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ADDITIONS OF FREE DIMETHYLGERMYLENE TO VINYL KETONES AND α-DIKETONES

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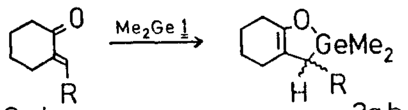
Summary: Derivatives of 1-oxa-2-germacyclopent-4-ene are obtained from germylenes with a number of cyclic or acyclic vinyl ketones, and 1,3-dioxa-2-germacyclopent-4-enes with different non-enolizable α-diketones. Structure-mechanism relationships are discussed.

The smooth thermolysis of 7-germanorbornadienes has been proved as useful for the thermal generation of singlet germylenes[1] giving both insertion reactions into σ bonds[2], and additions to π-systems such as styrenes[3], or stereospecific, cheletropic [4+2]cycloadditions to 1,3-dienes[4].

So, we looked for the reactivity of free germylenes towards other 4-π-electron partners, and we report here the first Me_2Ge additions to vinyl ketones and α-diketones.

With thermally generated dimethyl germylene, Me_2Ge 1, and vinyl ketones 2, we found in all examples tried so far the products of a formal 1,4-addition, the corresponding substituted 1-oxa-2-germacyclopent-4-enes 3:

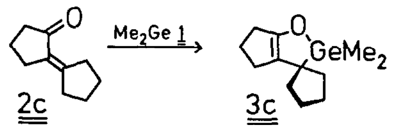


2a,b

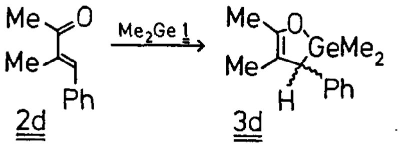
3a,b

3a, R = Ph. ^{1}H-NMR: 0.13 (s, 3H, GeMe); 0.6 (s, 3H, GeMe); 1.47-2.80 (m, 8H, CH_2); 3.17 (s, 1H, C_tH); 6.83-7.50 (m, 5H, Ar)
MS (70eV): m/e = 290 (M^+, 22%), 275 (M^+-Me, 7%), 261 (M^+-CH_2CH_3, 19%), 185 (M^+-Me_2, 100%)
yield (^{1}H-NMR): 85%

3b, R = Me. ^{1}H-NMR: 0.47 (s, 3H, GeMe); 0.53 (s, 3H, GeMe); 1.12 (d, 3H, CH_3); 1.50-2.60 (m, 9H, CH_2CH_2)
MS (70eV): m/e = 228 (M^+, 23%), 213 (M^+-Me, 100%), 197 (M^+-OMe, 28%), 107 (M^+-Me_2GeOH, 45%)
yield (^{1}H-NMR): 80%



^{1}H-NMR: 0.07 (s, 3H, GeMe); 0.50 (s, 3H, GeMe); 1.2-2.8 (m, 14H, CH_2)
MS (70eV): m/e = 254 (M^+, 67%); 239 (M^+-Me, 100%); 225 (M^+-CH_2CH_3, 83%),; 149 (M^+-Me_2GeH, 25%)
yield (^{1}H-NMR): 50%



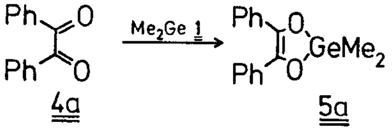
^{1}H-NMR: 0.09 (s, 3H, GeMe); 0.53 (s, 3H, GeMe); 1.50 (s, 3H, CH_3); 1.83 (s, 3H, $OCCH_3$); 3.12 (s, 1H, CH); 6.77-7.27 (m, 5H, Ar)
MS (70eV): m/e = 264 (M^+, 34%), 249 (M^+-Me, 100%), 187 (M^+-C_6H_5, 7%), 143 (M^+-Me_2GeOH, 52%)
yield (^{1}H-NMR): 70%

In all reactions the rate is identical with the rate of the first order spontaneous thermolysis of the germylene precursor, the Ph_4-7-germanorbornadiene . The yields (^{1}H-NMR) are given above, the lacking Ge residues are found as Me_2Ge polymers. More diluted reaction mixtures give lower yields, and more polygermane, as to be postulated. This points strongly to the intermediate occurrence of free **1**, adding to the π-systems. No further transients could be detected, and no stereospecifity can be expected. Therefore, it remains open at present whether a synchroneous 1,4-addition occurs, or a 1,2-addition across the C=O group giving a short-lived oxagermirane[5] rearranging then to **3a**-**d**. An initial addition to the electron deficient vinyl group giving a transient germirane also has to be discussed[6]. Anyway, a rigid s-cis system is not compulsory for a high reactivity and good yields as in the case of 1,3-dienes[7], since with the s-cis/s-trans mobile educt **2d** the yield is equivalent to the others.

In a typical procedure, 2.0g (3.7 mmol) of Ph_4-7-Ge-norbornadiene[1] is heated 4 h at 70°C with 7 mmol of the vinyl ketone **2a**-**d** in 15 ml of abs. benzene (**2c** without solvent), and the product isolated by Kugelrohr vacuum distillation. Isolated yields: 30-54%.

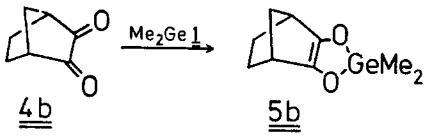
α-Diketones **4**, open-chained (**4a**) or alicyclic (**4b**) ones, as well as orthoquinones (**4c**-**e**), give 1,3-dioxa-2-germacyclopent-4-enes **5a**-**e** via a similar treatment with **1**. With excess diketone the yield (^{1}H-NMR) mostly is high or even quantitative. The reactivity increases in the sequence **4a** < **4c** ~ **4d** < **4e**.

Only such diketones could be used not decomposing spontaneously at 70°C, and not forming enols. Otherwise Me_2Ge **1** inserts predominantly into the O-H bond[8]. tBuCO-COtBu gives no product, apparently because no s-cis conformer is allowed by the bulky tBu-groups. This is in contrast to the action of free Me_2Si, giving an 1,3-dioxa-2-silacyclopent-4-ene, probably via an 1,2-addition, and rearrangement of the intermediate oxasilirane[9]. This points, in the case of Me_2Ge **1**, to an 1,4-addition mechanism giving products **5a**-**e** with **4a**-**e**. In no case, ESR signals of an intermediate



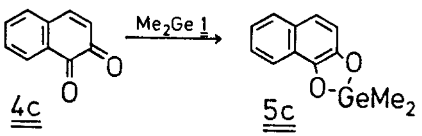
4a 5a

^{1}H-NMR: 0.52 (s, 6H, GeMe); 7.27-8.07 (m, 10H, Ar)
MS (70eV): m/e 314 (M^+, 3%); 299 (M^+-Me, 9%); 193 (M^+-Me_2GeOH, 37%)
yield (^{1}H-NMR): 80%



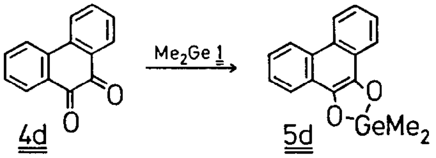
4b 5b

^{1}H-NMR: 0.48 (s, 6H, GeMe); 1.07-2.63 (m, 8H, CH, CH_2)
MS (70eV): m/e = 228 (M^+, 5%); 214 (M^+-CH_2, 4%); 198 (M^+-$2CH_3$, 3%); 125 (M^+-GeMe, CH_2, 28%)
yield (^{1}H-NMR): 55%



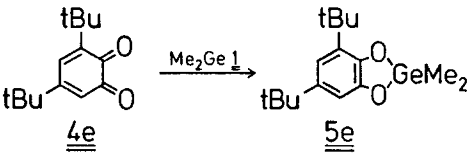
4c 5c

^{1}H-NMR: 1.12 (s, 6H, GeMe); 6.80-7.40 (m, 6H, Ar)
MS (70eV): m/e = 262 (M^+, 7%); 247 (M^+-Me, 27%); 158 (M^+-Me_2Ge, 100%); 105 (Me_2GeH, 14%)
yield (^{1}H-NMR): 70%



4d 5d

^{1}H-NMR: 1.15 (s, 6H, GeMe); 6.82-7.70 (m, 8H, Ar)
MS (70eV): m/e = 312 (M^+, 14%); 297 (M^+-Me, 27%); 282 (M^+-2Me, 8%)
yield (^{1}H-NMR): 60%



4e 5e

^{1}H-NMR: 0.93 (s, 6H, GeMe); 1.25 (s, 9H, tBu); 1.35 (s, 9H, tBu); 6.53-6.70 (m, 2H, Ar)
MS (70eV): m/e = 324 (M^+, 40%); 309 (M^+-Me, 100%); 293 (M^+-$2CH_3$, H, 14%); 279 (M^+-3Me, 3%)
yield (^{1}H-NMR): 100%

could be detected. The rate of the reactions always equals that of the spontaneous thermolysis of the germylene precursor . This and the fact that lacking Ge moieties are found as $(Me_2Ge)_n$ are seen as evidence for the action of a free germylene here.

But, a complicated ESR signal, and a greenish colour with red fluorescence could be observed when we mixed the orthoquinone 4e (excess) with the precursor of 1, Ph_4-7-germanorbornadiene. Exactly the same observations can be made when mixing 1,2,3,4-Ph_4-naphthalene, the product of Me_2Ge-extrusion, with 4e, and are attributed to a radical ion pair built up from 4e and Ph_4-naphthalene. They have, hence, nothing to do with the cycloadditions of 1 described above.

The typical procedure resembles that for 2a-d given above, but 20 mmol of the α-diketone 4a-e are used, and the workup is done by thick layer chromatography, using silica gel and n-hexane/CH_2Cl_2 as eluent. Isolated yields: 30-80%.

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