REACTION OF BIS(TRIETHYLGERMYL)MERCURY WITH CARBOXYLIC ACID CHLORIDES

L. I. Rybin, D. V. Gendin,
O. A. Vyazankina, and N. S. Vyazankin

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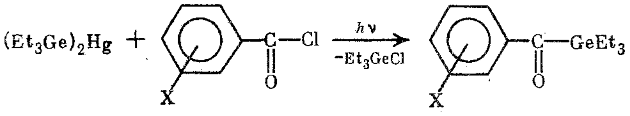
Methods for the synthesis of acylsilanes and acylgermanes are being actively developed in recent years [1-3]. These compounds are the heteroorganic analogs of ketones, but they are quite different from the latter in a number of physicochemical properties [4, 5].

We proposed a simple one-step method for the synthesis of benzoylgermanes, which consists in the photochemical reaction of bis(triethylgermyl)mercury (BTG) with benzoyl chlorides in benzene as the medium.

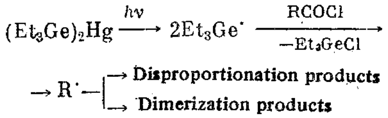


(1)

$X = H$ (I), m-CH_3 (II), p-F (III)

This method does not permit obtaining aliphatic acylgermanes. Thus, in the photochemical reaction of BTG with pivalyl chloride only CO, isobutane, isobutylene, mercury, and Et_3GeCl were detected in the reaction products. The reaction of phenylacetyl chloride with BTG gives dibenzyl, CO, mercury, and Et_3GeCl.

It is known [6] that bis(trimethylsilyl)- and bis(trimethylgermyl)mercury react with alkyl and aryl halides in the presence of UV light by the radical route. It may be assumed that the photochemical reactions of BTG with acyl chlorides also proceed by the radical route with the intermediate formation of acyl radicals. Benzoyl radicals are probably more stable than the aliphatic acyl radicals due to resonance stabilization and succeed in recombining with the triethylgermyl radical. However, the pivalyl and phenylacetyl radicals eject CO and form the tert-butyl and benzyl radicals, which then undergo either disproportionation [7] or recombination [8], which are characteristic reactions for them.



$$(Et_3Ge)_2Hg \xrightarrow{h\nu} 2Et_3Ge^{\cdot} \xrightarrow[-Et_3GeCl]{RCOCl} R\dot{C}{=}O \xrightarrow[-CO]{} R^{\cdot} - \begin{cases} \to \text{Disproportionation products} \\ \to \text{Dimerization products} \end{cases} \quad (2)$$

The presence of CO, isobutane, and isobutylene in the reaction gases was determined by chromato-mass spectrometry. Dibenzyl and Et_3GeCl were identified by GLC.

EXPERIMENTAL

The experiments were run in evacuated molybdenum glass ampuls as described in [9].

Benzoyltriethylgermane (I). To 2.7 g of benzoyl chloride in 15 ml of benzene was added 5.0 g of bis(triethylgermyl)mercury (BTG). The ampul was irradiated with a DRT-375 lamp for 35 min at 45-50°C (the distance from the light source was 10 cm). We isolated 1.8 g (94%) of Hg. Fractional distillation of the reaction mixture gave 1.6 g (62%) of (I), bp 95-97° (1 mm), n_D^{20} 1.5312. Infrared spectrum (ν, cm^{-1}): 1627 (C=O). Found: C 58.63; H 7.75; Ge 26.87%. $C_{13}H_{20}GeO$. Calculated: C 58.95; H 7.61; Ge 27.40%.

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m-Toluyltriethylgermane (II). We obtained (II) in a similar manner from 4.3 g of BTG and 2.5 g of m-toluyl chloride. Yield of Hg ~ 100%. In addition, we isolated 1.52 g (65%) of (II), bp 110-112° (1 mm), n_D^{20} 1.5270. PMR spectrum (TMS, CCl_4, δ, ppm): 2.39 s (3H,3H, CH_3), 7.35 m (5H, C_6H_4). Infrared spectrum (ν, cm^{-1}): 1628 (C=O). Found: C 59.25; H 7.74; Ge 25.93%. $C_{14}H_{22}GeO$. Calculated: C 60.29; H 7.95; Ge 26.02%.

p-Fluorobenzoyltriethylgermane (III). Obtained in a similar manner in 69% yield, bp 93–96° (1 mm), n_D^{20} 1.5252. PMR spectrum (TMS, CCl_4, δ, ppm):: 7.72, 7.08 m (4H, C_6H_4). Infrared spectrum (ν, cm^{-1}): 1628 (C=O). Found: 55.61; H 7.29; Ge 26.31%. $C_{13}H_{19}GeFO$. Calculated: C 55.20; H 6.77; Ge 25.66%.

Reaction of Bis(triethylgermyl)mercury with Pivalyl Chloride. To a solution of 2.1 g of pivalyl chloride in 10 ml of benzene was added 4.5 g of BTG. The mixture was irradiated with UV light until the characteristic orange color of BTG disappeared. Yield of Hg ~ 100%. The reaction mixture was analyzed by chromato-mass spectrometry (MAT-212 instrument). The following molecular ions were identified: CO 28, isobutane 58, and isobutylene 56. In addition, Et_3GeCl was identified by GLC.

Reaction of Bis(triethylgermyl)mercury with Phenylacetyl Chloride. To a solution of 3.0 g of phenylacetyl chloride in 10 ml of benzene was added 5.0 g of BTG. The mixture was irradiated as described above. We isolated 1.8 g (94%) of Hg and 270 ml of CO. As the main products in the benzene solution we identified by GLC: dibenzyl (83% yield) and Et_3GeCl (89% yield).

CONCLUSIONS

The photolysis of an equimolar mixture of bis(triethylgermyl)mercury with the benzoyl, m-toluyl, and p-fluorobenzoyl chlorides proceeds to give Hg metal and the corresponding acyltriethylgermanes. In the case of the pivalyl and phenylacetyl chlorides, together with the formation of Hg and Et_3GeCl, are generated the acyl radicals $Me_3C\dot{C}O$ and $PhCH_2\dot{C}O$, and the products of their subsequent transformations are obtained.

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