

CXXXI.—*Applications of Thallium Compounds in Organic Chemistry. Part III. Alkylations.*

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THE preparation of alkyl derivatives by heating organic thallos compounds with alkyl iodides, suggested by the resemblance between thallos and silver halides, proceeds smoothly if the thallos compound is soluble in the alkylating agent, or if, being of an amorphous nature, it presents to it a large surface, whilst sparingly soluble, well-crystallised substances enter into the reaction slowly, if at all.

Thallos palmitate, for instance, which is appreciably soluble in methyl iodide, is completely converted into methyl palmitate by boiling with this solvent for 4 hours. Again the thallos salt of ethyl acetoacetate, readily soluble in cold ethyl iodide, requires 3 hours for ethylation, and the amorphous yellow *trithallium methylglucoside*, insoluble in methyl iodide, gives, after treatment for 5 hours, a trimethyl methylglucoside in good yield. On the other hand, treatment of the well-crystallised, sparingly soluble tetrathallium tartrate with boiling methyl iodide for 100 hours gives an incompletely methylated product, whilst an attempt to methylate the thallos salt of *o*-nitrophenol had to be discontinued. The preparation of trimethyl methylglucoside from trithallium methylglucoside is interesting in view of McKenzie's suggestion (*J.*, 1899, **75**, 765) that the most plausible explanation of methylation by Purdie's silver oxide method is that an intermediate unstable silver derivative is formed which subsequently undergoes double decomposition with the alkyl halides (see also Lander, *J.*, 1900, **77**, 747; 1903, **83**, 416).

The rotations observed both in this case and in that of the product of methylation of tetrathallium tartrate indicate that at any rate in these instances racemisation does not occur.

## E X P E R I M E N T A L.

Treatment of their thallos salts with alkyl iodides affords a useful means of preparing small quantities of the esters of higher fatty acids. Thus from 0.47 g. and 0.55 g. of thallos stearate, 0.18 g. (m. p.  $38.5^{\circ}$ ; yield 62%) and 0.26 g. (m. p.  $37.5^{\circ}$ ; yield 79%) of methyl stearate were obtained, respectively, after refluxing for 4 hours with methyl iodide, and recovery of excess of this solvent, by extracting the resulting mixture of methyl stearate and thallos iodide with ether (Found in the latter sample: C, 76.4; H, 12.9. Calc., C, 76.4; H, 12.8%). By using larger quantities of material and benzene as solvent, almost theoretical yields may be obtained, thus 3.24 g. (theory, 3.26 g.) of methyl stearate (m. p.  $38.5^{\circ}$ ) were produced by boiling 5.33 g. of thallos stearate with methyl iodide in benzene, a quantitative yield of thallos iodide also resulting.

The smaller-scale preparations, however, illustrate a convenient technique when small quantities of the higher fatty acids are under examination, it being easy to obtain from less than 1 g. of the acid its titration value, and its ethyl or methyl ester pure and in quantity sufficient for analysis and determination of melting point. Thus 0.579 g. and 0.557 g. of palmitic acid dissolved in alcohol required respectively 7.5 c.c. and 7.0 c.c. of 0.307*N*-aqueous thallos hydroxide (calc., 7.35 c.c. and 7.0 c.c.). On evaporation of the solution resulting from the former titration and treatment of the residual dry thallos palmitate with boiling methyl iodide, 0.4 g. of methyl palmitate was obtained (yield 66%; m. p. after recrystallisation from methyl alcohol  $29.5^{\circ}$ . Found: C, 75.4; H, 13.0. Calc., C, 75.5; H, 12.7%). Evaporation to dryness before treatment with methyl iodide is essential, as, on addition of methyl iodide to the solution resulting from the second titration and boiling under reflux as before, a product was obtained which had an acid reaction and a high melting point ( $31.5^{\circ}$ ).

By using propyl iodide, 2 g. of *propyl palmitate* were obtained from 5 g. of thallos palmitate by boiling for 1 hour (yield 63%; m. p.  $15.3$ — $15.4^{\circ}$ , b. p.  $209^{\circ}/22$  mm. Found: C, 76.5; H, 12.95.  $C_{19}H_{38}O_2$  requires C, 76.4; H, 12.8%). The low yield was due to loss in manipulation.

*Ethylation of Ethyl Acetoacetate.*—A boiling solution of 23.4 g. of thallos ethyl acetoacetate (Christie and Menzies, J., 1925, 127, 2372) in ethyl iodide rapidly deposited thallos iodide as a brick-red powder which became yellow after 2 hours. After boiling for a further hour, it was filtered off from the cooled mixture (yield, 21.8 g.; calc., 23.3 g.). On fractionation, 8.6 g. of ethyl ethyl-acetoacetate (yield 77.5%) distilled between  $192^{\circ}$  and  $195^{\circ}$  (uncorr.)/

756 mm. (Found: C, 60.7; H, 9.0. Calc., C, 60.7; H, 8.9%.  $D_{15}^{15}$  0.9924,  $n_D^{15}$  1.4237.  $R_D$ , 40.72. Calc. for keto-form, 40.98, for enol-form, 41.92; and for the isomeric ethyl  $\beta$ -ethoxycrotonate, 42.08. Compare Lander, *loc. cit.*, p. 738).

*Trithallium methylglucoside* may be obtained in good yield as a yellow, amorphous powder by adding methylglucoside dissolved in a little water to a hot concentrated solution of thallos hydroxide. If 4 equivalents of the latter be used to each molecular equivalent of methylglucoside, the thallium content of the product approximates closely to that required for trithallium methylglucoside (Found as iodide: Tl, 76.4, 76.15.  $C_7H_{11}O_6Tl_3$  requires Tl, 76.2%). The trithallium methylglucoside used for the methylation described below was prepared from 21.6 g. of  $\alpha$ -methylglucoside (m. p. 165.5°;  $[\alpha]_D + 158.8^\circ$  for a 5.2% solution in water) in 13 c.c. of water and 206 c.c. of 1.62*N*-thallos hydroxide (3 equivs.), which immediately before the addition of the methylglucoside was concentrated by boiling to about half-bulk; 76.8 g. (yield 85%) separated at once (Found as iodide: Tl, 73.8%). 36.5 G. of this product were boiled with methyl iodide for 5 hours; the reaction was then complete. The excess of methyl iodide was removed, and the residue extracted with methyl alcohol; 9.8 g. of syrup (dried in a vacuum at 100°) were obtained, the theoretical yield calculated for trimethyl methylglucoside being 10.7 g. On distillation three fractions were obtained: (1) 2.25 g., b. p. 137°/2.2 mm.; (2) 4.35 g., b. p. 136.6°/2.3 mm. to 137.2°/1.5 mm.; (3) 1 g., b. p. 140°/2.5 mm. to 164°/1.8 mm. The optical and analytical data are in the following table:

$n_D$ .	$[\alpha]_D$ in water.	$[\alpha]_D$ * in ethyl alcohol.	C %.	H %.	OMe %.
(1) 1.4569	164° (1.6%)	165.9° (0.8%)	50.4	8.65	50.4
(2) 1.4592	153.1° (1.2%)	154.6° (1.2%)	50.9	8.5	49.0
(3) 1.464					46.0
	Calc. for trimethyl methylglucoside:		50.8	8.5	52.5

\* Compare Purdie and Bridgett, J., 1903, **83**, 1037, and Haworth, J., 1915, **107**, 13.

*Attempted Preparation of Methyl Dimethoxysuccinate.*—From 75 g. of tetrathallium tartrate, boiled under reflux with methyl iodide for approximately 100 hours, 12.5 g. of a syrup were obtained, which distilled as a homogeneous liquid, b. p. 146°/25 mm. to 146.1°/23 mm.,  $n_D$  1.4363,  $[\alpha]_D$  72.17° (Found: OMe, 50.8, 51.6. Calc. for four methoxy-groups, OMe, 60.2%; for three methoxy-groups, OMe, 48.4%). The syrup did not solidify and a nucleus of methyl dimethoxysuccinate, kindly supplied by Professor Haworth, was dissolved.

*Preparation of o-Methoxybenzaldehyde.*—From 20.2 g. of thallos

salicylaldehyde, refluxed for 50 hours with methyl iodide in benzene, after removal of unchanged thallium salicylaldehyde by agitation with aqueous sodium hydroxide and subsequent distillation in steam, 5.2 g. of *o*-methoxybenzaldehyde, m. p. 36.3° (yield 62%) were obtained (Found: OMe, 21.0. Calc., OMe, 22.8%) (compare Irvine, J., 1901, **79**, 668).

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