

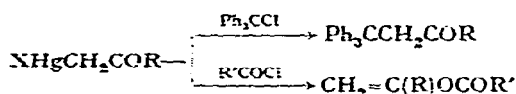
THE SYNTHESIS AND THE REARRANGEMENT OF *O*-SILYL-*O*-ALKYL KETENEACETALS INTO ESTERS OF SILYLACETIC ACID

I. F. LUTSENKO, Yu. I. BAUKOV, G. S. BURLACHENKO AND B. N. KHASAPOV

Chemistry Department, Moscow State University "M. V. Lomonosov", Moscow (USSR)

(Received April 13th, 1965)

In recent years the study of the chemical behaviour of aldehydes, ketones and esters of carboxylic acids in which the α -hydrogen atom is replaced by an atom of Hg, Sn, Ge, P, etc. has been carried out by Nesmeyanov and one of us. The first investigation of α -mercurated carbonyl compounds had already shown that reciprocal action of a Hg atom and a carbonyl group (σ, π -conjugation) resulted in a decrease in the stability of the Hg-C bond and dual reactivity without tautomerism¹.

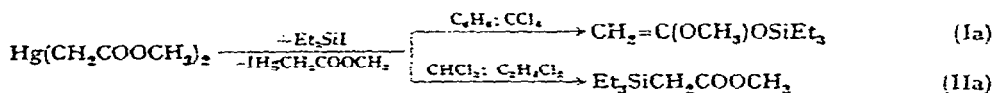


In the first case the metal atom is substituted. In the second case the acylating reaction proceeds with transfer of the reaction center (Nesmeyanov) resulting in a vinyl ester only. A further study of functionally substituted organotin and organomercury compounds showed that esters of α -metalated carboxylic acids also showed dual reactivity^{2,3}.

This work reports the results of an investigation on the reaction of halosilanes with esters of α -metalated carboxylic acids, and the conditions of the rearrangement of *O*-silyl-*O*-alkylketeneacetals (I) into esters of silylacetic acid (II).

By the interaction of trialkylsilylanes with esters of α -metalated carboxylic acids, (I) or (II) (the reactions with and without transfer of reaction centre) may be obtained by adjusting the structure of the original reactants and the conditions of the reaction*.

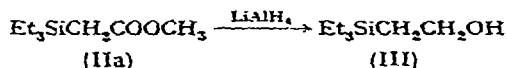
Thus, as a result of the action of triethylsilyl iodide on bis(carbomethoxymethyl)-mercury in dichloroethane or chloroform, methyl(triethylsilyl) acetate (IIa) is obtained with a yield of 60%. Using solvents with less ionizing capacity (e.g., benzene, carbon tetrachloride) we obtained the *O*-derivative (Ia)** in 50% yield.



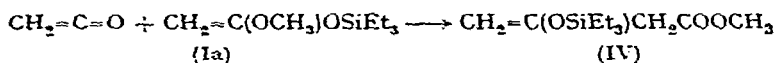
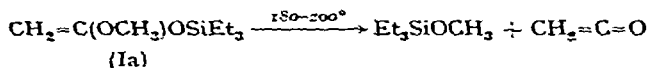
* Organosilicon esters having the ester group on the α -carbon atom have been synthesized previously by different methods⁴⁻¹². Only a few examples of the *O*-silyl-*O*-alkylketeneacetals have been described more recently by some authors^{12,13} and by us^{2,14} and their properties are not very well defined.

** The reaction of Et_3SiI and $\text{Pr}_3\text{SnCH}_2\text{COOCH}_3$ also leads to (Ia), as reported in our previous paper¹⁴.

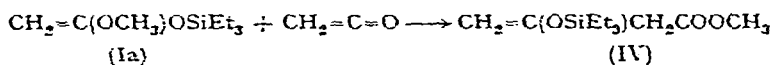
The compounds (Ia) and (IIa) differ appreciably in their physical and chemical properties, e.g., (Ia) is easily hydrolysed with water to give methyl acetate and triethylsilanol but (IIa) is unchanged under similar conditions; the reduction of (Ia) with LiAlH_4 leads to triethylsilane, while (IIa) gives the appropriate alcohol.



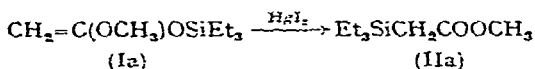
(IIa) may be distilled at atmospheric pressure. On heating (Ia) at 180–200° methyl 3-(triethylsiloxy)-3-butenolate (IV) and triethylmethoxysilane are obtained. The reaction can be explained as follows:



The structure of (IV) is deduced from the infrared and NMR absorption spectra and the reaction scheme confirmed by interaction between (Ia) and ketene. The latter reaction is exothermic, yielding 90% of (IV).



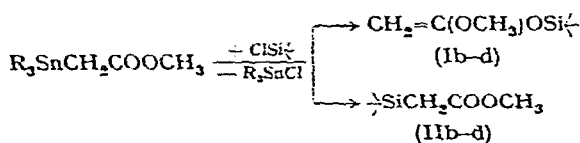
Different behaviour may be observed when (Ia) is heated gently in the presence of a small amount of HgI_2 when the isomerisation of (Ia) to (IIa) occurs as follows:



This rearrangement is apparent from the change in physical constants and spectral data and the reduction of the original and final products of the reaction, respectively.

The rearrangement takes place under such mild conditions that in any cases of dual reactivity it must be assumed that the reaction products isolated are not necessarily the initial reaction products. We confirmed that this was the case by studying the reaction of methyl (trialkylstannyl)acetates with some halosilanes: SiCl_4 (b), MeSiCl_3 (c), Me_2SiCl_2 (d).

O- Or *C*-derivatives may be isolated by this reaction by adjusting the temperature and the duration of the reaction.



The reaction was checked by infrared spectra. On adding organotin compounds to chlorosilane the absorption at $1710\text{--}1714\text{ cm}^{-1}$ ($\text{R}_3\text{SnCH}_2\text{COOCH}_3$) disappears and a $\text{C}=\text{C}$ stretching vibration at $1650\text{--}1680\text{ cm}^{-1}$ appears; this corresponds to the formation of (Ib-d), which may be isolated with a yield of about 70%. If, however, the reaction mixture is heated at $80\text{--}90^\circ$ for some hours without isolating (Ib-d), the $\text{C}=\text{C}$ stretching vibration disappears and simultaneously an intensive absorption band at $1740\text{--}1750\text{ cm}^{-1}$ appears, corresponding to the $\text{C}=\text{O}$ stretching vibration of

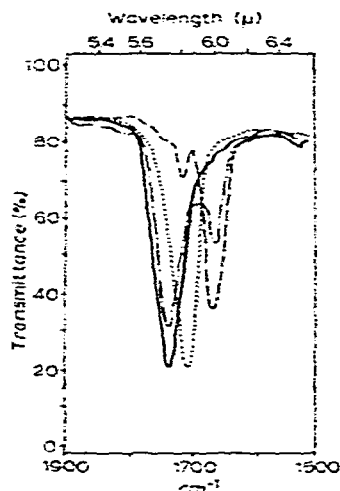
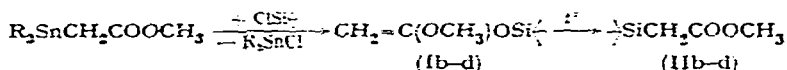
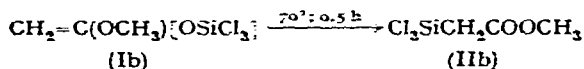


Fig. 1. ·····, IR spectrum of organotin ester; ----, IR spectrum of the reaction mixture after addition of organotin ester to SiCl_4 ; - - - -, IR spectrum of the reaction mixture after heating at 40° for 0.5 h; ———, IR spectrum of the reaction mixture after heating at 40° for 2 h.

organosilicon esters (Fig. 1) and (IIb-d) may be isolated with a yield of about 60%. This reaction may be represented by the following scheme:



It was possible by studying the isomerisation conditions to establish that the more Cl atoms were attached to the Si atom, the easier the thermal rearrangement of the *O*-derivative. (Ib) can, therefore, be isomerised slowly to (IIb) at room temperature and in 0.5 h by heating at 70° .



This extremely easy Si-O fission may be due to the presence of three electro-negative Cl atoms at the Si atom. The replacement of the Cl atoms by alkyl groups decreases the isomerisation capacity of *O*-derivatives. If one atom of chlorine is replaced by methyl [in (Ic)] the time required for isomerisation is increased to 5 h at 90° , and to 12 h by the replacement of two Cl atoms by methyl [(Id)]. When all the

Cl atoms are replaced by ethyl, the thermal isomerisation is repressed completely but the thermal decomposition of (Ia) occurs, as already described.

The structure of all the newly-prepared substances were proved by IR and ^1H NMR spectra. In the IR spectra of (IIa-d) intensive absorption bands were detected at 1720–1750 cm^{-1} corresponding to the valency oscillations of an ester group. In the spectra of (Ia-d)* a C=C stretching vibration was detected at 1650–1680 cm^{-1} . Figures 2 and 3 show the IR spectra of (IIa) and (IIb) and their *O*-derivatives. The infrared absorption spectrum of (IV) (Fig. 4) shows a C=C stretching vibration at 1654 cm^{-1} and a C=O stretching vibration at 1744 cm^{-1} compared with those at 1628 and 1714 cm^{-1} , respectively, of siloxycrotonate prepared according Gilman and

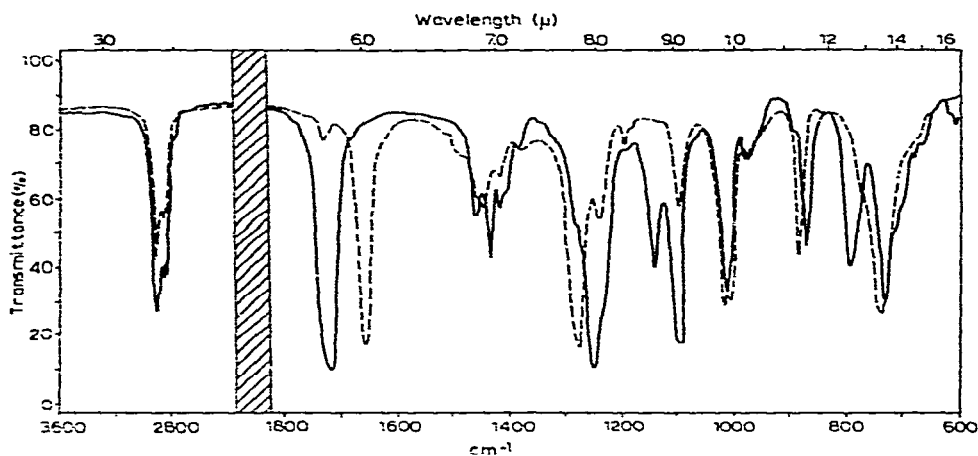


Fig. 2. —, IR spectrum of methyl (triethylsilyl)acetate; ----, IR spectrum of *O*-(triethylsilyl)-*O*-methylketeneacetal.

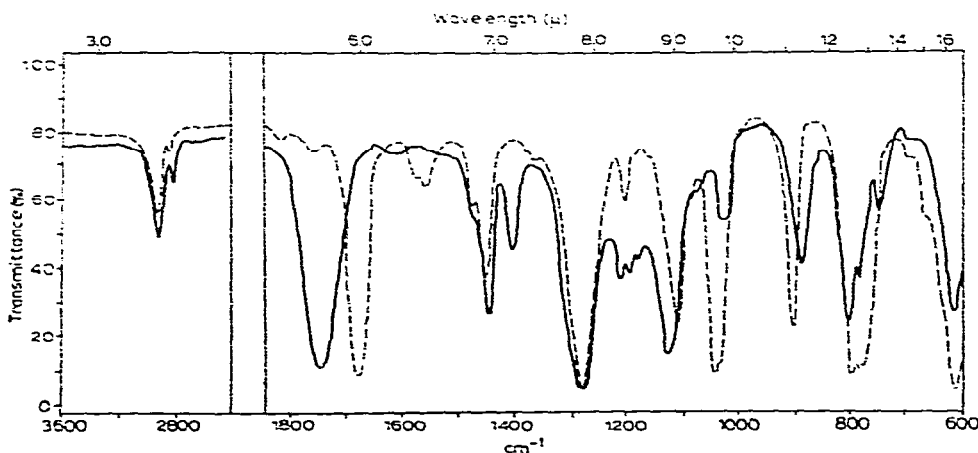


Fig. 3. —, IR spectrum of methyl (trichlorosilyl)acetate; ----, IR spectrum of *O*-(trichlorosilyl)-*O*-methylketeneacetal.

* IR spectra of (Ib-d) show a very small admixture of (IIb-d).

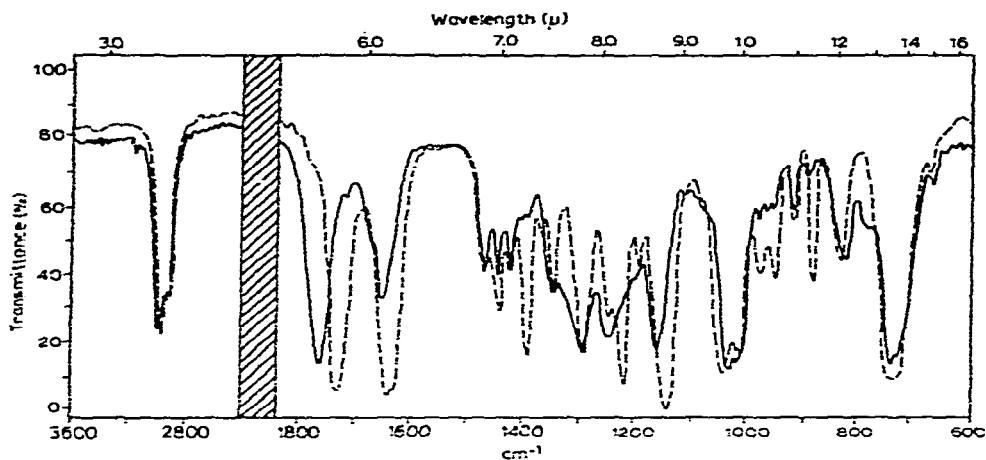


Fig. 4. ———, IR spectrum of methyl 3-(triethylsiloxy)-3-butenoate; - - - - -, IR spectrum of methyl 3-(triethylsiloxy)crotonate.

Clark¹⁵. Investigation of the ¹H NMR spectra of all the compounds prepared gave similar results. The chemical shifts of the Si-CH₂ group in (IIa-d) and the terminal =CH₂ group (a typical AB pattern), together with the values of the coupling constant *J* in (Ia-d) and data for (IV) are listed in Table I.

TABLE I
CHEMICAL SHIFTS (in ppm) AND *J* VALUES

	=CH ₂		δ(-CH ₂ -)		δ(Si-CH ₂ -)
	<i>J</i> _{AB}	δA	δB		
CH ₂ =C(OCH ₃)OSiEt ₃	2.6	2.94	3.09		Et ₃ SiCH ₂ COOCH ₃ 1.82
CH ₂ =C(OCH ₃)OSiCl ₂		ca. 3.20-3.60*			Cl ₃ SiCH ₂ COOCH ₃ 2.77
CH ₂ =C(OCH ₃)OSi(CH ₃)Cl ₂		ca. 3.20-3.50*			Cl ₂ (CH ₃)SiCH ₂ COOCH ₃ 2.45
CH ₂ =C(OCH ₃)OSi(CH ₃) ₂ Cl	2.6	3.22	3.32		Cl(CH ₃) ₂ SiCH ₂ COOCH ₃ 2.16
CH ₂ =C(OSiEt ₃)CH ₂ COOCH ₃		4.2	4.2	3.2	

* Together with -OCH₃ group.

EXPERIMENTAL

The starting materials: bis(carbomethoxymethyl)mercury, methyl (trialkylstannyl)acetates and triethyliodosilane were prepared according to reported procedures^{16,17}. Freshly distilled commercial halosilanes were used without additional purification. The IR spectra were obtained with thin films using a spectrometer "Jasko", IR-S(KCl). The NMR spectra were taken in carbon tetrachloride solution with tetramethylsilane as internal reference with a spectrograph CLA-40 constructed by Lubimov.

I. Reaction of triethyliodosilane with bis(carbomethoxymethyl)mercury

(a) In benzene; O-derivative, CH₂=C(OCH₃)OSiEt₃ (Ia). A mixture of 43.5 g (0.18 mole) of triethyliodosilane and 30 ml of benzene was added dropwise with

stirring, at room temperature, to 69.3 g (0.2 mole) of bis(carbomethoxymethyl)mercury dissolved in 300 ml of benzene. The reaction mixture was treated with 500 ml of petroleum ether and cooled to -30° . An insoluble material was separated by filtration. Recrystallisation from benzene gave 72 g (90%) of iodo(carbomethoxymethyl)mercury, m.p. $107-108^{\circ}$. (Found: C, 8.99; H, 1.41; Hg, 49.95. $C_3H_5HgIO_2$ calcd.: C, 8.99; H, 1.26; Hg, 50.08%.) The organic layer after removal of the solvent was distilled. The yield of (Ia) was 17.7 g (53%), b.p. $65-66.5^{\circ}$ (7 mm), n_D^{20} 1.4355, d_4^{20} 0.8870; MR_D 55.45, calcd. 55.56. (Found: C, 57.24; H, 10.80; Si, 15.13. $C_9H_{20}SiO_2$ calcd.: C, 57.40; H, 10.71; Si, 14.90%.)

(b) *In dichloroethane; C-derivative, Et₃SiCH₂COOCH₃ (IIa)*. A mixture of 14.6 g (0.06 mole) of triethylsilylchloride and 10 ml of dichloroethane was added with stirring at room temperature, to 22.8 g (0.066 mole) of bis(carbomethoxymethyl)mercury dissolved in 50 ml of dichloroethane. Treatment of the reaction mixture as in (Ia) gave 6.8 g (60%) of (IIa), b.p. $75-77^{\circ}$ (7 mm), n_D^{20} 1.4399, d_4^{20} 0.9019; MR_D 55.02, calcd. 55.18. (Found: C, 57.50; H, 10.94; Si, 15.30. $C_9H_{20}SiO_2$ calcd.: C, 57.40; H, 10.71; Si, 14.90%.)

2. Reduction of *O*- and *C*-derivatives with lithium aluminium hydride

(a) *Reduction of (Ia)*. An ethereal solution of 9.5 g (0.05 mole) of (Ia) was added to 3 g (0.08 mole) of $LiAlH_4$ in ether. The reaction mixture was stirred for 30 min at room temperature, refluxed for 30 min, hydrolyzed with moist ether and then with water. The ether layer was separated, treated in the usual manner and distilled. The yield of triethylsilyl ether was 4.1 g (71%), b.p. $106-110^{\circ}$ (760 mm), n_D^{20} 1.4123, d_4^{20} 0.7325; MR_D 39.51, calcd. 39.76. The literature values¹⁸ were: b.p. 109° (760 mm), n_D^{20} 1.4119, d_4^{20} 0.7318.

(b) *Reduction of IIa; (2-hydroxyethyl)triethylsilyl ether, Et₃SiCH₂CH₂OH (III)*. This reduction was carried out essentially in the same manner as in (2a): 7.1 g (0.038 mole) of (IIa), and 1.44 (0.038 mole) of $LiAlH_4$, gave 4.5 g (74%) of (III), b.p. $92-94^{\circ}$ (8.5 mm), n_D^{20} 1.4510, d_4^{20} 0.8623; MR_D 50.04, calcd. 50.31. (Found: C, 59.98; H, 12.44; Si, 18.16. $C_8H_{20}SiO$ calcd.: C, 59.94; H, 12.58; Si, 17.93%.)

3. Hydrolysis of *O*- and *C*-derivatives with water

(a) *Hydrolysis of (Ia)*. (Ia) (5.2 g, 0.028 mole) and 5 g (0.28 mole) of water were distilled together. The organic layer produced was separated, dried with sodium sulphate and distilled. The products isolated were methyl acetate, 1.5 g (72%), b.p. $53-57^{\circ}$ (760 mm), n_D^{20} 1.3600, d_4^{20} 0.9243, and triethylsilyl ether, 3.1 g (84%), b.p. $148-150^{\circ}$ (760 mm), n_D^{20} 1.4300, d_4^{20} 0.8620; MR_D 39.63, calcd. 40.05. The literature values¹⁹ were: b.p. 77.5° (28 mm), n_D^{20} 1.4239, d_4^{20} 0.8638.

(b) *Hydrolysis of (IIa)*. IIa undergoes no change when boiled with water under the conditions of experiment 3a.

4. Reaction of silicon tetrachloride with methyl (tripropylstannyl)acetate

(a) **O*-(Trichlorosilyl)-*O*-methylketeneacetal, CH₂=C(OCH₃)OSiCl₃ (IIb)*. Methyl (tripropylstannyl)acetate (61 g, 0.19 mole) was added dropwise with intensive stirring to 42.5 g (0.25 mole) of silicon tetrachloride. The reaction mixture was stirred for 1 h at 40° after the addition. Fractionation yielded 25 g of silicon tetrachloride and 14.6 g of (Ib) (70% based on reacted silicon tetrachloride), b.p. $20-25^{\circ}$ (7 mm) n_D^{20} 1.4260,

d_4^{20} 1.3244; MR_D 40.47, calcd. 40.14. (Found: C, 17.40; H, 2.69. $C_3H_5Cl_3O_2Si$ calcd.: C, 17.36; H, 2.43 %.) In addition 5 g (24 %) of (IIb) was isolated, b.p. 54–56° (7 mm), n_D^{20} 1.4450 (see 4b).

(b) *Methyl (trichlorosilyl)acetate*, $Cl_3SiCH_2COOCH_3$ (IIb). Methyl tripropylstannylacetate (61 g, 0.19 mole) was added dropwise to 58 g (0.34 mole) of silicon tetrachloride. The reaction mixture was stirred for 1.5 h at 70° and 1 h at 90°. Fractionation yielded (after removing of excess silicon tetrachloride) 26.5 g of (IIb) (67 % of theoretical), b.p. 60–61° (10 mm), n_D^{20} 1.4425, d_4^{20} 1.3801; MR_D 39.82, calcd. 39.93. (Found: C, 17.72; H, 2.63; Si, 13.54; $C_3H_5Cl_3O_2Si$ calcd.: C, 17.36; H, 2.43; Si, 13.52 %.) Further fractionation gave 50 g (93 %) of tripropylchlorostannane, b.p. 120–122° (13 mm), n_D^{20} 1.4927. The literature values²⁰ were: b.p. 123° (13 mm), n_D^{20} 1.4910.

5. Reaction of methyltrichlorosilane with methyl (tributylstannyl)acetate

(a) *O-(methylchlorosilyl)-O-methylketeneacetal*, $CH_2=C(OCH_3)OSiMeCl_2$ (Ic). Methyl (tributylstannyl)acetate (77 g, 0.21 mole) was added dropwise with stirring at room temperature to 47.5 (0.32 mole) of methyltrichlorosilane. The reaction mixture was stirred for 2.5 h at 50°. Fractionation yielded (after removing of excess methyltrichlorosilane, 27 g) 14.1 g of (Ic) (55 % based on reacted methyltrichlorosilane), b.p. 39–40° (12 mm), n_D^{20} 1.4274, d_4^{20} 1.1823; MR_D 40.67, calcd. 40.58. (Found: C, 25.51; H, 4.41; Si, 14.43. $C_4H_9Cl_3O_2Si$ calcd.: C, 25.68; H, 4.31, Si, 15.00 %.) Further fractionation gave 3 g (12 %) of (IIc) (see 5b), b.p. 47.5–48° (12 mm), n_D^{20} 1.4362, d_4^{20} 1.2132.

(b) *Methyl (methylchlorosilyl)acetate*, $Cl_2MeSiCH_2COOCH_3$ (IIc). To 16.8 g (0.11 mole) of methyl trichlorosilane was added dropwise with constant stirring 27 g (0.074 mole) of methyl (tributylstannyl)acetate; the mixture was heated for 12 h at 80–90°. Fractionation yielded 7.7 g of (IIc) (56 % of theoretical), b.p. 46–47° (12 mm), n_D^{20} 1.4390, d_4^{20} 1.2158; MR_D 40.33, calcd. 40.36. (Found: C, 25.65; H, 4.50; Si, 15.02. $C_4H_9Cl_2O_2Si$ calcd.: C, 25.68; H, 4.31; Si, 15.00 %.)

6. Reaction of dimethyldichlorosilane with methyl trialkylstannylacetate

(a) *O-(dimethylchlorosilyl)-O-methylketeneacetal*; $CH_2=C(OCH_3)OSiMe_2Cl$ (Id). To 19.2 g (0.15 mole) of dimethyldichlorosilane was added dropwise with constant stirring 75.3 g (0.23 mole) of methyl (tripropylstannyl)acetate; the mixture was heated for 2 h at 90°. Fractionation yielded (Id), 17 g (68 % of theoretical), b.p. 46–47° (20 mm), n_D^{20} 1.4185, d_4^{20} 1.0382; MR_D 40.84; calcd. 41.01. (Found: C, 35.72; H, 6.72; Si, 17.18. $C_3H_{11}ClO_2Si$ calcd.: C, 36.03; H, 6.65; Si, 16.84 %.) Further fractionation gave 1 g (4 %) of (IIId) (see 6b), b.p. 63–64° (18 mm), n_D^{20} 1.4258, d_4^{20} 1.0483.

(b) *Methyl (dimethylchlorosilyl)acetate*, $ClMe_2SiCH_2COOCH_3$ (IIId). To 14.9 g (0.11 mole) of dimethyldichlorosilane was added dropwise 28.3 g (0.078 mole) of methyl (tributylstannyl)acetate, stirred for 16 h at 80–90°. Fractionation yielded 7.5 g of (IIId) (58 % of theoretical), b.p. 46–48° (8 mm) n_D^{20} 1.4290, d_4^{20} 1.0521; MR_D 40.80, calcd. 40.80. (Found: C, 35.77; H, 6.80; Si, 17.55. $C_3H_{11}ClO_2Si$ calcd.: C, 36.03; H, 6.65; Si, 16.84 %.) Further fractionation gave 24.5 g (96 %) of tributylchlorostannane, b.p. 129–130° (1 mm), n_D^{20} 1.4925. The literature values²¹ were: b.p. 145–147° (5 mm), n_D^{20} 1.4908.

7. *Thermal isomerisation of O-(chlorosilyl)-O-alkylketeneacetals; isomerisation of (Ib).*

(Ib) (4.4 g) was heated for 0.5 h at 70°. Fractionation yielded 3.7 g (85 % of theoretical) of (IIb) (see 4b), n_D^{20} 1.4460; d_4^{20} 1.3790.

(IIc) (5 h at 90°) and (IId) (12 h at 90°) were prepared similarly.

8. *Thermal decomposition of O-(triethylsilyl)-O-methylketeneacetal (Ia).*

(Ia) (6 g, 0.032 mole) was heated at 180–200° and the distillate of triethylmethoxysilane collected. Fractionation of the reaction products gave 2 g (86 %) of triethylmethoxysilane, b.p. 54–56° (36 mm), n_D^{20} 1.4123, d_4^{20} 0.8199; MR_D 44.42, calcd. 44.88. (lit.²²: b.p. 140.5° (760 mm), n_D^{20} 1.4129, d_4^{20} 0.8203) and 2.7 g of (IV) (74 %), b.p. 87–89° (3 mm), n_D^{20} 1.4427, d_4^{20} 0.9498; MR_D 64.26, calcd. 64.83. (Found: C, 57.67; H, 9.59; Si, 12.40. $C_{11}H_{22}O_3Si$ calcd.: C, 57.35; H, 9.63; Si, 12.18 %.)

9. *Reaction of O-(triethylsilyl)-O-methylketeneacetal with ketene*

On passing the excess ketene through 4.1 g of (Ia) there is evolution of heat and 4.3 g (85 %) of (IV) are obtained, b.p. 78–80° (1.5 mm), n_D^{20} 1.4433, d_4^{20} 0.9509; MR_D 64.25, calcd. 64.83. (Found: C, 57.07; H, 9.49; Si, 12.62. $C_{11}H_{22}O_3Si$ calcd.: C, 57.35; H, 9.63; Si, 12.18 %.) The infrared spectra of the substances obtained in experiments 8 and 9 were identical.

10. *Rearrangement of O-(triethylsilyl)-O-methylketeneacetal into methyl (triethylsilyl)-acetate*

(Ia) (7 g) and 1 g of HgI_2 were stirred for 0.5 h at room temperature and then for 1 h at 70°. After separation from HgI_2 , the reaction product was distilled. 5.8 g (83 %) of (IIa) was obtained (see 1b), b.p. 79–82° (8 mm), n_D^{20} 1.4412, d_4^{20} 0.9030; MR_D 55.08, calcd. 55.18.

ACKNOWLEDGEMENT

The authors express their appreciation to E. I. FEDIN and L. P. PETROVSKAJA who provided the NMR spectra and assisted in interpreting them.

SUMMARY

1. The conditions of dual reactivity of the esters of α -metalated carboxylic acids with the halides of some organosilicon compounds were examined.

2. The rearrangement of *O*-silyl-*O*-alkylketeneacetals into esters of silylacetic acid is reported.

REFERENCES

- 1 A. N. NESMEYANOV, I. F. LUTSENKO AND Z. M. TUMANOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 601 (1949); *Uch. Zap. Mosk. Gos. Univ.*, 132 (1950) 44.
- 2 Yu. I. BAUKOV, G. S. BURLACHENKO AND I. F. LUTSENKO, *Dokl. Akad. Nauk SSSR*, 157 (1964) 119.
- 3 S. V. PONOMAREV AND I. F. LUTSENKO, *Zh. Obshch. Khim.*, 34 (1964) 3450.
- 4 J. R. GOLD, L. H. SOMMER AND F. C. WHITMORE, *J. Am. Chem. Soc.*, 70 (1948) 2874.
- 5 C. R. HANCE AND C. R. HAUSER, *J. Am. Chem. Soc.*, 75 (1953) 994.
- 6 F. RIJKENS, M. J. JANSSEN, W. DRENTH AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 2 (1964) 347.

- 7 K. A. KRAMER AND A. K. WRIGHT, *J. Chem. Soc.*, (1963) 6604.
- 8 L. GOODMAN, R. M. SILVERSTEIN AND A. BENITEZ, *J. Am. Chem. Soc.*, 79 (1957) 3073; L. GOODMAN, R. M. SILVERSTEIN AND J. N. SHOOLERY, *J. Am. Chem. Soc.*, 78 (1956) 4493.
- 9 L. H. SOMMER, F. P. MACKAY, O. W. STEWARD AND P. G. CAMPBELL, *J. Am. Chem. Soc.*, 79 (1957) 2764.
- 10 L. SPEIER, J. A. WEBSTER AND G. H. BARNES, *J. Am. Chem. Soc.*, 79 (1957) 974.
- 11 K. A. ANDRIANOV AND L. I. MAKAROVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1956) 702.
- 12 A. D. PETROV, S. I. SADYKH-ZADE AND E. I. FILATOVA, *Zh. Obshch. Khim.*, 29 (1959) 2936.
- 13 C. R. KRÜGER AND E. G. ROCHOW, *J. Organometal. Chem.*, 1 (1964) 476.
- 14 YU. I. BAUEOV, G. S. BURLACHENKO AND I. F. LUTSENKO, *J. Organometal. Chem.*; 3 (1965) 478; *Zh. Obshch. Khim.*, 35 (1965) 757.
- 15 H. GILMAN AND R. N. CLARK, *J. Am. Chem. Soc.*, 69 (1947) 967.
- 16 I. F. LUTSENKO, V. L. FOSS AND N. L. IVANOVA, *Dokl. Akad. Nauk SSSR*, 141 (1961) 1107; I. F. LUTSENKO AND S. V. PONOMAREV, *Zh. Obshch. Khim.*, 31 (1961) 2025.
- 17 M. G. VORONKOV AND YU. I. KHUDOBIN, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1956) 713.
- 18 S. TANNENBAUM, S. KAYE AND G. F. LEWENZ, *J. Am. Chem. Soc.*, 75 (1953) 3753.
- 19 L. H. SOMMER, E. W. PIETRUSZA AND F. C. WHITMORE, *J. Am. Chem. Soc.*, 68 (1947) 2282.
- 20 G. GRÜTTNER AND E. KRAUSE, *Ber.*, 50 (1917) 1802.
- 21 Z. M. MANULKIN, *Zh. Obshch. Khim.*, 18 (1948) 299.
- 22 B. N. DOLGOV, N. P. KHARITONOV AND M. G. VORONKOV, *Zh. Obshch. Khim.*, 24 (1954) 1178.

J. Organometal. Chem., 5 (1966) 20-28