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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XXV*. PREPARATIONS AND REACTIONS OF TETRAMETHYLENE-[(α-TRIMETHYLSILYL- OR α-TRIMETHYLSTANNYL)PHENACYL]-SULPHONIUM SALTS AND YLIDES

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SUMMARY

Tetramethylene[(α-trimethylsilyl- and α-trimethylstannyl)phenacyl]sulphonium salts $[(CH_2)_4S^+{-}CH(MMe_3){-}CO{-}Ph]Cl^-$ (M = Si and Sn) have been prepared by the reaction of tetramethylenesulphonium phenacyclide (I) with the relevant Me_3MCl. The thermal rearrangement of tetramethylene[(α-trimethylsilyl)phenacyl]-sulphonium chloride (II) unexpectedly afforded $Cl(CH_2)_4S{-}CH{=}C(OSiMe_3)Ph$ (III) by a 1,3-migration of the trimethylsilyl group to the oxygen atom accompanied by simultaneous ring-opening. Tetramethylene[(α-trimethylstannyl)phenacyl]sulphonium chloride (IV) gave the corresponding ylide (VI) by reaction with n-butyllithium.

INTRODUCTION

Few publications on the sulphonium salts or ylides containing Group IV organometallyl groups have appeared and only studies concerning $(Me_2S^+{-}CH_2{-}SiMe_3)I^-$ [2], $(Me_2S^+{-}SnMe_3)I^-$ [3] and $Me_2S^+{-}CH^-SiMe_3$[2] have been reported to date.

In this paper the preparation of new α-trimethylmetal substituted sulphonium salts and ylides stabilized by a benzoyl group is reported. In addition, the chemical behavior of these compounds, 1,3-migration of the trimethylsilyl group in their reactions and carbene formation in the case of silyl- and tin-substituted sulphonium salts have been investigated.

RESULTS AND DISCUSSION

When tetramethylenesulphonium phenacylide (I) was added to an excess of trimethylchlorosilane at −30° the extremely hygroscopic tetramethylene[(α-tri-

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* For part XXIV see ref. 1.

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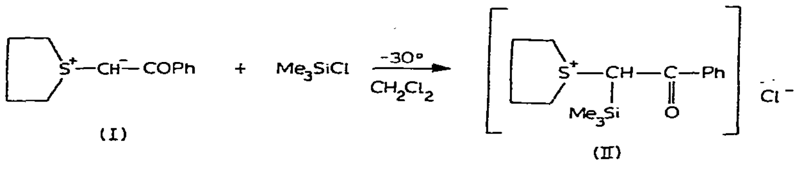
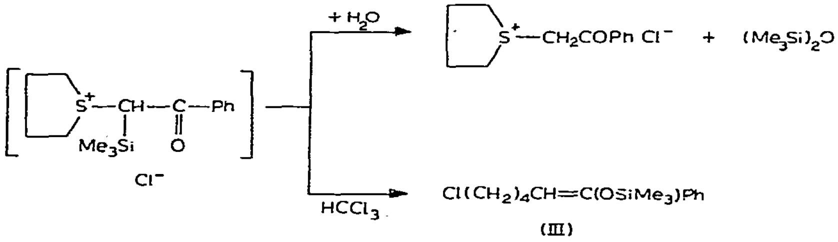
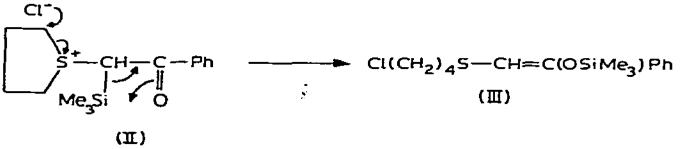
methylsilyl)phenacyl]sulphonium salt (II) was isolated in 83% yield. The structure of (II) was elucidated by elemental analysis, as well as by the presence of a strong ν(C=O) frequency at 1675 cm^{-1} and the fact that the hydrolysis of (II) gave tetramethylenephenacylsulphonium chloride and hexamethyldisiloxane.





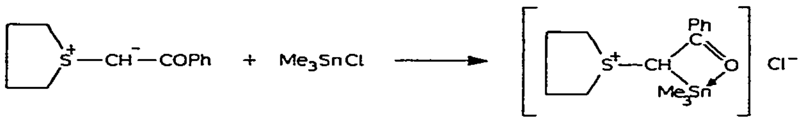
The sulphonium salt (II) rearranged slowly in chloroform solution at room temperature to give a silyl enol ether, 1-phenyl-1-(trimethylsiloxy)-2-[(4-chlorobutyl)-thio]ethylene (III). The structure of (III) was identified by elemental analysis and by NMR spectroscopy, its spectrum exhibiting a triplet due to CH_2–Cl at τ 6.53, a triplet due to CH_2–S at τ 7.35 and a singlet due to the olefinic proton at τ 4.40.

This rearrangement process is presumably induced by the 1,3-migration of the trimethylsilyl group from the carbon to the carbonyl oxygen as well as by the simultaneous opening of the tetramethylenesulphonium ring.



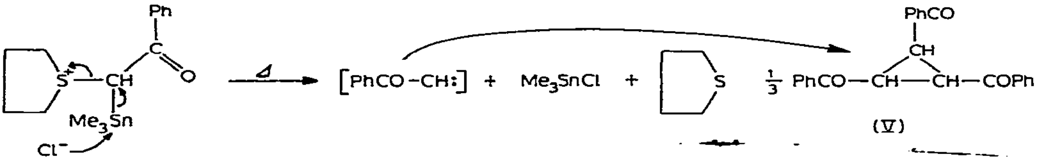
The silyl enol ether (III) was also prepared directly by reverse addition; thus, addition of trimethylchlorosilane to tetramethylenesulphonium phenacylide (I) at room temperature in methylene chloride gave (III) selectively in 43% yield.

Treatment of trimethyltin chloride with (I) gave a stable tetramethylene[(α-trimethylstannyl)phenacyl]sulphonium salt (IV) in excellent yield. Extremely low carbonyl stretching frequencies in the infrared spectrum at 1524 and 1487 cm^{-1} suggest strong coordination of the carbonyl oxygen to the trimethyltin moiety in this compound, this coordination presumably increasing the stability of (IV) towards hydrolysis, which is a ready process in the case of the corresponding silicon analogue (II).



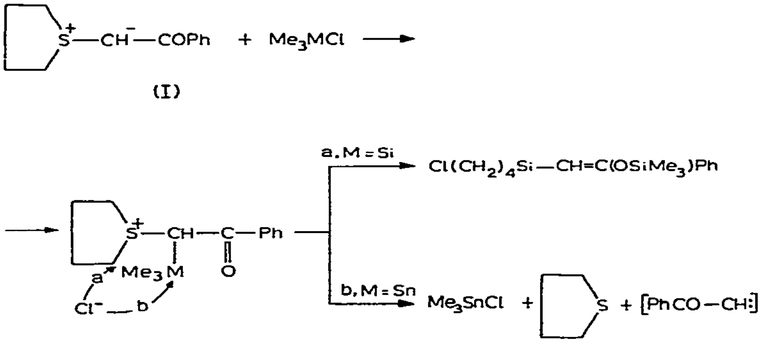
(I) (IV)

Thermal decomposition at 150° or photochemical reaction of (IV) gave tribenzoylcyclopropane (V), trimethyltin chloride and tetramethylene sulphide. A fragmentation reaction of this kind may be ascribed to nucleophilic attack of the chloride anion on the trimethyltin moiety to give benzoyl carbene as follows:



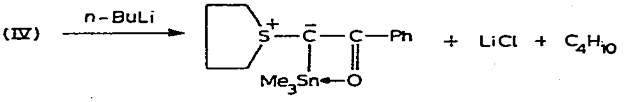
(V)

Thus, the reactions of the Group IV sulphonium chlorides (II) and (IV) may be summarized as follows;



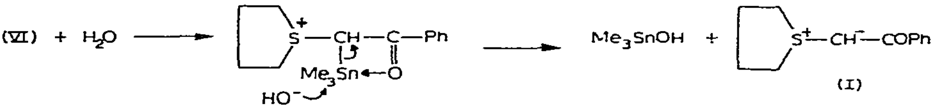
(I)

Treatment of (IV) with n-butyllithium in tetrahydrofuran in an attempt to prepare tetramethylene[(α-trimethylstannyl)phenacylide] (VI) gave a deep orange solution with the liberation of n-butane. The infrared spectrum in tetrahydrofuran showed ν(C=O) at 1528 cm^{-1} which again indicated coordination of the carbonyl oxygen to the tin atom. Hydrolysis of the ylide (VI) gave the parent tetramethylenesulphonium phenacylide (I) (73% yield) and trimethyltin hydroxide (83% yield).



(VI)

The hydrolysis would be induced by primary protonation to the carbanion and subsequent nucleophilic attack of the hydroxide ion on the trimethyltin group as follows



Addition of phenyl isocyanate to a tetrahydrofuran solution of the ylide (VI) resulted in trimerization to yield triphenyl isocyanurate.

EXPERIMENTAL

Tetramethylenesulphonium phenacylide (I)

To tetramethylenephenacylsulphonium bromide (2.87 g; 10 mmoles), prepared by reaction of tetramethylene sulphide with phenacyl bromide, in 20 ml of THF, was added sodium hydride (10 mmoles) at 0° with vigorous stirring. The reaction mixture was kept for 5 h at the temperature of a salt bath (0°), when, after removal of sodium bromide by centrifugation and of the solvent under reduced pressure, tetramethylenesulphonium phenacylide (I) was obtained as a pale yellow crystalline solid. Recrystallization from chloroform/petroleum ether (boiling range 30–40°) mixture gave 2.0 g (97%) of (I); m.p. 92–93° [92–93°[4]]. IR (KBr), 1512 (vs) cm^{-1} ν(C=O). NMR ($CDCl_3$), τ 6.4–7.5 m (CH_2 of ring); τ 5.70 s (CH^-–) and τ 2.60 m (C_6H_5).

Tetramethylene[(α-trimethylsilyl)phenacyl]sulphonium chloride (II)

Tetramethylenesulphonium phenacylide (I); (1.03 g; 5 mmoles) dissolved in 5 ml of methylene chloride was slowly added to 2 ml of a solution of trimethylchlorosilane (1.1 g; 10 mmoles) in petroleum ether (boiling range 30–40°) at −30°. After three minutes, excess trimethylchlorosilane and solvent were removed under vacuum at −10°. The residue was washed in ether/petroleum ether (1/1) mixed solvent and dried *in vacuo* when tetramethylene[(α-trimethylsilyl)phenacyl]sulphonium chloride (II) was obtained as a colourless oil in 83% yield. IR (CCl_4), 1675 (vs) and 1250 (vs) cm^{-1} (CH_3–Si). (Found; C, 57.02; H, 7.13. $C_{15}H_{23}ClOSSi$ calcd.: C, 57.21; H, 7.32%.)

1-*Phenyl*-1-(*trimethylsiloxy*)-2-[(4-*chlorobutyl*)*thio*]*ethylene* (*III*)

Trimethylchlorosilane (1.08 g; 10 mmoles) in 2 ml of methylene chloride was added to tetramethylenesulphonium phenacylide ((I); 1.03 g; 5 mmoles) in 5 ml of methylene chloride. The mixture was stirred for 15 min at room temperature and the lower boiling fractions were evaporated off under vacuum at the same temperature. The residue was purified by column chromatography (silica gel and ether/petroleum ether (1/9) mixed solvent) to give a deep yellow oily product (III) in 43% yield. (Found: C, 57.32; H, 7.55. $C_{15}H_{23}ClOSSi$ calcd.: C, 57.21; H, 7.32%.) NMR (CCl_4), τ 9.82 s (CH_3–Si), τ 8.1–8.25 (CH_2 ring), τ 7.35 t (CH_2–S), τ 6.53 t (CH_2–Cl), τ 4.40 s (H–C=) and τ 2.5–2.9 m (C_6H_5). IR (liquid film) 1670 (w) (C=C), 1250 (vs) (Me–Si), 852 (s) (δC–H).

Hydrolysis of tetramethylene[(α-trimethylsilyl)phenacyl]sulphonium chloride (II)

A chloroform solution (10 ml) of (II) (1.57 g; 5 mmoles) was stirred for one hour at −20° in air. The precipitated materials were recrystallized from ether to give tetramethylenephenacylsulphonium chloride; 1.1 g (91%) m.p. 115–116, which was identified by mixed melting point and by comparison of its infrared spectrum with that of an authentic sample prepared by the reaction of tetramethylene sulphide with phenacyl chloride. Distillation of the filtrate after removal of solvent gave hexamethyldisiloxane 0.35 g (85%).

Conversion of (II) to (III)

The rearrangement of tetramethylene[(α-trimethylsilyl)phenacyl]sulphonium chloride (II) (1.57 g; 5 mmoles in 10 ml of chloroform) was accomplished by storing at room temperature for three days. Chromatographic separation of the residue after the removal of low boiling fractions under reduced pressure, in a similar manner to that mentioned above, gave (III) as a yellow oily product; 0.79 g (52%).

Tetramethylene[(α-trimethylstannyl)phenacyl]sulphonium chloride (IV)

Trimethyltin chloride (1.0 g; 5 mmoles) dissolved in 5 ml of chloroform was added dropwise to a chloroform solution of (I) (5 mmoles in 5 ml). The mixture was constantly stirred for 10 min at room temperature, when, after removal of the chloroform under reduced pressure, the crystalline product was obtained by addition of small portions of an acetone/petroleum ether (boiling range 30–40°) 1/1 mixture. Filtration of the reaction product gave tetramethylene[(α-trimethylstannyl)phenacyl]sulphonium chloride (IV) in 95% yield; m.p. 106–107°. (Found: C, 43.84; H, 5.52. $C_{15}H_{23}ClOSSn$ calcd.: C, 44.21; H, 5.62%.) Mol.wt. Found: 400; calcd.: 408. NMR ($CDCl_3$), τ 9.38 s with satellites (CH_3–Sn), $\sim\tau$ 7.5 m (ring CH_2), τ 6.75 m (CH_2–S^+), τ 5.50 s (C–H) and $\sim\tau$ 2.6 m (C_6H_5). IR (KBr), 1524 and 1487 (C=O), 1270, 795 cm^{-1} (Me–Sn).

Thermal decomposition of (IV)

(*A*). Sulphonium chloride (IV) (0.82 g; 2 mmoles) was heated at 150° for 3 h in a sealed tube under an argon atmosphere. Small portions of chloroform were then added to give a brown solid which was recrystallized from benzene to give tribenzoylcyclopropane (V) 0.4 g (35%) as crystalline needles; m.p. 213–214°. The compound was characterized by comparison of its melting point and infrared spectrum with those of an authentic sample.

(*B*). A methanol solution (15 ml) of (IV) (0.82 g; 2 mmoles) was heated under reflux for 24 h. The crystalline precipitate was filtered off and recrystallized to give tribenzoylcyclopropane; 0.47 g (58%). Distillation of the filtrate gave tetramethylene sulphide and trimethyltin chloride (0.13 g).

Photochemical decomposition of (IV)

Irradiation of a methanol (15 ml) solution of (IV) (0.82 g; 2 mmoles) by UV light for 15 h, led to the formation of 0.12 g (30%) of crystalline tribenzoylcyclopropane (V). Careful distillation of the filtrate gave trimethyltin chloride (39%) and tetramethylene sulphide (46%).

Tetramethylenesulphonium (α-trimethylstannyl)phenacylide (VI)

The sulphonium salt (VI) (0.82 g; 2 mmoles) in 5 ml of tetrahydrofuran was treated with equimolar amounts of 1.7 *M* n-butyllithium at −30° and for an additional hour at room temperature. After removal of lithium chloride by filtration and of the solvent under vacuum, small portions of ether were added to give the unstable orange coloured ylide (VI) (0.63 g) in 80% yield. This material was extremely unstable both thermally and hydrolytically, and for this reason no spectroscopic measurements, except the observation of ν(C=O) at 1528 cm^{-1} in THF, were made. Consequently, all reactions of (VI) should be performed *in situ* during the formation of (VI) in THF.

Hydrolysis of (VI)

A tetrahydrofuran solution of (VI), formed *in situ* by treatment of 2 mmoles of (IV) with 2 mmoles of n-butyllithium and by the rapid filtration of lithium chloride, was stirred at room temperature overnight in air. After the removal of solvent, the crystalline residues were washed with small amounts of dry acetone to give trimethyltin hydroxide, 0.31 g (84%). The washing solutions were combined and the acetone evaporated off. Tetramethylenesulphonium phenacylide (I) was isolated in 73% yield (0.28 g) by the addition of a chloroform/petroleum mixture (1/1).

Reaction of ylide (VI) with phenyl isocyanate

To a tetrahydrofuran solution containing 2 mmoles of (VI) was added a petroleum ether solution of phenyl isocyanate (0.24 g; 2 mmoles). The mixture was kept stirring at room temperature for 2 h, when triphenyl isocyanurate began to precipitate and was finally obtained in 93% yield.

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