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NOTE

RING EXPANSION OF 1,1-DIETHYL-1-GERMACYCLOBUTANE VIA DICHLOROCARBENE INSERTION INTO THE GERMANIUM–CARBON BOND

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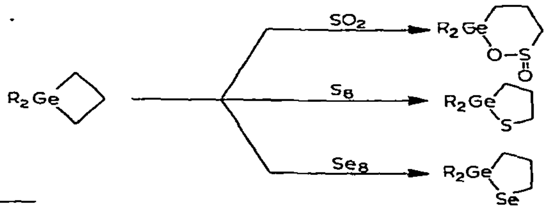
During the development of new dichlorocarbene reaction chemistry based on the phenyl(bromodichloromethyl)mercury reagent, we discovered the first example of dichlorocarbene insertion into a silicon–carbon bond, the ring expansion reaction, 1,1-dimethyl-1-silacyclobutane → 1,1-dimethyl-2,2-dichloro-1-silacyclopentane[1]. That dichlorocarbene could insert into this particular Si–C bond and not into others (*e.g.*, not into those of 1,1-dimethyl-1-silacyclopentane and 1,1-dimethyl-1-silacyclohexane) was attributed to the large ring strain energy of the silacyclobutane system. On this basis, one would predict that the strained germacyclobutane ring should react with phenyl(bromodichloromethyl)mercury-derived dichlorocarbene in similar fashion.

Germacyclobutanes were first reported in 1965[2], and these and subsequent studies showed that this ring system is opened by a large variety of reagents with great facility: alcoholic silver nitrate[2], mercuric chloride[2], bromine[2,3], hydrogen halides[2,3], other protonic acids[3], germanium tetrachloride[3], sulfuryl chloride[3], lithium aluminum hydride[2,3], organosilicon and organogermanium hydrides[4,5], strong bases[3], alkali metal alcoholates[6] and n-butyl- and phenyllithium[6]. Of special significance in terms of the objective of the present study was the observation that elemental sulfur[7], elemental selenium[7] and sulfur dioxide[8] reacted with 1,1-dialkyl-1-germacyclobutanes with expansion of the GeC_3 ring:



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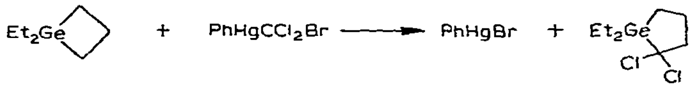
When 1,1-diethyl-1-germacyclobutane was allowed to react with phenyl(bromodichloromethyl)mercury in slight excess in benzene solution at reflux, four volatile products—one major and three minor—were obtained. The major product, obtained in 35% yield, was shown to be 1,1-diethyl-2,2-dichloro-1-germacyclopentane, and thus the expected ring expansion had indeed occurred. This represents the first case of carbene insertion into a carbon–germanium bond:



The NMR spectrum (in carbon tetrachloride) of this product confirmed the structure shown: a sharp singlet at 1.15 ppm overlapping with a complex pattern of lesser intensity at *ca.* 0.9–1.4 ppm (12 H total; $EtGeCH_2$-ring); a multiplet of at least nine lines from 1.6–2.1 ppm centered at 1.8 ppm [2 H; $GeCH_2CH_2$–] and two overlapping doublets at 2.25 ppm (2 H; $-CH_2CCl_2-$).

The minor products could not be obtained in quantity sufficient to permit their identification. In the case of 1,1-dimethyl-1-silacyclobutane, the β-C–H insertion product, 1,1-dimethyl-3-dichloromethyl-1-silacyclobutane, was a second product which was formed in smaller quantity than the ring expansion product[1], and thus a similar by-product might be expected in the case of the germacyclobutane. On the other hand, one or more of the by-products may only be artifacts, since the germacyclobutane used contained 5–8% of an impurity, diethyl-n-propylgermane, $(C_2H_5)_2$-$(n\text{-}C_3H_7)GeH$, and phenyl(bromodichloromethyl)mercury is known to insert CCl_2 into the Ge–H bond[9].

The low yield of phenylmercuric bromide obtained in this reaction, 43%, was noteworthy. It is probable that this is a result of an undesired side-reaction which consumes both germacyclobutane and phenylmercuric bromide, *i.e.*, ring opening to give $Et_2BrGe(CH_2)_3HgPh$ or a derived product. In support of this idea was the finding that in one such reaction thin layer chromatographic examination of the trap-to-trap distillation residue showed the presence of a mercury compound which was not $PhHgCCl_2Br$ or PhHgBr. Further confirmation of the idea that a phenylmercuric bromide–germacyclobutane reaction was diverting significant amounts of the latter from the inserting reaction of CCl_2 was given by the finding that use of a higher $PhHgCCl_2Br$/germacyclobutane ratio (1.5 instead of *ca.* 1) served to raise the 1,1-diethyl-2,2-dichloro-1-germacyclopentane yield to nearly 70%. Increasing the $PhHgCCl_2Br$-to-substrate ratio serves to increase the amount of CCl_2 which can react with substrate at any given instant, but the concentration of the very insoluble phenylmercuric bromide should not be changed significantly. The net effect is that the desired reaction is promoted and the undesired side-reaction with phenylmercuric bromide is minimized.

EXPERIMENTAL

Reaction of phenyl(bromodichloromethyl)mercury with 1,1-diethyl-1-germacyclobutane

A mixture of the germacyclobutane[2,3] (2.39 g, 13.8 mmoles)* and 6.69 g (15.2

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* Found by GLPC analysis (General Electric Co. SE-30 silicone rubber gum on Chromosorb P) to contain *ca.* 85% of the germacyclobutane, *ca.* 7% of diethyl-n-propylgermane and 7% of toluene.

mmoles) of phenyl(bromodichloromethyl)mercury[10] in 20 ml of dry benzene under nitrogen was placed in a 50 ml, three-necked flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring assembly. The flask was immersed in an oil bath, and the reaction mixture was stirred while the bath was heated. As the temperature reached 80°, a white, flaky solid precipitated from the initially clear solution. The bath was maintained at 82–85° for 3.5 h. At the end of this time, the reaction mixture was cooled to room temperature and filtered into a dry 100 ml flask under nitrogen. The residue was washed with 5 ml of benzene which was added to the initial filtrate, and the white solid was dried to give 2.31 g (43% yield) of phenylmercuric bromide, m.p. 276–279°.

Volatile components were removed from the filtrate by trap-to-trap distillation at 0.03 mm (pot heated with a heat lamp) into a liquid nitrogen-cooled trap. The residue consisted of brown solid and pale yellow liquid. Benzene was removed from the distillate by distillation at atmospheric pressure and the remaining liquid was analyzed by GLPC (MIT isothermal unit, 2.5 m glass column packed with 20% SE-30 on Chromosorb W, 190°, 15 psi helium). A major component with a retention time of 12.0 min (35% yield) was eluted after the benzene, as well as three other minor components at 5.5, 16.5 and 21.5 min (*ca.* 5% each). The relative amount of each component was established by adding a weighed amount of n-butyrophenone to the mixture as an internal standard (response factor of 1 assumed).

The major component was identified as 1,1-diethyl-2,2-dichloro-1-germacyclopentane. (Found: C, 37.65; 37.39; H, 6.27; 6.35. $C_8H_{16}Cl_2Ge$ calcd. C, 37.57; H, 6.31%.) An analytical sample had n_D^{25} 1.5061. The IR spectrum (liquid film) showed absorptions at 2950 s, 2940 (sh), 2905 (sh), 2875 s, 2820 (sh), 2715 w, 1460 m, 1435 m, 1420 (sh), 1380 w, 1315 w, 1305 w, 1258 w, 1225 w, 1118 m, 1034 m, 1020 m, 968 m, 950 (sh), 880 w, 780 m, 735 m, 678 s, 665 (sh), 595 w, and 578 w cm^{-1}.

The minor products of this reaction could not be identified, sufficient quantities not being available.

A similar reaction between 15 mmoles of $PhHgCCl_2Br$ and 10 mmoles of the germacyclobutane in 20 ml of benzene at reflux for 3 h gave phenylmercuric bromide in 95% yield and 1,1-diethyl-2,2-dichloro-1-germacyclopentane in *ca.* 70% yield.

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