

REACTIONS OF GERMYL ETHERS AND GERMYLCARBINOLS

G. J. D. PEDDLE AND J. E. H. WARD

Chemistry Department University of Alberta, Edmonton, Alberta (Canada)

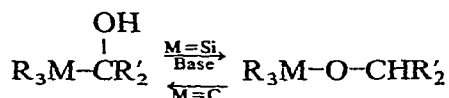
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SUMMARY

It was shown that germyl ethers do not undergo a Wittig type rearrangement but that α -germylcarbinols do rearrange to germyl ethers.

INTRODUCTION

In comparing the reactions of the organic compounds of Group IVB an interesting alternation in properties is often observed^{1,2}. The rearrangement of α -silylcarbinols to silyl ethers^{3,4} is the reverse of the Wittig rearrangement⁵.

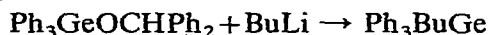


Since it has been reported that α -germylcarbinols do not rearrange to germyl ethers^{6,7}, it seemed of interest to determine whether or not germyl ethers would undergo a Wittig rearrangement.

RESULTS AND DISCUSSION

(Diphenylmethoxy)triphenylgermane (I) was prepared by an exchange reaction between triphenylmethoxygermane and benzhydrol. It was very sensitive to moisture and hydrolyzed readily in moist air or in wet ether to hexaphenyldigermoxane and benzhydrol.

Treatment of (I) with *n*-butyllithium, with *tert*-butyllithium or with the complex of *n*-butyllithium and tetramethylethylenediamine⁸ gave in each case the corresponding triphenylbutylgermane as the principal product.



(I)

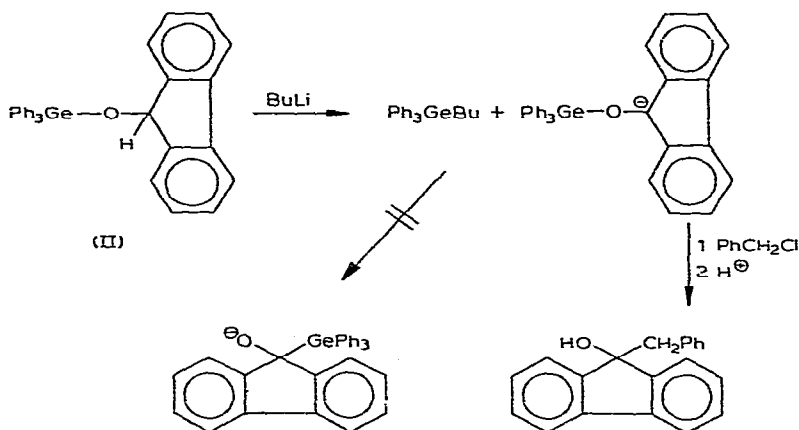
Thin layer chromatography of the mother liquors confirmed the absence of the Wittig type rearrangement product (triphenylgermyl)diphenylmethanol.

Treatment of (I) with *N*-bromosuccinimide in an attempt to prepare the α -bromoether gave benzophenone and triphenylbromogermane.



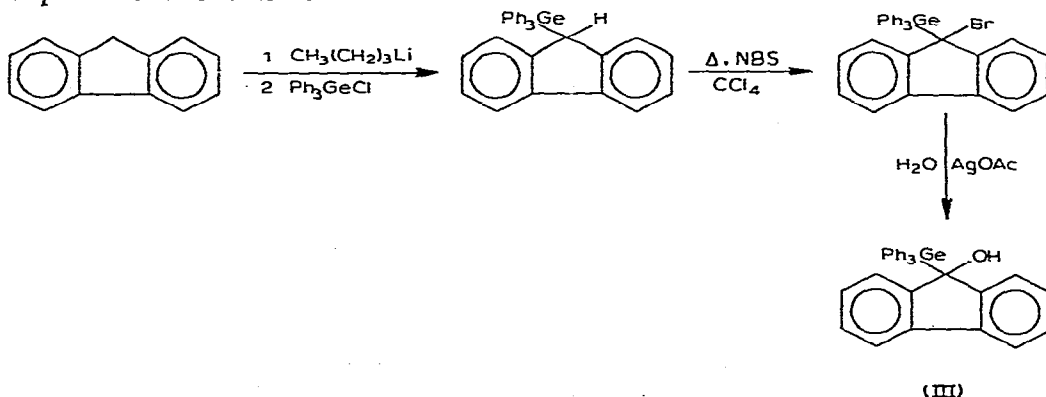
9-(Triphenylgermyloxy)fluorene (II), in which the proton should be much more acid than the proton in (I), was prepared by the reaction of sodium 9-fluorenoxide with triphenylchlorogermane.

Treatment of (II) with *n*-butyllithium gave a black solution. When benzyl chloride was added followed by refluxing and then acid work-up triphenylbutylgermane, hexaphenyldigermoxane, 9-fluorenol and 9-benzyl-9-fluorenol were obtained. In addition small amounts of fluorenone*, probably formed by the facile autoxidation of 9-fluorenol⁹, were present. None of the Wittig type rearrangement product, 9-(triphenylgermyl)-9-fluorenol (III) was detected.

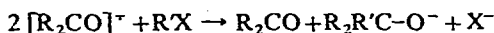


Since no evidence of a Wittig rearrangement of the germyl ether was observed it seemed possible that the α -germyl carbinols might rearrange to the germyl ether but not under the same mild conditions as the α -silylcarbinols.

Of all the α -silylcarbinols investigated 9-(triphenylsilyl)-9-fluorenol rearranged most rapidly⁴. The germanium analog (III), was prepared by the reaction sequence shown below:



* Since the amount of fluorenone present was less than 2%, fluorenone ketyl can be ruled out as a major intermediate:

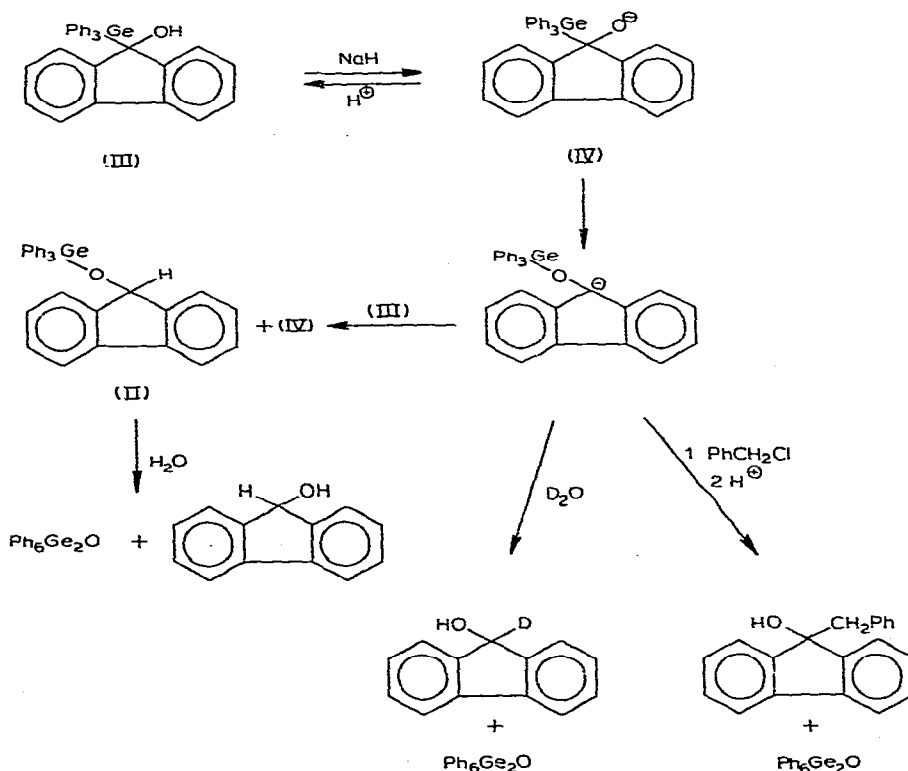


When a solution of (III) in THF was treated with sodium hydride a gas, likely hydrogen, was evolved. Immediate acidification regenerated (III). If the colorless solution of the anion of (III) was stirred for 2 h at 50° it slowly became black. Acid work-up gave hexaphenyldigermoxane and 9-fluorenol. Addition of deuterium oxide gave 9-deutero-9-fluorenol. Addition of benzyl chloride followed by 3 h additional stirring at 50° and then acid work-up gave 9-benzyl-9-fluorenol.

Similar results have been reported by Schwartz and Brook in their study of the reactions of (triphenylsiloxy)diphenylmethanopotassium¹⁰.

More direct evidence for the formation of (II) from the rearrangement of (III) was obtained by treating (III) with 0.05 equivalents of sodium hydride. The rearrangement went to completion and acid work-up gave 9-fluorenol and hexaphenyldigermoxane. The germyl ether, (II), could be isolated by seeding a heptane solution of the rearrangement product with a crystal of (II).

Although these studies do not establish unambiguously the mechanism of this rearrangement, in the absence of conflicting evidence, it seems reasonable to assume that the mechanism is similar to that proposed in the silicon case⁴. The above results can therefore be rationalized on the basis of the reaction sequence outlined below.



The variation in rate of reaction between the silicon and germanium compounds therefore is a reflection of the more facile nucleophilic cleavage of C-Si bonds compared to C-Ge bonds¹¹. If a similar difference in rate of rearrangement occurs between the 9-(triphenylgermyl)fluorenol and (triphenylgermyl)diphenylmethanol (V) as has been observed between the silicon analogs, it would take approxi-

mately 1000 h for (V) to rearrange under the same conditions. It is therefore not surprising that the rearrangement of (V) has not been observed under the mild conditions usually employed with silicon compounds.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of prepurified nitrogen. The THF used was distilled from lithium aluminum hydride. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Nashville, Tennessee or by Mrs. D. Mahlow and Mrs. A. Dunn, Department of Chemistry, University of Alberta. Mass spectra, NMR and IR data were determined on Metropolitan-Vickers MS-9, Varian Associates A-56/60A and Perkin-Elmer 421 spectrometers, respectively.

Preparation of (diphenylmethoxy)triphenylgermane (I)

To a solution of sodium methoxide prepared by the addition of 2.0 g (0.088 g-atom) of sodium to 100 ml of methanol, 30.0 g (0.088 mole) of triphenylchlorogermane was slowly added. After refluxing for 15 h, 100 ml of xylene was added and the methanol slowly distilled off. Following the addition of 16.3 g (0.089 mole) of benzhydrol slow distillation of solvent was continued for 18 h. The reaction mixture was then cooled and the liquid portion decanted from the white solid which had formed.

Distillation of the liquid gave 23 g (54%) of (I) as a viscous oil, b.p. 220–240° (1 mm). (Found: C, 76.5; H, 5.55. $C_{31}H_{26}GeO$ calcd.: C, 76.4; H, 5.38%.)

The NMR spectrum of (I) (CCl_4) consisted of a singlet at τ 4.27 ppm and a multiplet at 2.3–3.1 ppm with relative areas of 1:26, respectively.

Reaction of (I) with *n*-butyllithium

To a solution of 1.1 g (0.0023 mole) of (I) in 20 ml of THF, 2.8 ml (0.0045 mole) of *n*-butyllithium in hexane was slowly added. The reaction mixture rapidly turned red and became warm to touch. Within 5 min the red color had turned to yellow. The solution was stirred for 1 h and then added to ethyl ether and a saturated aqueous solution of ammonium chloride. The ether layer was washed with water, dried with sodium sulfate and concentrated on a rotary evaporator. The resultant yellow solid was recrystallized from 95% ethanol to obtain 0.28 g (35%) of triphenyl-*n*-butylgermane, m.p. 82–84°, reported m.p. 84.5–85.5°¹².

An NMR, IR and thin layer chromatographic study of the mother liquor showed the presence of additional triphenyl-*n*-butylgermane and of benzhydrol but no (triphenylgermyl)diphenylmethanol.

Reaction of (I) with *n*-butyllithium–tetramethylethylenediamine complex

A solution of 2.0 g (0.0041 mole) of (I) in 30 ml of heptane was added to a stirred solution of 1.0 g (0.0086 mole) of tetramethylethylenediamine and 5.1 ml (0.0082 mole) of *n*-butyllithium in hexane in 25 ml of heptane. The solution turned yellow and a pink precipitate formed. After stirring for 2 h work-up as above gave 1.1 g (74%) of crude triphenyl-*n*-butylgermane. Spectroscopic examination of the

mother liquor showed the presence of additional triphenyl-*n*-butylgermane and benzhydrol and the absence of (VII). These results were confirmed by thin-layer chromatography.

Reaction of (I) with tert-butyllithium

A solution of 3.7 ml (0.005 mole) of tert-butyllithium in pentane was added to 1.0 g (0.002 mole) of (I) in 25 ml of xylene. The resultant solution turned gold and then red. After refluxing for 1 h the solution was deep red. Work-up as above gave 0.4 g (40%) of triphenyl-*tert*-butylgermane, m.p. 165–166°. (Found: C, 72.3; H, 6.30. $C_{22}H_{24}Ge$ calcd.: C, 72.4; H, 6.63%.)

The NMR spectrum (CCl_4) consisted of a singlet at τ 8.75 ppm and a multiplet from τ 2.2–2.9 ppm with relative areas of 11 : 20, respectively.

Reaction of (I) with NBS

A mixture of 0.2 g (0.0011 mole) of NBS, 0.5 g (0.001 mole) of (I) and a crystal of benzoyl peroxide in 40 ml of carbon tetrachloride was refluxed for 48 h. The reaction mixture was cooled and filtered. An IR spectrum of the filtrate indicated that it was primarily a mixture of triphenylbromogermane and benzophenone. This was confirmed by removing the solvents under reduced pressure and recrystallizing the resultant solid from ethanol to obtain triphenylbromogermane, m.p. 133–135, mixed m.p. 133–135°. The benzophenone was isolated as its 2,4-dinitrophenylhydrazone, m.p. 239–240, mixed m.p. 239–240°.

Preparation of 9-(triphenylgermoxy)fluorene, (II)

A solution of 8.6 g (0.047 mole) of 9-fluorenol in 100 ml of THF was added to 1.12 g (0.047 mole) of sodium hydride. When gas evolution ceased 15 g (0.044 mole) of triphenylchlorogermane was added to the brown solution. The brown color was immediately discharged. After stirring for 2 h 100 ml of heptane was added and the solvents distilled off until a total volume of approximately 50 ml remained in the pot. Following the addition of 100 ml of heptane, the mixture was immediately centrifuged to remove approximately 10–15 g of a gummy solid. The supernatant liquid was filtered and 6.3 g (29%) of 9-(triphenylgermoxy)fluorene (II), m.p. 124–126°, crystallized from the filtrate. (Found: C, 76.5; H, 5.30; mol. wt. by mass spectrometry, 486. $C_{31}H_{24}GeO$ calcd.: C, 76.8; H, 4.99%; mol. wt., 486.)

The NMR spectrum (CCl_4) consisted of a singlet at τ 4.20 and a multiplet from τ 2.3 to 3.0 with approximate relative areas of 1 : 23.

*Reaction of (II) with *n*-butyllithium*

When 1.1 ml (0.0018 mole) of *n*-butyllithium in hexane was added to 0.8 g (0.0016 mole) of (II) in 40 ml of THF the solution rapidly became black. After stirring for 5 min 0.23 g (0.0018 mole) of benzyl chloride was added and the reaction mixture was refluxed for 3 h. The resultant light yellow solution* was added to dilute hydrochloric acid, extracted with ether and concentrated under reduced pressure. Following

* A comparison of the ϵ of the UV spectrum of an aliquot of the reaction mixture following work-up with that of a standard solution of fluorenone showed that the yield of fluorenone from the reaction was less than 2%.

a series of crystallizations from carbon tetrachloride and then from mixtures of carbon tetrachloride and ethanol and chromatography on silica gel eluted with mixtures of cyclohexane and benzene the following products were isolated: 0.08 g (27%) of 9-fluorene, 0.18 g (35%) hexaphenyldigermoxane, 0.26 g (44%) of triphenyl-*n*-butylgermane and 0.13 g (29%) of 9-benzyl-9-fluorene.

During these separations the mother liquor slowly became more yellow due to the formation of fluorenone which was isolated as the 2,4-dinitrophenylhydrazone, m.p. 282–284°, mixed m.p. 281–284°.

Preparation of 9-(triphenylgermyl)fluorene

A solution of 9-fluorenyllithium, prepared from 172 ml (0.31 mole) of *n*-butyllithium in hexane and 46.8 g (0.28 mole) of fluorene in 250 ml of THF, was stirred for 1 h with 81.5 g (0.24 mole) of triphenylchlorogermane. Work-up with dilute acid as above followed by crystallization from 95% ethanol gave 66 g (57%) of 9-(triphenylgermyl)fluorene, m.p. 166–168°. (Found: C, 79.2; H, 5.12. $C_{31}H_{24}Ge$ calcd.: C, 79.4; H, 5.16%.)

The NMR spectrum (CCl_4) consisted of a singlet at τ 5.34 ppm and a multiplet from τ 2.1–3.2 ppm with relative areas of 1 : 23, respectively.

Preparation of 9-(triphenylgermyl)-9-bromofluorene

A mixture of 3.9 g (0.022 mole) of NBS, 10.0 g (0.021 mole) of 9-(triphenylgermyl)fluorene and a few crystals of benzoyl peroxide in 100 ml of carbon tetrachloride was refluxed for 1 h. The mixture was cooled, the succinimide filtered off and the solvent removed under reduced pressure. The 9-(triphenylgermyl)-9-bromofluorene was used without further purification. Recrystallization of a small amount from ethanol/chloroform gave an analytical sample, m.p. 166°. (Found: C, 67.8; H, 4.13. $C_{31}H_{23}BrGe$ calcd.: C, 67.9; H, 4.23%.)

Preparation of 9-(triphenylgermyl)-9-fluorene (III)

The 9-(triphenylgermyl)-9-bromofluorene prepared from 10 g of 9-(triphenylgermyl)fluorene and 3.9 g (0.022 mole) of NBS was dissolved in 150 ml of acetone and 20 ml of water. After the addition of 31.0 g (0.14 mole) of silver trifluoroacetate the mixture was stirred for 18 h. The solids were removed by filtering through Celite. The filtrate was reduced to a volume of about 50 ml and then added to ether and water. The ether layer was washed with a saturated aqueous solution of sodium chloride, and then water. It was dried over sodium sulfate and concentrated under reduced pressure. The resultant solid was recrystallized from mixtures of 95% ethanol/chloroform/heptane to obtain 4.5 g (44%) of (III), m.p. 150–151°. (Found: C, 76.9; H, 5.14. $C_{31}H_{24}GeO$ calcd.: C, 76.8; H, 4.99%.)

The NMR spectrum (CCl_4) of (III) consisted of a singlet at τ 8.12 ppm and a multiplet from τ 2.4–3.0 ppm with relative areas of 1 : 24, respectively. The singlet at τ 8.12 ppm disappeared when deuterium oxide and acid were added.

Reaction of (III) with sodium hydride

A. When a solution of 0.485 g (0.001 mole) of (III) in 10 ml of THF was added to a suspension of 0.025 g (0.0011 mole) of sodium hydride in 20 ml of THF a colorless gas was evolved. The mixture was stirred at 50° for 2 h during which time it turned

from colorless to yellow to brown to black. The solution was divided into 3 fractions of approximately 10 ml each which were worked up as described below:

(a) Addition of 10 ml of the reaction mixture to ethyl ether and dilute hydrochloric acid discharged the black color and gave a light yellow ether layer. The ether layer was washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resultant solid was warmed under reduced pressure in a sublimation apparatus and 0.04 g (66%) of 9-fluorenol, m.p. 152–154°, sublimed from the reaction mixture. Recrystallization of the residue from ethanol gave 0.08 g (76%) of hexaphenyldigermoxane, m.p. 179–182°.

(b) When a sample was added to deuterium oxide and then worked up as above, the NMR and mass spectra of the sublimed 9-fluorenol obtained when compared with the spectra of 9-fluorenol confirmed at least partial (> 30%) formation of a mono deuterated 9-fluorenol.

(c) A 10 ml sample was added to 0.042 g (0.00033 mole) of benzyl chloride and the resultant solution stirred for 3 h at 50°. Work-up as above followed by repeated recrystallization from carbon tetrachloride and ethanol gave 0.05 g (58%) of 9-benzyl-9-fluorenol, m.p. 140°, identical in all respects to an authentic sample prepared by the addition of fluorenone to benzyl Grignard reagent¹³.

B. A solution of 2.0 g (0.0041 mole) of (III) and 0.005 g (0.0002 mole) of sodium hydride in 50 ml of THF was stirred at 50° for 4 h. Approximately 50 ml of heptane was added and the mixture was concentrated under reduced pressure to a total volume of about 10 ml. The addition of 40 ml of heptane and a seed of the germyl ether (II) gave 1.4 g (70%) of (II), m.p. 124–126°.

When a similar reaction mixture was worked up with dilute hydrochloric acid and ether the products obtained were 9-fluorenol (77%), m.p. 150–154°, and hexaphenyldigermoxane (70%), m.p. 175–80°.

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