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A new spirogermole: its synthesis, and some aspects of its reactivity

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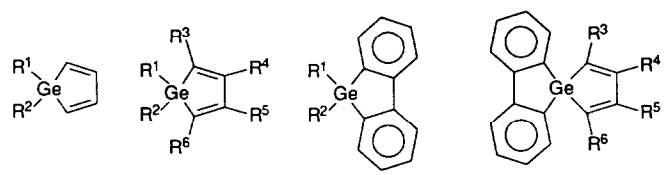
Abstract

The (6-7,8-9)-dibenzo-2,3-dimethyl-5-germa [4.4]-spironona-1,3-diene **6**, the first representative of a new type of germole, has been synthesized. This spirogermole reacts with maleic anhydride and t-butylphosphaacetylene by [2+4] cycloadditions, which involve exclusively the 2,3-dimethylgermole moiety. The adduct **9** obtained with the phosphaalkyne undergoes a thermal decomposition leading to the corresponding phosphabenzene.

Introduction

Three main types of germole are known [1]: the C-unsubstituted germoles I, the C-substituted germoles, II, and the germafluorenes III:



I II III IV

We report here a new type of germole IV, that belongs to both of the types II and III. Such a species brings together on a single germanium atom a "pseudo-germole" unit and a "true" germole ring. We thought it possible that such a dissymmetric

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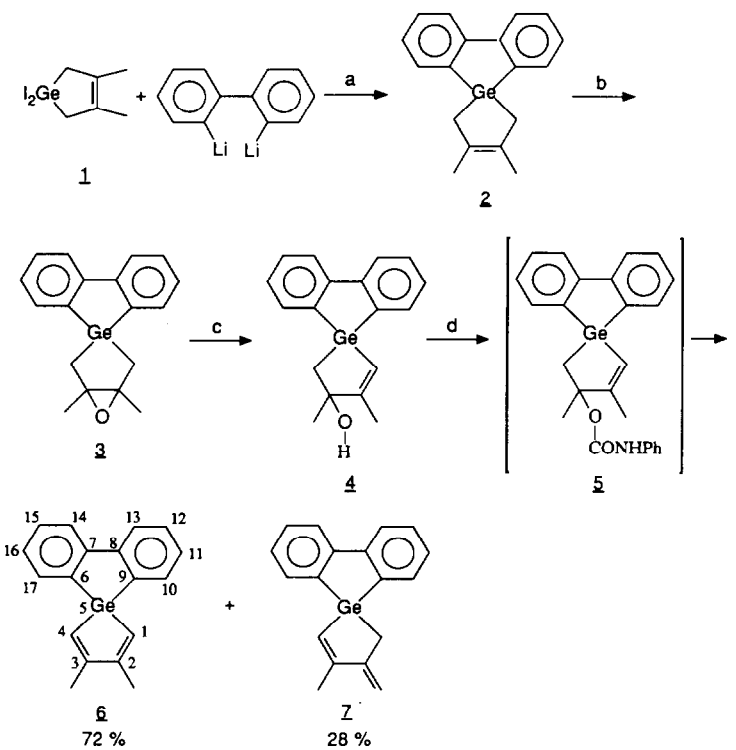
spirogermole IV might have some properties different from those of separate species II and III.

Results and discussion

The spirogermole **6**, (6-7,8-9)-dibenzo-2,3-dimethyl-5-germa [4.4] spironona-1,3-diene, belonging to type IV, was obtained in four steps from the known 4,4-diiodo-1,2-dimethyl-4-germacyclopent-1-ene **1** [2], as shown in Scheme 1. The first step (a) involves the reaction of **1** and 2,2′-dilithiobiphenyl [3] leading to the crystalline spirogermacyclopentene **2**.

The second step (b) involves the ready epoxidation of the tetrasubstituted double bond of the germacyclopentene ring of **2** by *meta*-chloroperbenzoic acid in ether [2b,4]. In step c the resulting oxirane **3** is completely isomerised to the corresponding allylic alcohol **4** by lithium diethylamide, a reaction very typical of 6-oxa-3-germabicyclo[3.1.0]hexanes [5].

The last step (d) involves a "one pot" synthesis of the expected germole **6**: the germacyclopentenol **4** is first transformed into its carbamate **5** by reaction with



a) pentane, THF, -78°C then 20°C
b) MCPBA, Et_2O, 15°C then reflux
c) Et_2NLi , Et_2O, pentane, 20°C
d) 2 PhNCO, CCl_4, tin (II) octanoate, reflux

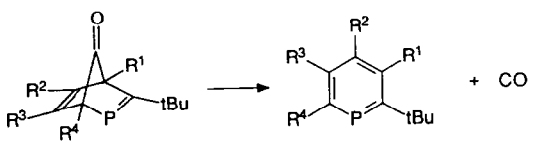
Scheme 1. Synthesis of (6-7,8-9)-dibenzo-2,3-dimethyl-5-germa[4.4]spironona-1,3-diene **6**.

phenylisocyanate, and this tertiary phenyl carbamate **5** is decomposed *in situ* in refluxing carbon tetrachloride to give dienes **6** and **7**, aniline, and carbon dioxide. Aniline is readily removed by reaction with an excess of phenyl isocyanate to give solid diphenylurea. After filtration, evaporation of the filtrate and purification, recrystallization gives a mixture of germole **6** and its "transoïd" isomer **7**. The two compounds have similar solubilities and cannot be separated by fractional crystallization. The **6**/**7** ratio (72:28) does not change during several months in the solid state or in chloroform solution. Compound **6** is thus evidently much more stable than germoles of types I and II; for example, partial isomerisation of 1,1,3,4-tetramethylgermole into its "transoïd" isomer, the 1,1,3-trimethyl-4-methylene-1-germacyclopent-2-ene occurs at 20 °C or during distillation [1].

The mixture of dienes **6** and **7** was treated with two dienophiles, maleic anhydride and t-butylphosphaacetylene [7]. As expected, **6** was very reactive towards maleic anhydride; the adduct **8**, obtained quantitatively at room temperature (Scheme 2), was isolated by fractional crystallization from chloroform and fully characterized by ^{1}H and ^{13}C NMR spectroscopy. The solution contained mainly **7**.

In contrast, the reaction of **6** with t-butylphosphaacetylene took place only in a pressure tube at 120 °C (cycloaddition reactions between t-butylphosphaalkynes and dienes generally need such heating [7]). The spiro adduct **9** decomposed to a totally insoluble material and a pure phosphorus compound. The insoluble material is probably formed by polymerisation of the transient germylene **10**. The phosphorus derivative formed was identified as the phosphabenzene **11**, 2-t-butyl-4,5-dimethyl-λ^3-phosphinine, from its NMR data [8]. The reaction was quantitative.

Decomposition of the adduct **9** may be compared to both the CO extrusion from a phosphanorbornadiene, such as **13**, leading to a stable phosphabenzene ring [7]



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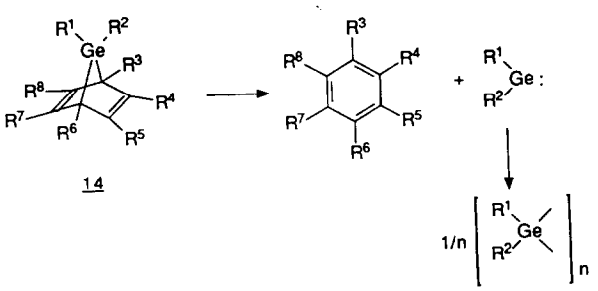
and also to the germylene extrusion from germanorbornadiene species **14** [1a] with formation of a stable aromatic ring:



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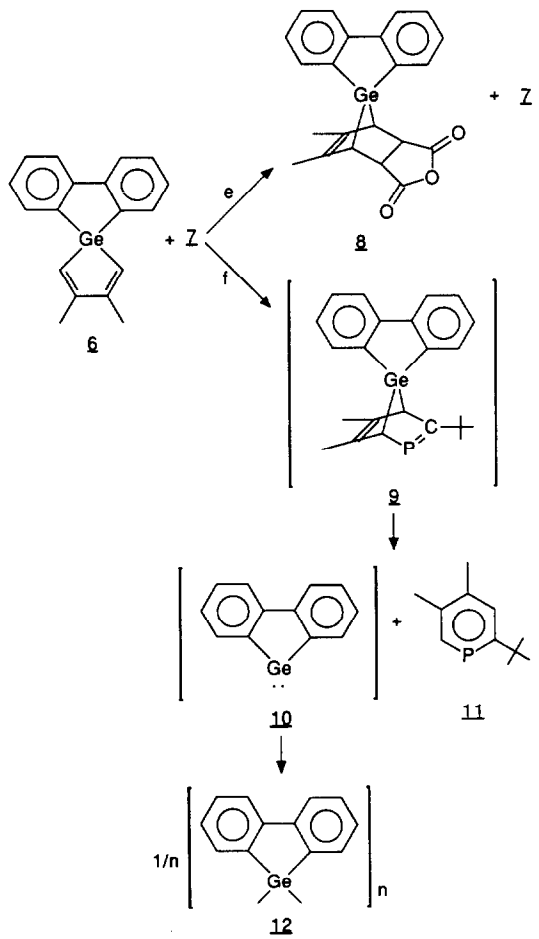
The above synthesis of germole **6** involves combination of the two different previously published methods used to prepare germoles of types II and III, respectively [1].



e) maleic anhydride, 20°C
f) t-BuC≡P , pressure tube, 120°C, 24 h.

Scheme 2. Cycloaddition reactions of germole **6**.

The crystalline spirogermole **6** of type IV, in contrast to germoles of type II, exhibits good stability towards isomerisation into its transoïd form. The observed chemical reactions involve only the "true" germole ring, which reacts normally as a diene with double and hetero-triple bond systems. [2 + 4] Cycloaddition of germoles to phosphaalkynes provides a new route to phosphabenzenes.

Experimental

General data

^{1}H NMR spectra were recorded on Bruker AC 80 and AC 250 spectrometers respectively, at 80.1 and 250.1 MHz. ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 at 50.3 and 62.9 MHz (TMS internal standard), and ^{31}P on a Bruker AC 200 spectrometer at 81.01 MHz (H_3PO_4 85% external standard). IR

spectra were recorded on a Perkin Elmer 1600 (FT) spectrometer. Mass spectra were obtained with a Nermag R10 010 spectrometer. Melting points were determined with a Reichert apparatus.

(6-7,8-9)-Dibenzo-2,3-dimethyl-5-germa[4.4]spironona-2-ene **2**

A pentane solution of 1 (prepared from 3.44 g (10.5 mmol) of GeI_2 and 1.0 g (12 mmol of DMB) [2]) was slowly added to a stirred THF solution of 2,2'-dilithiobiphenyl [3] at −78 °C (the dilithio compound was prepared from 3.27 g (10.4 mmol) of 2,2'-dibromobiphenyl [9] and butyllithium 1.6 M in hexane (13.5 ml)). The mixture was magnetically stirred for 12 h at 20 °C and then filtered. The white precipitate formed was filtered off and thoroughly extracted with hot ether. The washings then were combined with the filtrate and the combined solution then evaporated. Crystallization from ether gave 2.21 g of white crystals identified as **2**. (69% yield), m.p. 188° C. ^{1}H NMR ($CDCl_3$): δ 1.88 (s, ^4J(HH) 1.2 Hz, 6H, Me), 2.05 (q, ^4J(HH) 1.2 Hz, 4H, CH_2), 7.28–7.96 (m, 8H, GeR_2). ^{13}C NMR ($CDCl_3$): δ 19.36 (Me), 24.62 (C1, C4), 121.49 (C13, C14), 127.73, 129.73, 133.26 (C10, C11, C12, C15, C16, C17), 131.33 (C2, C3), 138.96, 146.52 (C6, C7, C8, C9). IR ν(C=C): 1647.4 cm^{-1}. MS (EI, ^{74}Ge): 308 (M^+, 37), 226 (R_2Ge^+, 90), 152 (R_2H^+, 100).

(6-7,8-9)-Dibenzo-2,3-epoxy-2,3-dimethyl-5-germa[4.4]spirononane **3**

Compound **2** (1.48 g, 5.2 mmol) in 150 ml of Et_2O (it has a low solubility) was added with magnetic stirring to a 100 ml Et_2O solution of 90% pure metachloroperbenzoic acid (1.09 g, 6.3 mmol). After 1 h refluxing 10% aqueous NaOH solution was added at 0 °C. The organic layer was washed several times with water, dried over sodium sulfate, and evaporated, to give 1.51 g of white crystals of **3** (4.7 mmol, 89% yield) m.p. 189 °C. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 6H, Me), 1.73 (s, 2H, CH_2), 1.78 (s, 2H, CH_2), 7.17–7.96 (m, 8H, GeR_2). ^{13}C NMR ($CDCl_3$): δ 20.08 (Me), 23.16 (C1, C4), 68.39 (C2, C3), 121.21 (C13, C14), 127.74, 130.00, 134.02 (C10, C11, C12, C15, C16, C17), 138.15, 146.20 (C6, C7, C8, C9). MS (EI, ^{74}Ge): 324 (M^+, 4), 309 ($M^+ - Me$, 7), 267 ($M^+ - CH_3COCH_2$, 14), 226 (R_2Ge^+, 25), 152 (R_2^+, 36), 43 (MCO^+, 44), 41 (CH_2CMe^+, 100).

(6-7,8-9)-Dibenzo-2,3-dimethyl-5-germa[4.4]spironona-1-ene-3-ol **4**

A suspension of diethyllithium amide was prepared from 2.3 g (30 mmol) of diethylamine and 10 ml of ^{n}BuLi 1.6 M in hexane (16 mmol) in 20 ml of pentane and 1.36 g (42 mmol) of epoxide **3** in 100 ml of Et_2O was added. The mixture was stirred overnight at 20 °C and then hydrolysed. The organic layer was washed with H_2O, extracted with 100 ml of Et_2O, dried over Na_2SO_4 and evaporated to give 1.46 g (4.5 mmol) of pale yellow crystals of **4** (96% yield), m.p. 191–193 °C. ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 3H, MeCO), 1.69 (s, 1H, CHGe), 1.76 (s, 1H, CHGe), 2.11 (d, ^4J(HH) 1.3 Hz, 3H, MeC=), 5.81 (q, ^4J(HH) 1.3 Hz, 1H, HC=), 7.25–7.93 (m, 8H, GeR_2). ^{13}C NMR ($CDCl_3$): δ 18.09 (Me), 29.67 (C4), 30.75 (Me), 62.73 (C3), 121.49, 121.64, 121.92 (C13, C14, C1), 127.60, 127.92, 130.06, 130.11, 133.28, 133.38 (C10, C11, C12, C15, C16, C17), 137.04, 146.30, 146.52 (C6, C7, C8, C9), 166.61 (C2). IR ν(OH): 3601.5 cm^{-1}. MS (EI, ^{74}Ge): 324 (M^+, 15), 226 (R_2Ge^+, 58), 152 (R_2^+, 100).

(6-7,8-9)-Dibenzo-2,3-dimethyl-5-germa[4.4]spironona-1,3-diene **6**

Alcohol **4** (1.40 g, 4.3 mmol) was added to a solution of PhNCO (1.24 g, 10 mmol) in 80 ml of CCl_4 in the presence of a drop of stannous octanoate. The mixture was refluxed for 8 h to complete the reaction. The diphenylurea was filtered off and the solvent evaporated. The residue was stirred for 1 h with 3 g of silica and 150 ml of pentane. After filtration, the clear solution was evaporated to give 0.86 g of a mixture of **6** and **7** in the ratio 72:28 (overall yield 65%). **6**: ^{1}H NMR (C_6D_6): δ 2.19 (d, ^4J(CH) 0.9 Hz, 6H, Me), 5.80 (q, ^4J(CH) 0.9 Hz, 2H, CHGe), 7.13–7.99 (m, CHR_2). ^{13}C NMR (C_6D_6): δ 20.74 (Me), 111.09 to 147.10 (ethylenic and aromatic CH). **7**: ^{1}H NMR (C_6D_6): δ 2.19 (d, ^4J(CH) 0.9 Hz, 3H, Me), 5.22–5.39 (m, 2H, C=CH_2), 6.16–6.23 (m, 1H, CHGe), 7.13–7.99 (m, CR_2). ^{13}C NMR (C_6D_6): δ 19.33 (Me), 24.61 (C1), 111.09–147.10 (ethylenic and aromatic CH).

Adduct **8**

Maleic anhydride (0.030 g, 0.31 mmol) was added to 0.14 g of a mixture of **6** and **7** (0.30 mmol of **6**) in 0.5 ml $CDCl_3$ contained in an NMR tube. Slow evaporation of the solvent led to formation of crystals, which were identified by ^{1}H and ^{13}C NMR spectroscopy as compound **8** (quantitative yield from **6**); white crystals, m.p. 200–205 °C. The remaining $CDCl_3$ solution contained mainly unchanged **7**. ^{1}H NMR (C_6D_6): δ 1.60 (s, 6H, Me), 2.40 (AA'XX', 2H, CHGe), 3.16 (AA'XX', 2H, CHCO), 6.97–7.67 (m, 8H, CHR_2). ^{13}C NMR (C_6D_6): δ 16.11 (Me), 42.16 (C1, C4), 48.55 (CHCO), 122.12, 122.18, 122.21, 122.25, 131.52, 132.62, 133.07 (C10–C17), 133.97 (C2, C3), 132.21, 135.41, 145.09, 145.97 (C6–C9), 172.62 (CO).

Reaction of germole with t-butylphosphaacetylene

t-Butylphosphaacetylene [10] (0.13 g, 1.28 mmol) and a mixture of **6** and **7** containing 0.39 g of **6** (1.28 mmol) in benzene (2 ml) were heated together for 24 h at 120 °C in a sealed tube. Filtration gave 0.23 g of a white powder, insoluble in common organic solvents, and judged to be the polygermylene **12** (m.p. > 350 °C). The solution was evaporated *in vacuo* and ^{1}H and ^{31}P NMR showed the residue to be of 2-t-butyl-4,5 dimethyl-λ^3-phosphinine **11** [9], formed in nearly quantitative yield.

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