27. *Promoters for the Dropwise Condensation of Steam. Part I. Preparation of Compounds containing Monofunctional Sulphur Groups.*

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A number of compounds in which a hydrocarbon chain is attached to a single sulphur- or selenium-containing group have been prepared, for test as promoters of dropwise condensation of steam.

This paper begins a series describing the preparation of possible promoters for the dropwise condensation of steam on metal surfaces. The compounds now reported contain a hydrocarbon residue attached to a single sulphur- or selenium-containing group, namely, xanthates, thioxanthates, thiocyanates and derivatives, selenocyanates, thiolic esters, thiols, and sulphides. The underlying theory will be discussed in Part IV of this series.

Alkyl xanthates were prepared by alkylation of potassium ethyl xanthate, $EtO{\cdot}CS_2K$, and potassium octadecyl xanthate, themselves obtained by the action of carbon disulphide on a mixture of the corresponding alcohol and powdered potassium hydroxide. The salts were alkylated by slightly more than the equivalent amount of alkyl, or substituted alkyl, bromide in boiling ethanol.

Ethyl dodecyl trithiocarbonate, $C_{12}H_{25}{\cdot}S{\cdot}CS{\cdot}SEt$, was prepared by the action of dodecanethiol on ethyl chlorodithioformate,[1] $Cl{\cdot}CS_2Et$. Dodecyl chlorodithioformate and didodecyl trithiocarbonate were prepared by the action of dodecanethiol (1 and 2 mols. respectively) on thiocarbonyl chloride. Attempts to replace the chlorine in the chloro-compound by hydroxyl and thiol groups (to give free di- and tri-thio-acids) proved unsuccessful. Hydroxylation (*a*) in aqueous dioxan, and (*b*) in alkaline aqueous acetone yielded pale yellow solids whose analyses and m. p.s corresponded closely to those of didodecyl disulphide, which was possibly formed by oxidation of dodecanethiol formed as an intermediate by loss of carbonyl sulphide from the desired acid. Thiolation was attempted (*a*) by addition of the chloro-compound in dry ether to an ether suspension

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[1] Braun, *Ber.*, 1902, **35**, 3377.

of anhydrous sodium hydrogen sulphide, and (*b*) by passing dry hydrogen sulphide into a dry ether–pyridine solution of the compound: in both cases a red colour developed, but attempts to isolate the free acid or its barium salt were unsuccessful.

Unsuccessful attempts were also made to prepare the following compounds: (*a*) Dodecyl tridecanedithioate, $C_{12}H_{25}\cdot CS\cdot SC_{12}H_{25}$, by the action of dodecylmagnesium bromide on dodecyl chlorodithioformate. Although almost the theoretical amount of magnesium bromide chloride was formed, the only product isolated from the ether solution was a pale yellow solid (m. p. 62—63·5°) which contained only a trace of sulphur. This was probably formed from the intermediate desired dithio-ester by loss of carbon disulphide, but the analytical figures did not indicate $C_{24}H_{50}$. (*b*) Nonadecanedithioic acid by the action of carbon disulphide on octadecylmagnesium bromide. (*c*) Pentacosane-13-thione and heptatriacontane-19-thione by the action of the corresponding alkylmagnesium bromides on thiocarbonyl chloride in ether at room temperature. Although thioketones of low molecular weight react further with Grignard reagents, it was hoped that the presence of the long hydrocarbon chain would cause the Grignard reagents to react with the thiocarbonyl chloride. However, no thioketone was isolated. A second attempt to prepare pentacosane-13-thione, this time at —40°, gave only a polymeric product, possibly formed from the expected thione. These failures are consistent with the fact that no similar compounds of high molecular weight have been reported to date. In all preparations involving Grignard reagents, very intense colours (pink, red, or purple) were formed, possibly indicating free-radical intermediates.

Alkyl, and substituted alkyl, thiocyanates and selenocyanates were prepared from the corresponding bromides by treatment with potassium thiocyanate or selenocyanate in boiling ethanol. Alkyl *N*-acetyldithiocarbamates, $Ac\cdot NH\cdot CS_2R$, were prepared from the thiocyanates and refluxing thioacetic acid,[2] and were yellow high-melting solids which crystallised readily from ethanol. The corresponding selenium compounds could not be prepared. The thiocyanates were converted into thiolcarbamates, $NH_2\cdot CO\cdot SR$, by treatment with ice-cold concentrated sulphuric acid followed by acid hydrolysis.[3] The corresponding selenium compounds again could not be prepared.

Alkane- and substituted alkane-thiols were prepared by alkaline decomposition of the corresponding thiuronium bromides,[4] and were characterised qualitatively by precipitation as yellow lead mercaptides with alcoholic lead acetate.

Unsymmetrical sulphides were prepared by heating alcoholic solutions of the sodium alkyl sulphide and bromide.

Esters of thiolic acids were prepared by the action of acid chlorides on thiols, the rate of reaction and the yield being higher when no solvent was used.

EXPERIMENTAL

Potassium Octadecyl Xanthate.—Carbon disulphide (52 g.) was added slowly to a well-stirred, finely powdered, mixture of octadecanol (57 g.) and potassium hydroxide (11·2 g.). The resulting pale yellow paste was kept at room temperature for 15 hr., and the *xanthate* (73 g.) recrystallised several times from ethanol, forming very pale yellow plates, m. p. 206° (decomp.) (Found: C, 59·2; H, 9·7. $C_{19}H_{37}OS_2K$ requires C, 59·3; H, 9·7%).

S-*Ethyl* O-*Octadecyl Xanthate.* —Ethyl bromide (1·1 g.) and potassium octadecyl xanthate (3·8 g.) were heated under reflux in ethanol (20 ml.) for 2 hr. Water (5 ml.) was added and the solution evaporated to 10 ml. A further quantity (5 ml.) of water was added, and the *xanthate* was extracted with ether. The ether was removed and the product recrystallised three times from acetone–methanol, forming white plates, m. p. 38—39° (3·4 g.) (Found: C, 67·0; H, 11·3; S, 17·3. $C_{21}H_{42}OS_2$ requires C, 67·3; H, 11·3; S, 17·1%).

Similar reactions gave *dioctadecyl xanthate*, white plates (from acetone), m. p. 54·5° (Found: C, 74·1; H, 12·2. $C_{37}H_{74}OS_2$ requires C, 74·2; H, 12·5%), S-*benzyl* O-*octadecyl xanthate*, b. p.

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[2] Wheeler and Merriam, *J. Amer. Chem. Soc.*, 1901, **23**, 283.

[3] Schmidt and Kolleck-Bos, *ibid.*, 1953, **75**, 6067.

[4] *Org. Synth.*, 1941, **21**, 36.

160°/3 mm., f. p. *ca.* 20° (Found : C, 71·3; H, 10·0; S, 14·4. $C_{26}H_{44}OS_2$ requires C, 71·5; H, 10·2; S, 14·7%), and *O-ethyl S-octadecyl xanthate*, white plates (from ethanol), m. p. 41·5—42° (Found : C, 67·4; H, 11·3. $C_{21}H_{42}OS_2$ requires C, 67·3; H, 11·3%).

Ethyl Chlorodithioformate.—Thiocarbonyl chloride (12·5 g.) was added dropwise during 12 hr. to ethanethiol (6·75 g.) in carbon disulphide (40 ml.). The mixture was kept at room temperature, in the absence of moisture, for 6 days. The product (7·6 g.) was isolated by fractional distillation as a yellow-orange liquid, b. p. 90°/34 mm. Diethyl trithiocarbonate (3·4 g.), b. p. 110°/34 mm., was also obtained.

Similarly was obtained *dodecyl chlorodithioformate*, b. p. 176—178°/1·5 mm., n_D^{20} 1·5196 (Found : C, 55·4; H, 8·9; S, 22·4. $C_{13}H_{25}S_2Cl$ requires C, 55·6; H, 9·0; S, 22·8%).

Ethyl Dodecyl Trithiocarbonate.—Dodecanethiol (5·0 g.) and ethyl dithiochloroformate (3·5 g.) in carbon disulphide (20 ml.) were kept at room temperature, in the absence of moisture, for 6 days. The *trithiocarbonate* was isolated by distillation as a light-orange oily liquid, b. p. b. p. 116—118°/4 mm., n_D^{20} 1·4872 (Found : C, 58·9; H, 10·0. $C_{15}H_{30}S_3$ requires C, 58·8; H, 9·9%).

Didodecyl trithiocarbonate.—Dodecanethiol (8·1 g.) and thiocarbonyl chloride (2·3 g.) in carbon disulphide (20 ml.) were kept at room temperature, in the absence of moisture, for 6 days. The solvent was removed on a steam-bath, and the solid residue crystallised from ethanol in pale yellow plates (7·1 g.), m. p. 51—52·5° (lit.,[5] 49·5—50°) (Found : C, 67·1; H, 11·4; S, 22·0. Calc. for $C_{25}H_{50}S_3$: C, 67·2; H, 11·3%; S, 21·5).

Octadecyl Thiocyanate.—Octadecyl bromide (16·7 g.) and potassium thiocyanate (5·3 g.) were heated under reflux in ethanol (80 ml.) for 3 hr. Water (20 ml.) was added and the alcohol removed under reduced pressure. The residual solution was extracted with ether, and the product (13·5 g.) isolated by fractional distillation as a colourless oil, b. p. 120°/0·9 mm., f. p. *ca.* 25° (lit., 23°) (Found : C, 73·1; H, 11·8; N, 4·8. Calc. for $C_{19}H_{37}NS$: C, 73·4; H, 12·0; N, 17·5%).

Octadecyl Selenocyanate.—Octadecyl bromide (16·7 g.) and potassium selenocyanate (8·5 g.) in hot ethanol (80 ml.) gave the *selenocyanate* (15 g.) which crystallised from ether in pale yellow-green plates, m. p. 59·5—60° (Found : C, 63·5; H, 10·3; N, 4·1. $C_{19}H_{37}NSe$ requires C, 63·7; H, 10·4; N, 3·9%).

Octadecyl Acetyldithiocarbamate.—Octadecyl thiocyanate (3·1 g.) was heated under reflux for 3 hr. with an excess of thioacetic acid (4 ml.). The excess of acid was removed under reduced pressure, and the pale yellow residual ester (3·6 g.) recrystallised from ethanol as pale yellow needles, m. p. 95—96° (Found : C, 65·0; H, 10·7; S, 16·2; N, 3·7. $C_{21}H_{41}ONS_2$ requires C, 65·0; H, 10·7; S, 16·6; N, 3·6%).

Octadecyl Thiolcarbamate.—Octadecyl thiocyanate (1 g.) was dried over phosphoric oxide in a vacuum for 24 hr., then treated with ice-cold 96% sulphuric acid (5 ml.). The mixture was stirred to a homogeneous paste and placed in an ice-box for 24 hr. Chips of ice were added and the mixture allowed slowly to attain room temperature. Ice-cold aqueous acetone (40%; 10 ml.) was added with stirring and the white solid collected at the pump. This was washed well with aqueous acetone (10%) and recrystallised from acetone to give the *thiolcarbamate* (0·8 g.) as a white microcrystalline powder, m. p. 111—112° (Found : C, 69·0; H, 11·8; S, 9·5; N, 4·5. $C_{19}H_{39}ONS$ requires C, 69·2; H, 11·9; S, 9·7; N, 4·2%).

Octadecanethiol.—This compound was prepared by the general method of Frank and Smith[4] as a white waxy solid, b. p. 145—148°/1 mm., m. p. 55—56° (lit., 55·5—56°).

Octadecylthiuronium Picrate.—Octadecylthiuronium bromide solution was heated under reflux for 10 min. with alcoholic picric acid. The solution was cooled in an ice-box for 1 hr. The yellow solid was collected at the pump and washed with ice-cold ethanol (3 × 2 ml.) followed by light petroleum. The *picrate* recrystallised from ethanol as yellow needles, m. p. 124·5—125° (Found: C, 53·6; H, 7·8; S, 5·6; N, 11·8. $C_{25}H_{43}O_7N_5S$ requires C, 53·8; H, 7·8; S, 5·8; N, 12·6%).

Octadecylthiododecane.—Dodecanethiol (2·95 g.) was heated under reflux for 15 min. with sodium hydroxide (0·6 g.) in alcohol. Octadecyl bromide (4·93 g.) in ethanol was added, and the mixture heated under reflux for a further 2 hr., then kept at 0° for 2 hr. The *sulphide* (6·5 g.) was collected and recrystallised from ethanol as white plates, m. p. 53·5° (Found : C, 76·3; H, 13·7; S, 7·1. $C_{30}H_{62}S$ requires C, 76·2; H, 13·8; S, 7·0%).

Dodecyl Octadecanethiolate.—Octadecanoyl chloride (3·0 g.) was liquefied (*ca.* 30°), treated with

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[5] Stevens, Frank, Drake, and Smith, *J. Polymer Sci.*, 1948, **3**, 50.

dodecanethiol (2·0 g.), and kept at room temperature until hydrogen chloride was no longer evolved (2 hr.). The white solid product was then warmed at 60° for 1 hr., cooled to 40°, treated with light petroleum (20 ml.), and placed at 0° for 1 hr. The *ester* (4·3 g.) was collected and recrystallised from acetone as white plates, m. p. 53·5° (Found : C, 76·6; H, 12·7; S, 7·0. $C_{30}H_{60}OS$ requires C, 76·8; H, 12·9; S, 6·8%).

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