28. *Promoters for the Dropwise Condensation of Steam. Part II.*[1] *Preparation of Compounds containing Polyfunctional Sulphur Groups.*

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A series of compounds has been prepared containing two or more surface-active groups associated with one or more hydrocarbon residues.

IN this paper the preparation of a series of possible promoters for the dropwise condensation of steam is described in which two or more surface-active groups are present in an otherwise non-polar molecule. The types of compound are analogous to the monofunctional ones described in Part I.[1]

The bromine atoms of decamethylene dibromide, dodecyl 11-bromoundecanethiolate, and decamethylene di-(11-bromoundecanethiolate) were replaced as described in Part I, to give the corresponding alkyl, and substituted alkyl, xanthates, selenocyanates, thiocyanates and derivatives, thiols, and thiuronium picrates. In some instances the purity of the reagents had a very marked effect on the success of the reactions; for example, dodecyl 11-bromoundecanethiolate could be obtained only when the acyl chloride was quite free from phosphorus trichloride. Further, traces of impurities can affect the melting point of compounds by several degrees in either direction. In several cases it was found that although recrystallisation produced an analytically pure product it caused a lowering of the melting point. Westlake and Dougherty[2] report that in their preparation of dioctadecyl disulphide they obtained a product which gave an almost perfect analysis but melted 6° below the pure compound (m. p. 62—62·5°); repeated recrystallisations and treatment with charcoal did not raise the melting point, and they assumed that a small amount of octadecanol caused the effect.

A series of substituted glycerides of high molecular weight was prepared from glycerol tri-11-bromoundecanoate by the usual replacement of the bromine atoms. The tribromoglyceride was prepared by the action of 11-bromoundecanoyl chloride on glycerol in the presence of quinoline.

EXPERIMENTAL

OO-*Decamethylene Di(potassium Xanthate)*.—A finely powdered mixture of decane-1 : 10-diol (4·4 g.) and potassium hydroxide (2·8 g.) reacted with carbon disulphide (4 g.) to form the *dixanthate* (7·3 g.) which separated from ethanol as a white microcrystalline powder, m. p. 290° (Found : C, 35·5; H, 5·0. $C_{12}H_{20}O_2S_4K_2$ requires C, 35·8; H, 5·0%).

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[1] Part I, preceding paper.

[2] Westlake and Dougherty, *J. Amer. Chem. Soc.*, 1942, **64**, 149.

OO-*Decamethylene Di*(*ethyl Xanthate*).—Ethyl bromide (0·22 g.) and the above xanthate (0·4 g.) in hot ethanol gave the *dixanthate* (0·28 g.), which crystallised from light petroleum (b. p. 40—60°) as a white microcrystalline powder, m. p. 49—50° (Found : C, 50·1; H, 7·8; S, 33·7. $C_{16}H_{30}O_2S_4$ requires C, 50·2; H, 7·9; S, 33·5%).

The S-*octadecyl analogue* formed plates, m. p. 53·5—54° (Found : C, 69·4; H, 11·5; S, 15·2. $C_{48}H_{94}O_2S_4$ requires C, 69·3; H, 11·4; S, 15·4%).

SS-*Decamethylene Di*(*ethyl Xanthate*).—Decamethylene dibromide (3·0 g.) and potassium ethyl xanthate (3·2 g.) in hot ethanol gave this *dixanthate* (2·6 g.), which crystallised from ice-cold light petroleum (b. p. 40—60°) as a white powder, m. p. 34—35° (Found : C, 50·1; H, 7·9; S, 33·2. $C_{16}H_{30}O_2S_4$ requires C, 50·2; H, 7·9; S, 33·5%).

The O-*octadecyl analogue* formed plates (from acetone), m. p. 55·5—56° (Found : C, 69·4; H, 11·1; S, 15·2. $C_{48}H_{94}O_2S_4$ requires C, 69·3; H, 11·4; S, 15·4%).

Decamethylene Dithiocyanate.—Decamethylene dibromide (6·0 g.) and potassium thiocyanate (3 g.) in hot ethanol (40 ml.) gave the *dithiocyanate* (2·1 g.) as a colourless oil, b. p. 224—227°/2 mm. (Found : C, 56·3; H, 7·9;.S, 24·9. $C_{12}H_{20}N_2S_2$ requires C, 56·2; H, 7·9; S, 25·0%).

The *diselenocyanate*, similarly prepared, crystallised from toluene as a bright yellow powder, m. p. 63—63·5°, possessing a disgusting odour (Found : C, 40·9; H, 5·8; N, 7·5. $C_{12}H_{20}N_2Se_2$ requires C, 41·2; H, 5·8; N, 8·0%).

Decamethylene Bis-N-*Acetyldithiocarbamate*.—Decamethylene dithiocyanate (1·3 g.) was heated under reflux with an excess of thioacetic acid (2 ml.) for 3 hr. The excess of acid was removed under reduced pressure, and the pale yellow residual *ester* (0·5 g.) recrystallised from ethanol as pale yellow needles, m. p. 158—159° (Found : C, 48·3; H, 7·1; S, 30·8; N, 6·8. $C_{16}H_{28}O_2N_2S_4$ requires C, 47·0; H, 6·9; N, 6·9; S, 31·4%).

Decamethylene Bisthiolcarbamate.—The dithiocyanate (1 g.) with ice-cold 96% sulphuric acid (5 ml.) (cf. Part I [1]) gave the *bisthiolcarbamate* (1 g.), which recrystallised from acetone–light petroleum (3 : 1) as a white microcrystalline powder, m. p. 185·5—187° (Found : C, 49·2; H, 8·2; S, 21·5; N, 9·8. $C_{12}H_{24}O_2N_2S_2$ requires C, 49·3; H, 8·3; S, 21·9; N, 9·6%).

Didodecyl Decane-1 : 10-*dithiolate*.—Decane-1 : 10-dioyl dichloride (12·0 g.) was treated with dodecanethiol (20 g.) and kept at room temperature in the absence of moisture until hydrogen chloride was no longer evolved (2 hr.). The white solid product was then warmed at 60° for 1 hr., diluted when cool with light petroleum (20 ml.), and cooled at 0° for 1 hr. The *ester* (27 g.) was collected and recrystallised from acetone in white plates, m. p. 64—64·5° (Found : C, 71·7; H, 11·7; S, 10·9. $C_{34}H_{66}O_2S_2$ requires C, 71·5; H, 11·7; S, 11·2%).

1 : 10-*Di*(*octadecanoylthio*)*decane*.—Octadecanoyl chloride (6·0 g.) and decane-1 : 10-dithiol (2·0 g.) reacted likewise, to give the *compound* (7·0 g.) which crystallised from acetone–chloroform in white plates, m. p. 81—81·5° (Found : C, 74·5; H, 12·0; S, 8·5. $C_{46}H_{90}O_2S_2$ requires C, 74·7; H, 12·3; S, 8·7%).

11-*Bromoundecanoyl Chloride*.—11-Bromoundecanoic acid (37·5 g.) and phosphorus trichloride (6·5 g.) were heated together under reflux in anhydrous benzene (250 ml.) for 5 hr. The clear solution was decanted from the deposited phosphorous acid, and the benzene removed by distillation. Benzene (50 ml.) was added and then removed again by distillation. This was repeated. Finally the acid chloride was warmed in a high vacuum at 70° for 20 min., all phosphorus trichloride being thus removed. The product was a very pale straw-coloured oil, f. p. *ca.* 20°. It was characterised by formation of the 11-bromo-amide, m. p. 88° (lit., 88°).

Dodecyl 11-*Bromoundecanethiolate*.—11-Bromoundecanoyl chloride (14·1 g.) and dodecanethiol (10·1 g.) at room temperature (4 hr.) gave the *ester* (17·8 g.) which crystallised from acetone in white plates, m. p. 43—44° (Found : C, 61·4; H, 10·0; S, 7·1; Br, 17·9. $C_{23}H_{45}OSBr$ requires C, 61·4; H, 10·1; S, 7·1; Br, 17·8).

Dodecyl 11-[*Ethoxy*(*thiocarbonyl*)*thio*]*undecanethiolate*, $C_{12}H_{25}S{\cdot}CO{\cdot}[CH_2]_{10}{\cdot}S{\cdot}CS{\cdot}OEt$.—Dodecyl 11-bromoundecanethiolate (1·0 g.) and potassium ethyl xanthate (0·36 g.) in hot ethanol gave the new *xanthate* (0·8 g.) which crystallised from light petroleum as a white powder, m. p. 39·5—40·5° (Found : C, 63·7; H, 10·3; S, 19·9. $C_{26}H_{50}O_2S_3$ requires C, 63·6; H, 10·3; S, 19·6%).

Dodecyl 11-[*Octadecyloxy*(*thiocarbonyl*)*thio*]*undecanethiolate*.—Dodecyl 11-bromoundecanethiolate (0·7 g.) and potassium octadecyl xanthate (0·6 g.) in hot ethanol gave this *ester* (0·85 g.) which, crystallised from ether, had m. p. 54—55° (Found : C, 70·4; H, 11·4; S, 13·0. $C_{42}H_{82}O_2S_3$ requires C, 70·5; H, 11·6; S, 13·4%).

Dodecyl 11-*Selenocyanatoundecanethiolate*.—Dodecyl 11-bromoundecanethiolate (0·7 g.) and potassium selenocyanate (0·23 g.) were heated under reflux in ethanol (5 ml.) for 2 hr. Water (5 ml.) was added and heating continued for a further 10 min. The solution was reduced to *ca.* 3 ml. by distillation and then extracted with ether. The white solid (0·7 g.) obtained after removal of the ether crystallised from ether, to give the *selenocyanato-ester* as a white microcrystalline powder, m. p. 71—72° (Found: C, 60·6; H, 9·6; S, 6·4. $C_{24}H_{45}ONSSe$ requires C, 61·0; H, 9·6; S, 6·8%).

Dodecyl 11-*Thiocyanatoundecanethiolate.*—Dodecyl 11-bromoundecanethiolate (2·4 g.) and potassium thiocyanate (0·52 g.) likewise gave the *thiocyanate* (2·2 g.), m. p. 40·5—41° (from light petroleum) (Found: C, 67·1; H, 10·5; S, 14·7; N, 3·1. $C_{24}H_{45}ONS_2$ requires C, 67·4; H, 10·6; S, 15·0; N, 3·3%).

Dodecyl 11-(N-*Acetylthiocarbamoylthio*)*undecanethiolate.*—Dodecyl 11-thiocyanatoundecanethiolate (0·5 g.) with an excess of hot thioacetic acid (2 ml.) gave the *compound* as a pale yellow solid (0·5 g.) which crystallised from ethanol–light petroleum in pale yellow needles, m. p. 88—89° (Found: C, 61·8; H, 10·0; S, 19·2; N, 2·7. $C_{26}H_{49}O_2NS_3$ requires C, 62·0; H, 9·8; S, 19·1; N, 2·8%).

Dodecyl 11-*Carbamoylthioundecanethiolate.*—Dodecyl 11-thiocyanatoundecanethiolate (0·5 g.) with ice-cold 96% sulphuric acid (5 ml.) gave the *carbamoylthio-ester* (0·42 g.), which, crystallised from ethanol–light petroleum, had m. p. 97—99° (Found: C, 64·2; H, 10·4; S, 14·3; N, 3·0. $C_{24}H_{47}O_2NS_2$ requires C, 64·7; H, 10·7; S, 14·4; N, 3·1%).

Dodecyl 11-*Mercaptoundecanethiolate.*—Dodecyl 11-bromoundecanethiolate (2·2 g.) and thiourea (0·4 g.) were heated under reflux in ethanol (15 ml.) for 6 hr., then treated with sodium hydroxide (0·2 g.) in alcohol and heated under reflux in nitrogen for a further 2 hr. Water (5 ml.) was added and the solution was reduced to about 8 ml. by distillation. The residual solution was extracted with ether, and the solid extract (0·8 g.) recrystallised from acetone–light petroleum to give the *mercapto-ester* in white plates, m. p. 73—74° (Found: C, 68·3; H, 11·3; S, 15·8. $C_{23}H_{46}OS_2$ requires C, 68·6; H, 11·5; S, 15·9%).

Picrate of Dodecyl 11-(*Amidinothio*)*undecanethiolate.*—The thiuronium bromide solution obtained in the first stage of the preceding preparation was heated with alcoholic picric acid for 10 min. The yellow *picrate* that separated at 0° was collected, and washed with three portions of ice-cold ethanol. It recrystallised from ethanol in yellow needles, m. p. 109—110° (Found: C, 53·6; H, 7·7; S, 9·7; N, 9·9. $C_{30}H_{51}O_8N_5S_2$ requires C, 53·5; H, 7·6; S, 9·5; N 10·4%).

Dodecyl 11-*Dodecylthioundecanethiolate.*—Dodecanethiol (0·45 g.) was heated under reflux for 15 min. with sodium hydroxide (0·09 g.) in alcohol. Dodecyl 11-bromoundecanethiolate (1·0 g.) in ethanol (3 ml.) was added and the mixture heated for 3 hr. Water (5 ml.) was added and the majority of the alcohol was removed. The *thiolic ester* was isolated from the residual solution by ether-extraction. The white solid (0·6 g.), recrystallised from acetone, had m. p. 57—59° (Found: C, 73·4; H, 12·1; S, 11·5. $C_{35}H_{70}OS_2$ requires C, 73·6; H, 12·4; S, 11·2%).

Decamethylene Di-(11-*bromoundecanethiolate*).—11-Bromoundecanoyl chloride (28·3 g.) and decane-1 : 10-dithiol (10·3 g.) reacted at room temperature (5 hr.) to give the *compound* (28 g.), which crystallised from acetone in white plates, m. p. 67—68° (Found: C, 54·5; H, 9·1; Br, 23·2; S, 9·1. $C_{32}H_{60}O_2S_2Br_2$ requires C, 54·8; H, 8·7; S, 9·1; Br, 22·8%).

Decamethylene Di-[11-*ethoxy*(*thiocarbonyl*)*thioundecanethiolate*].—Decamethylene di-(11-bromoundecanethiolate) (0·5 g.) and potassium ethyl xanthate (0·23 g.) in hot ethanol gave the *dixanthate* (0·4 g.), m. p. 48—49° (from light petroleum) (Found: C, 58·6; H, 9·1; S, 24·0. $C_{38}H_{70}O_4S_6$ requires C, 58·3; H, 9·0; S, 24·6%).

Decamethamethylene Di-[11-*octadecyloxy*(*thiocarbonyl*)*thioundecanethiolate*], m. p. 69—70° (from ether) (Found: C, 68·3; H, 10·9; S, 15·8. $C_{70}H_{134}O_4S_6$ requires C, 68·2; H, 11·0; S, 15·6%), was similarly obtained.

Decamethylene Di-(11-*selenocyanatoundecanethiolate*).—Decamethylene di-(11-bromoundecanethiolate) (0·5 g.) and potassium selenocyanate (0·21 g.) in hot ethanol gave the *diselenocyanato-ester* (0·45 g.) which crystallised from ether as a white microcrystalline powder, m. p. 61—62° (Found: C, 54·6; H, 8·3; S, 8·3; N, 3·8. $C_{34}H_{60}O_2N_2S_2Se_2$ requires C, 54·2; H, 8·1; S, 8·5; N, 3·7%).

Decamethylene Di-(11-*thiocyanatoundecanethiolate*), m. p. 67—68° (from light petroleum) (Found: C, 62·0; H, 9·1; S, 19·3; N, 4·1. $C_{34}H_{60}O_2N_2S_4$ requires C, 62·1; H, 9·2; S, 19·5; N, 4·3%), was similarly obtained by use of potassium thiocyanate.

Decamethylene Di-[11-N-*acetyl*(*thiocarbamoyl*)*thioundecanethiolate*].—The preceding thiocyanate (0·5 g.) with an excess of hot thioacetic acid (2 ml.) gave this *compound* (0·45 g.) which crystallised from ethanol in pale yellow needles, m. p. 101—102·5° (Found : C, 56·2; H, 8·6; S, 23·5; N, 3·6. $C_{38}H_{68}O_4N_2S_6$ requires C, 56·4; H, 8·5; S, 23·8; N, 3·5%).

The same thiocyanato-undecanoylthiodecane (0·5 g.) with ice-cold 96% sulphuric acid (5 ml.) gave the *dicarbamoylthio-ester* (0·4 g.), m. p. 113—114·5° (from ethanol) (Found : C, 58·5; H, 9·1; S, 18·8; N, 3·7. $C_{34}H_{64}O_4N_2S_4$ requires C, 58·9; H, 9·3; S, 18·5; N, 4·0%).

Decamethylene Di-(11-*mercaptoundecanethiolate*).—The 11-bromoundecanethiolate (3·3 g.) and thiourea (0·72 g.) in ethanol formed the dithiuronium bromide solution, which with sodium hydroxide (0·37 g.) in alcohol under nitrogen gave the *mercapto-ester* (1·4 g.) which crystallised from ether–ethanol in white plates, m. p. 105—107° (Found : C, 63·2; H, 10·2; S, 21·5. $C_{32}H_{62}O_2S_4$ requires C, 63·3; H, 10·3; S, 21·1%).

Picrate of Decamethylene Di-[11-(*amidinothio*)*undecanethiolate*]—The thiuronium bromide solution obtained as above was treated with alcoholic picric acid, to give the *dipicrate*, yellow needles, m. p. 134—135·5° (from ethanol–light petroleum) (Found : C, 47·9; H, 6·3; S, 10·4; N, 11·9. $C_{46}H_{72}O_{16}N_{10}S_4$ requires C, 48·1; H, 6·3; S, 11·2; N, 12·2%).

Glycerol Tri-(11-*bromoundecanoate*).—11-Bromoundecanoyl chloride (9·5 g.), anhydrous glycerol (1·02 g.), and freshly distilled quinoline (4·32 g.) in dry ether (100 ml.) were kept at room temperature for 6 days. Hydrogen chloride was passed into the solution to precipitate unchanged quinoline. The mixture was filtered and the brownish filtrate was warmed under reflux with charcoal for 30 min., then filtered and evaporated. The light-grey residue, recrystallised five times from light petroleum, gave white plates of the *tribromo-compound* (4·4 g.), m. p. 50—50·5° (Found : C, 51·8; H, 7·7; Br, 28·3. $C_{36}H_{65}O_6Br_3$ requires C, 51·9; H, 7·9; Br, 28·8%).

Glycerol Tri-(11-*mercaptoundecanoate*).—Glycerol tri-(11-bromoundecanoate) (0·4 g.) and thiourea (0·11 g.) were heated in ethanol (6 ml.) for 6 hr. The thiuronium bromide solution was heated with sodium hydroxide (0·05 g.) in alcohol under nitrogen for a further 2 hr. Water (5 ml.) was added and the solution was reduced to *ca.* 3 ml. by distillation. The residue was extracted with ether, and the solid extract (0·14 g.) recrystallised from acetone–light petroleum, to give the *trimercapto-compound*, m. p. 67—68·5 (Found : C, 62·8; H, 9·8. $C_{36}H_{68}O_6S_3$ requires C, 62·4; H, 9·9%).

Tripicrate of Glycerol Tri-(11-*amidinothioundecanoate*).—The thiuronium bromide solution obtained as above was treated with alcoholic picric acid solution, to give the *tripicrate*, yellow needles, m. p. 165—167° (sinter at 160°) (from ethanol–chloroform) (Found : C, 45·2; H, 5·6; S, 6·4; N, 13·4. $C_{57}H_{83}O_{27}N_{15}S_3$ requires C, 45·4; H, 5·6; S, 6·4; N, 13·9%).

Glycerol Tri-(11-*dodecylthioundecanoate*).—Dodecanethiol (0·15 g.) was heated under reflux with sodium hydroxide (0·3 g.) in alcohol for 15 min. An alcoholic solution of glycerol tri-(11-bromoundecanoate) (0·2 g.) was added and the mixture heated under reflux for a further 2 hr. Water (5 ml.) was added and the solution reduced to a small volume. The *triglyceride* (0·13 g.) was then isolated by ether-extraction; recrystallised from light petroleum it had m. p. 64—65° (Found : C, 71·9; H, 11·7; S, 7·7. $C_{72}H_{140}O_6S_3$ requires C, 72·2; H, 11·8; S, 8·0%).

Glycerol Tri-[11-*ethoxy*(*thiocarbonyl*)*thioundecanoate*].—Glycerol tri-(11-bromoundecanoate) (1·67 g.) and potassium ethyl xanthate (0·98 g.) in hot ethanol gave the *triglyceride* (0·63 g.), m. p. 44—45° (from ethanol) (Found : C, 56·3; H, 8·5; S, 19·7. $C_{45}H_{80}O_9S_6$ requires C, 56·4; H, 8·4; S, 20·1%).

Glycerol Tri-[11-*octadecyloxy*(*thiocarbonyl*)*thioundecanoate*].—Glycerol tri-(11-bromoundecanoate) (0·21 g.) and potassium octadecyl xanthate (0·29 g.) likewise gave the *triglyceride* (0·26 g.), m. p. 65·5—66·5° (from acetone) (Found : C, 68·2; H, 10·7; S, 11·5. $C_{93}H_{176}O_9S_6$ requires C, 68·5; H, 10·9; S, 11·8%).

Glycerol Tri-(11-*selenocyanatoundecanoate*), m. p. 50—50·5° [from light petroleum–ether (10 : 1)] (Found : C, 51·4; H, 7·1; N, 4·3. $C_{39}H_{65}O_6N_3Se_3$ requires C, 51·5; H, 7·2; N, 4·6%), and *tri-*(11-*thiocyanatoundecanoate*), m. p. 32—32·5° [from light petroleum–ether (4 : 1)] (Found : C, 59·9; H, 8·7; S, 12·5; N, 5·65. $C_{39}H_{65}O_6N_3S_3$ requires C, 60·9; H, 8·6; S, 12·5; N, 5·5%), were similarly prepared.

Glycerol Tri-[11-N-*acetyl*(*thiocarbamoyl*)*thioundecanoate*].—Glycerol tri-(11-thiocyanoundecanoate) (0·38 g.) was heated with an excess of thioacetic acid (0·5 ml.) for 3 hr. The excess of acid was removed under reduced pressure, and the pale yellow solid residue (0·4 g.) was recrystallised from ethanol–light petroleum, to give pale yellow needles of the *triglyceride*, m. p. 118—119° (Found : C, 54·5; H, 8·0; S, 18·9; N, 3·9. $C_{45}H_{77}O_9N_3S_6$ requires C, 54·2; H, 7·8; S, 19·3; N, 4·2%).

Glycerol Tri-(11-carbamoylthioundecanoate).—Glycerol tri-(11-thiocyanatoundecanoate) (0·2g.) with ice-cold 96% sulphuric acid (1 ml.) gave the ***triglyceride*** (0·15 g.) which crystallised from acetone–light petroleum, had m. p. 123—124° (Found: C, 56·7; H, 8·5; S, 11·9; N, 4·8. $C_{39}H_{71}O_9N_3S_3$ requires C, 57·0; H, 8·7; S, 11·7; N, 5·1%).

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