thiophen. It is clear from these results that the compound must be 2 : 3 : 4 : 5-tetraphenylthiophen nonasulphide (II), and that it is a compound of high stability except in the presence of reagents which can extract the extra-nuclear sulphur.



(II.)

It is noteworthy that Fromm and Schmoldt (*Ber.*, 1907, 2863) claimed that the destructive distillation of thiobenzoic acid, dibenzoyl monosulphide, or dibenzoyl disulphide yielded " tolan tetrasulphide," $C_{14}H_{10}S_4$, m. p. 164°, in addition to other products, whilst similar treatment of lead dithiobenzoate produced " tolan disulphide," $C_{14}H_{10}S_2$, m. p. 174—175° ; molecular weight determinations in molten naphthalene apparently confirmed the molecular formula of the tetrasulphide but not that of the disulphide. These sulphides were assigned heterocyclic structures containing four and two atoms in the ring respectively. Fromm and Klinger

(*Annalen*, 1912, **394**, 342) showed later, however, that both compounds, when treated with aqueous ammonium sulphide, or when recrystallised from ether or ligroin, yielded 2 : 3 : 4 : 5-tetraphenylthiophen, and consequently they questioned the chemical identity of the original polysulphides. In view of our results, however, there is little doubt that Fromm and Schmoldt's sulphides were 2 : 3 : 4 : 5-tetraphenylthiophen heptasulphide and trisulphide respectively, and were definite compounds analogous in structure to our nonasulphide. (This conclusion ignores the molecular weight determinations in naphthalene, but the latter must have given unreliable results with compounds of this type.) Furthermore, we find that pure dibenzoyl disulphide, when destructively distilled under reduced pressure, gives a crude distillate which on repeated recrystallisation furnishes the nonasulphide (II); it is clear therefore that our nonasulphide and Fromm and Schmoldt's " heptasulphide " represent the thermal decomposition products of dibenzoyl disulphide under reduced and atmospheric pressure respectively. The nonasulphide (II) is therefore not a direct product of the thermal decomposition of the benzoyl ethyl xanthate, but of the dibenzoyl disulphide to which the xanthate gives rise.

The ethyl xanthates obtained from carboxylic acid chlorides are thus usually more stable than the analogous compounds obtained from sulphonyl chlorides, which apparently undergo spontaneous decomposition on formation (see Part IV).

Experimental.

The solvents used for recrystallisation are named in parenthesis after the compounds concerned. All molecular weight determinations, unless otherwise stated, were ebullioscopic, the concentrations recorded being g. solute/100 g. solvent. The ligroin used throughout had b. p. 60—80°.

O-*Ethyl* S-p-*Nitrobenzoyl Xanthate* (I).—Dry powdered potassium ethyl xanthate (8 g.) and *p*-nitrobenzoyl chloride (9·3 g., 1 mol.) were ground thoroughly together : the mixture became pasty as heat was evolved, but solidified on cooling. The pulverised product, when extracted with cold water, dried and recrystallised (ligroin), gave the *xanthate* (I), long yellow needles, m. p. 65° (Found : C, 44·3; H, 3·45; N, 5·2; S, 23·6. $C_{10}H_9O_4NS_2$ requires C, 44·25; H, 3·35; N, 5·15; S, 23·65%) : 12 g., 89%.

The xanthate, heated at 0·01 mm. pressure, boiled with very slight decomposition but the distillate, b. p. 120—123°, was almost pure xanthate, m. p. 64° (alone and mixed) after recrystallisation from ligroin (Found : C, 44·3; H, 3·55; S, 23·6%). The xanthate, heated at 18 mm. pressure, decomposed, giving a black charred residue, and a distillate which on cooling gave a yellow solid mixed with a red liquid. The latter was extracted with cold ligroin, and the yellow solid yielded *p*-nitrobenzoic acid (benzene), m. p. 235—235·5° (alone and mixed) (Found : C, 50·3; H, 3·0; N, 8·4. Calc. for $C_7H_5O_4N$: C, 50·3; H, 3·0; N, 8·4%). The solvent was evaporated from the ligroin extract, and the residual oily ethyl *p*-nitrobenzoate, when chilled in ice-salt, solidified : colourless crystals (alcohol), m. p. 56·5—57° (Found : C, 55·4; H, 4·7; N, 7·15. Calc. for $C_9H_9O_4N$: C, 55·35; H, 4·65; N, 7·2%).

Dry powdered potassium xanthate (2 g.) was slowly added with stirring to molten *p*-nitrobenzoyl chloride (2·3 g.; 1 mol.) maintained at 80°, and the mixture heated on the water-bath for 30 minutes. The cold greenish pasty product was extracted with cold ether, and the pale yellow solid residue, when washed with water, dried and recrystallised (benzene) gave *p*-nitrobenzoic anhydride, m. p. 193—193·5° (alone and mixed) (Found : C, 53·25; H, 2·65; N, 8·9. Calc. for $C_{14}H_8O_7N_2$: C, 53·15; H, 2·55; N, 8·85%). The ether extract was evaporated, and the residual oil solidified on cooling : crystallisation (alcohol) gave ethyl *p*-nitrobenzoate, m. p. 56·5—57° (alone and mixed) (Found : C, 55·5; H, 4·6; N, 7·1%).

O-*Ethyl* S-p-*Chlorobenzoyl Xanthate*.—This *xanthate* was prepared precisely as (I), using potassium xanthate (4·6 g.) and *p*-chlorobenzoyl chloride (5 g., 1 mol.) : yellow needles (ligroin), m. p. 70·5° (Found : C, 45·95; H, 3·6; Cl, 13·5; S, 24·7. $C_{10}H_9O_2ClS_2$ requires C, 46·05; H, 3·5; Cl, 13·6; S, 24·6%) (7 g., 94%). This xanthate underwent slight decomposition when heated at 0·1 mm. pressure, but the distillate, b. p. 122—125°, furnished the pure xanthate (ligroin), m. p. 69—69·5° (alone and mixed) (Found : C, 46·1; H, 3·75; Cl, 13·5%). It decomposed when heated at 19 mm. pressure, giving a black charred residue, but the distillate immediately solidified on cooling, and furnished *p*-chlorobenzoic anhydride (xylene), m. p. 193—194° (Found : C, 56·9; H, 2·75; Cl, 24·2. Calc. for $C_{14}H_8O_3Cl_2$: C, 56·95; H, 2·75; Cl, 24·05%).

O-*Ethyl* S-*Benzoyl Xanthate*.—Dry powdered potassium ethyl xanthate (8·8 g.) was added in small amounts to a solution of freshly distilled benzoyl chloride (7 g., 0·91 mol.) in ether (300 c.c.), the mixture being vigorously stirred and maintained at 0° throughout the addition : it was then shaken for 30 minutes at 0° and finally set aside at room temperature for 6 hours. The solution, filtered to remove precipitated potassium chloride and unchanged xanthate, was evaporated under reduced pressure below 15°, and the residual benzoyl xanthate, a golden yellow oil, when confined in a vacuum for several days, was pure (Found : C, 53·1; H, 4·55; S, 28·5; *M*, cryoscopic in 1·204% ethylene dibromide solution, 215. Calc. for $C_{10}H_{10}O_2S_2$: C, 53·05; H, 4·45; S, 28·35%; *M*, 226). The use of carbon disulphide (300 c.c.) as the solvent gave the same product (Found : C, 53·05; H, 4·5; S, 28·5%).

When the potassium xanthate (16 g.) was similarly added to chilled benzoyl chloride (14 g., 1 mol.) in the absence of a solvent, much heat was evolved, and the temperature rose to *ca.* 70°. Extraction of the cold yellowish pasty product with ligroin left a residue of potassium chloride, and the ligroin extract, when evaporated at reduced pressure, gave a yellow oil which was clearly the above benzoyl xanthate, since on thermal decomposition it behaved precisely as that prepared in ethereal solution. Experimental data are given only for the decomposition of the first sample of the xanthate, but the identity of the five products obtained from each sample (with and without a solvent) was determined by independent analysis in each case and thus doubly confirmed.

Thermal Decomposition.—(i) The xanthate, in small quantities, was cautiously heated at 18 mm. pressure until a violent decomposition ensued, when the heating was immediately stopped. The reddish-black residual oil partly solidified on cooling, and was then drained on the filter. Repeated recrystallisation of the solid product (alcohol or benzene) afforded colourless needles of dibenzoyl disulphide, m. p. 128° [Found : (a) from benzene, C, 61·4; H, 3·85; S, 23·6. (b) From alcohol, C, 61·3; H, 3·55; S, 23·25. Calc. for $C_{14}H_{10}O_2S_2$: C, 61·25; H, 3·7; S, 23·4%]. Engelhardt *et al.* (*loc. cit.*) give m. p. 128°, Weigart (*Ber.*, 1903, **36**, 1010) gives m. p. 129—130°, and Binz and Marx (*Ber.*, 1907, **40**, 3857) give m. p. 132°. (ii) After the above violent decomposition had subsided, the product was cautiously distilled at 20 mm. pressure, and the crude distillate collected in four main fractions having the b. p.s :— (*a*) 75—115°, (*b*) 115—150°, (*c*) 150—180°, (*d*) 200—220°. Fractions (*a*), (*b*), and (*c*) remained liquid, (*d*) rapidly solidified on cooling. A considerable black tarry residue remained in the flask.

Fraction (a). Repeated fractionation afforded ethyl benzoate, b. p. 90—92°/13 mm. (Found : C, 71·9; H, 6·55. Calc. for $C_9H_{10}O_2$: C, 71·95; H, 6·7%), which was further identified by nitration to ethyl *m*-nitrobenzoate, colourless crystals (ligroin), m. p. 42—42·5° (alone and mixed) (Found : C, 55·25; H, 4·75; N, 7·35. Calc. for $C_9H_9O_4N$: C,

55·35; H, 4·65; N, 7·2%). *Fraction* (b). Similar fractionation furnished colourless ethyl thiobenzoate, b. p. 131—133°/15 mm. (Found : C, 64·9; H, 6·05; S, 19·2. Calc. for $C_9H_{10}OS$: C, 65·0; H, 6·05; S, 19·3%). *Fraction* (c). Repeated fractionation afforded ethyl dithiobenzoate, a red liquid, b. p. 159—161°/13 mm. (Found : C, 59·25; H, 5·55; S, 35·3. Calc. for $C_9H_{10}S_2$: C, 59·25; H, 5·55; S, 35·2%). Hohn and Bloch (*J. pr. chem.*, 1910, **82**, 494) gave b. p. 158—162°/13 mm., 165—168°/19 mm. *Fraction* (d). Repeated crystallisation (alcohol) furnished pale yellowish-brown fibrous crystals of 2 : 3 : 4 : 5-*tetraphenylthiophen nonasulphide* (II), m. p. 165·5—166° (Found : C, 49·55; H, 3·1; S, 47·35; *M*, in 0·953% acetone solution, 665; in 0·491%, 0·882% alcoholic solution, 650, 656; in 0·603%, 0·762%, 1·427%, 1·479% benzene solution, 662, 660, 637, 660; in 0·692%, 1·095%, 1·33% 2 : 2 : 4-trimethyl-*n*-pentane solution, 330, 327, 324. $C_{28}H_{20}S_{10}$ requires C, 49·65; H, 3·0; S, 47·35%; *M*, 677). Elementary analyses similar to those above were obtained with several samples.

Properties of the Nonasulphide (II).—(a) A suspension of the powdered nonasulphide in an excess of aqueous alkaline permanganate was refluxed for 4 hours. After removal of the permanganate and manganese dioxide with sulphurous acid, the insoluble residue, recrystallised from alcohol, furnished unchanged (II), m. p. 164—164·5° (alone and mixed). (b) A solution of (II) (0·2 g.) and chloramine-T (0·9 g., 10 mols.) in alcohol (50 c.c.) was refluxed for 10 hours : the filtered solution deposited unchanged (II), m. p. 163·5—164·5° (alone and mixed). (c) A solution of (II) (0·5 g.) in methyl iodide (23 g.) was refluxed for 10 hours. After evaporation of the iodide, recrystallisation of the residue (alcohol) afforded unchanged (II), m. p. 165° (alone and mixed). (d) Powdered potassium permanganate (16 g. in all) was slowly added to a boiling solution of (II) (1 g.) in acetone (200 c.c.) until no further oxidation occurred. Filtration and evaporation of the solution furnished 2 : 3 : 4 : 5-tetraphenylthiophen, colourless crystals (ligroin), m. p. 186·5° (Found : C, 86·65; H, 5·3; S, 8·05. Calc. for $C_{28}H_{20}S$: C, 86·55; H, 5·2; S, 8·25%). Fromm and Schmoldt (*loc. cit.*) and Forst (*Annalen*, 1875, **178**, 376) give m. p. 184°. (e) The finely powdered (II) was shaken with an excess of cold concentrated aqueous ammonium sulphide solution for 8 hours. The collected solid product, washed with water and dried, had m. p. 179—181°, unchanged by admixture with the above thiophen : one recrystallisation (ligroin) gave the pure thiophen, m. p. 184·5—185° (Found : C, 86·45; H, 5·35%). (f) The compound (II), when thrice crystallised (ligroin), furnished the pure thiophen, m. p. 185—185·5° (alone and mixed) (Found : C, 85·55; H, 5·2%). (g) The compound (II), thrice recrystallised from 2 : 2 : 4-trimethyl-*n*-pentane, also gave the pure thiophen, m. p. 186—186·5° (alone and mixed).

Thermal Decomposition of Dibenzoyl Disulphide.—The disulphide, prepared by the method of Engelhardt *et al.* (*loc. cit.*) and recrystallised from alcohol, had m. p. 128°. When heated at 18 mm., considerable decomposition occurred, but the pure disulphide, b. p. 155—162°/16 mm., distilled over. When heated, however, under a constant pressure of 48 mm., a distillate of b. p. 240—250° was obtained which rapidly and completely solidified, and after repeated recrystallisation (alcohol) furnished the nonasulphide (II), m. p. 165·5—166° (alone and mixed) (Found : C, 49·85; H, 3·2; S, 47·1%).

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