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REACTION OF BIS(TRIETHYLSILYL)- AND BIS(TRIETHYLGERMYL)-MERCURY WITH ESTERS OF α-BROMOCARBOXYLIC ACIDS

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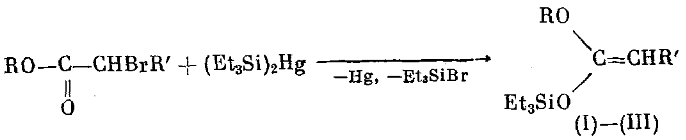
Methods for the synthesis of the silyl ethers of enols and their reactivity have been studied intensely in recent years [1, 2]. We established that the esters of α-bromocarboxylic acids react with bis(triethylsilyl)mercury to give the O-silylated acetals of ketenes.



$$RO{-}\underset{\overset{\|}{O}}{C}{-}CHBrR' + (Et_3Si)_2Hg \xrightarrow[-Hg,\ -Et_3SiBr]{} \begin{matrix} RO \\ & \diagdown C{=}CHR' \\ Et_3SiO \diagup \end{matrix} \qquad (1)$$

(I)–(III)

$R = Et,\ R' = H$ (I); $R = Et,\ R' = Me$ (II); $R = Me,\ R' = Et$ (III)

Catalytic amounts of HMPA accelerate reaction (1). The use of an equimolar ratio of the reactants and HMPA gives, along with compounds (I)-(III), an easily isolated complex of composition $Et_3SiBr{\cdot}HMPA$, mp 89-91°. The mechanism of such reactions was described previously [3].

The reaction of the esters of α-bromocarboxylic acids with bis(triethylgermyl)mercury (BTG) proceeds to give the corresponding esters of α-germylated carboxylic acids (IV)-(XI).

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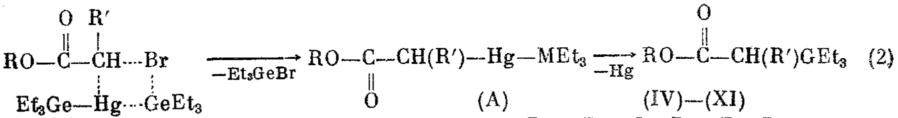
TABLE 1. Physicochemical Properties of Obtained Compounds

Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	Infrared spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm (TMS, CCl_4)
(I)	76	41–42 (1)	1,4345	1655 (C=C)	3,11 d (=CH_2), 2,89 d (=CH_2), 3,71 q (OCH_2)
(II)	83	74–75 (3)	1,4350	1682 (C=C)	4,07 q (=CH), 3,64 q (OCH_2)
(III)	69	52–54 (1)	1,4370	1680 (C=C)	1,94 d.t (CH_2), 3,59 t (=CH), 3,49 s (OCH_3)
(IV)	53	42–43 (1)	1,4606	1696 (C=O)	1,83 s (CH_2), 3,54 s (OCH_3)
(V)	85	92–95 (8)	1,4591	1695 (C=O)	2,20 q (CH), 1,20 d (CH_3). 3,56 s (OCH_3)
(VI)	67	70–71 (2)	1,4597	1695 (C=O)	3,56 s (OCH_3)
(VII)	75	45–46 (1)	1,4619	1700 (C=O)	1,80 s (CH_2), 4,00 q (OCH_2)
(VIII)	61	80–81 (4)	1,4600	1692 (C=O)	4,03 q (OCH_2), 2,17 q (CH)
(IX)	59	85–90 (4)	1,4592	1687 (C=O)	4,86 q (OCH), 2,15 q (CH)
(X)	86	101–104 (2)	1,4550	1685 (C=O)	
(XI)	47	64–65 (1)	1,4690	1712 (C=O)	3,92 s (CHCl), 4,10 q (OCH_2). 1,25 m (CH_3)

Reactions of this type probably proceed via the 4-center transition state [4] with the intermediate formation of the (A) intermediates, the demercuration of which gives compounds (IV)-(XI).



$$RO-\overset{\overset{O}{\|}}{C}-\overset{\overset{R'}{|}}{CH}\cdots Br \xrightarrow[-Et_3GeBr]{} RO-\underset{\underset{O}{\|}}{C}-CH(R')-Hg-MEt_3 \xrightarrow[-Hg]{} RO-\overset{\overset{O}{\|}}{C}-CH(R')GEt_3 \quad (2)$$

$$Et_3Ge-Hg\cdots GeEt_3 \qquad (A) \qquad (IV)-(XI)$$

R = Me, R′ = H (IV); R = R′ = Me (V); R = Me, R′ = Et (VI); R = Et, R′ = H (VII); R = Et, R′ = Me (VIII); R = *i*-Pr, R′ = Me (IX); R – *t*-Bu, R′ = Et (X); R = Et, R′ = Cl (XI).

In agreement with the discussed mechanism is the fact that when the methyl ester of α-bromobutyric acid (XII) is reacted with BTG we isolated in one of the parallel experiments, along with the expected product (VI), the crystalline dimethyl ester of α,α-mercuribisbutyric acid $Hg\cdot(CHEt-COOMe)_2$ (XIII) in 14% yield. The formation of (XIII) can be explained if it is assumed that intermediate (A), where R = Me, R' = Et, reacts with a second molecule of the starting ester (XII) by an analogous 4-center mechanism.

It was shown by the method of competing reactions that the rate of reaction (2) decreases with increase in the size of the R substituent (R' = Me). The ratio of the reaction rates when R = Me, Et, and i-Pr is 1.0, 0.9, and 0.7 respectively. When BTG is reacted with the dimethyl ester of α,α-dibromosebacic acid we isolated the dimethyl ester of α,α-bis(triethylgermyl)sebacic acid (XIV). The properties of the obtained compounds are given in Table 1.

EXPERIMENTAL

All of the experiments were run in evacuated sealed ampuls as described in [5]. Typical experiments are given below.

1-Triethylsiloxy-1-ethoxyethylene (I). To a solution of 1.8 g of ethyl α-bromoacetate in 10 ml of benzene was added 4.4 g of bis(triethylsilyl)mercury. After 3.5 h the solution was decanted from the Hg (2.0 g, 98%) and the solvent was removed. Fractional distillation gave 1.7 g (76%) of (I) (see Table 1). Found: C 59.47; H 11.00; Si 13.24%. $C_{10}H_{22}O_2Si$. Calculated: C 59.35; H 10.96; Si 13.89%. When this reaction was run in the presence of an equimolar amount of HMPA (1.9 g) the reaction was completed in 5-10 min. After removal of the benzene and recrystallization from hexane we isolated 2.9 g (76%) of the complex $Et_3SiBr \cdot$ HFMA, mp 89-91°. Found: C 38.16; H 8.55; Br 21.65%. $C_{12}H_{33}BrN_3OP$. Calculated: C 37.53; H 8.59; Br 20.83%.

Methyl Ester of α-Triethylgermylbutyric Acid (VI) and Dimethyl Ester of α,α-Mercuribisbutyric acid (XIII). To a solution of 3.1 g of (XII) in 15 ml of benzene was added 5.9 g of bis(triethylgermyl)mercury (BTG). After 3.5 h the solution was decanted from the Hg (1.8 g, 79%) and the solvent was removed. The residue was recrystallized from hexane to give 0.6 g (14%) of (XIII), mp 95-97°. PMR spectrum (TMS, C_6H_6, δ, ppm): 3.09 (OCH_3), 2.08 (CH), 0.83 m (CH_3). ^{199}Hg NMR spectrum (t-Bu_2Hg, C_6D_6, δ, ppm): +90.24. Infrared spectrum (ν, cm^{-1}): 1678 (C=O). Fractional distillation of the mother liquor gave 2.0 g (67%) of (VI) (see Table 1). Found: C 49.77; H 9.28; Ge 28.04%. $C_{11}H_{24}GeO_2$. Calculated: C 50.64; H 9.27; Ge 27.82%.

Dimethyl Ester of α,α-Bis(triethylgermyl)sebacic Acid (XIV). To a solution of 3.4 g of dimethyl α,α-dibromosebacate in 20 ml of benzene was added 8.9 g of BTG. The reaction was ended after 12 h with the deposition of 3.3 g (94%) of Hg. Fractional distillation gave 3.3 g (70%) of (XIV), bp 182-183° (10^{-3} mm), n_D^{20} 1.4837. PMR spectrum (TMS, CCl_4, δ, ppm): 3.30 s (OCH_3), 2.05 m (CH). Infrared spectrum (ν, cm^{-1}): 1717 (C=O). Found C 52.57; H 8.91; Ge 26.48%. $C_{24}H_{50}Ge_2O_4$. Calculated: C 52.62; H 9.20; Ge 26.50%.

Compounds (II)-(XI) were obtained in a similar manner.

CONCLUSIONS

A method was developed for obtaining the O-silylated acetals of ketenes and the esters of α-germylated carboxylic acids, which is based on the reaction of the esters of α-bromocarboxylic acids with bis(triethylsilyl)- and bis(triethylgermyl)mercury.

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