

An unexpected epoxidation of benzil derivatives in their reaction with a germene†

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The germene Mes₂Ge=CR₂ (Mes = 2,4,6-trimethylphenyl, CR₂ = fluorenylidene) reacts with various benzil derivatives to lead to germanium-containing bicyclic epoxides by an unexpected new type of epoxidation reaction.

Introduction

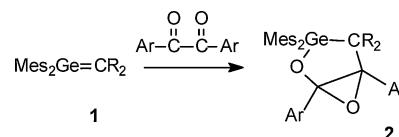
The study of compounds containing one low-coordinate silicon, germanium or tin element, analogous to olefins, has attracted much attention over the past few decades. Such doubly-bonded compounds display very high reactivity and constitute valuable building blocks for the synthesis of unusual derivatives owing to additions or cycloadditions onto the E=C (E = Si,¹ Ge,^{1g,2} Sn^{2a}) unsaturation. For example, the high synthetic potential of germenes is illustrated by their reaction with carbonyl compounds. Various types of reaction have been observed depending on the structure of the carbonyl derivatives: generally [2 + 2] cycloadditions with saturated aldehydes and ketones,³ and [2 + 4] cycloadditions with α -ethylenic aldehydes and -ketones⁴ or -esters⁵ but also ene-reactions, the germenes behaving either as ene⁶ or enophile.⁶ In the special case of benzophenone, besides a [2 + 2] cycloaddition, a [2 + 4] cycloaddition involving the phenyl group has also been observed.⁷ For compounds with two carbonyl functions, such as anhydrides or 1,3-diketones, [2 + 2] cycloadditions onto one or both carbonyl functions were reported.⁵

In order to learn more about the chemical behavior of germenes toward carbonyl compounds, we investigated their reactions with α -dicarbonyl derivatives. We have recently reported the reaction of α -diester EtOOC-COOEt with germene **1** giving a [2 + 2] cycloaddition onto one C=O group.⁵

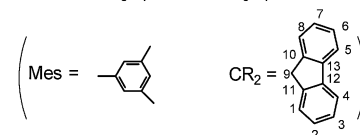
In this paper, we report the unexpected behavior of dimethylfluorenylidene germane Mes₂Ge=CR₂ **1** (Mes = 2,4,6-trimethylphenyl, CR₂ = fluorenylidene) towards α -diketones such as benzil and related 3,3' and 4,4'-disubstituted benzils, a class of carbonyl derivatives whose reactivity towards germenes has still not yet been explored.

Results and discussion

A [2 + 2] cycloaddition between the Ge=C double bond and one C=O group, or more reasonably a [2 + 4] cycloaddition involving the two C=O groups, was expected.^{8–10} To our surprise, when benzil was added to a cold solution of germene **1** in Et₂O, an unexpected reaction occurred leading quantitatively to the germanium-containing bicyclic epoxide **2a**.‡ The formation of **2a** is independent of the reaction conditions since either addition of germene **1** to the diketone or the reverse procedure, and use of either an excess of **1** or of benzil, led to the same result (Scheme 1).



Ar = Ph, **2a**; 4-FC₆H₄, **2b**; 3-MeOC₆H₄, **2c**;
4-MeOC₆H₄, **2d**; 4-MeC₆H₄, **2e**.



Scheme 1

To gain better insight into the formation of heterocycle **2a**, we investigated the reaction of germene **1** with various benzils substituted in positions 3,3' and 4,4' by electron-donor or electron-acceptor groups such as fluorine, methyl and methoxy groups. Similar clean reactions occurred to afford epoxides **2b–e**§ analogous to **2a** and proved that, whatever the benzil derivative, this epoxidation is a general reaction of this germene.

A possible mechanism for the formation of epoxides **2** is shown in Scheme 2. The first step is probably a nucleophilic attack of the oxygen atom of the carbonyl group on the germanium atom to lead to intermediate **3**. Ring closure leading to the strained oxagermetane **4** did not occur for steric reasons. Compound **2** could be obtained by either stepwise epoxidation followed by ring closure or by a single concerted step *via* the nucleophilic attack

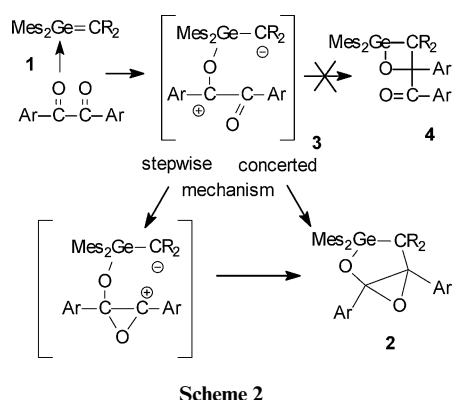
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† Electronic supplementary information (ESI) available: Complete experimental and physicochemical data for **2b**, **2c**, **2d** and **2e**. CCDC reference number 689531. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812694c

‡ Please see Experimental section for full procedure.

§ Please see Experimental section for selected NMR data.



of C⁻ at the C⁺(=O), which causes simultaneous epoxidation (Scheme 2).

The ¹H NMR spectra of heterocycles **2** showed the non-equivalence of the mesityl groups, with extremely broad signals for the *o*-methyl groups due to the hindered rotation of mesityl groups in the NMR time scale caused by the large steric hindrance. The ¹³C NMR spectra revealed resonances around 78 and 91 ppm for the carbon atoms of the oxirane ring (R₂CCO and OCO respectively) and mass spectra displayed the molecular peak. The results are wholly consistent with the structures proposed for **2**; that of **2a** was unambiguously established by an X-ray analysis (Fig. 1).

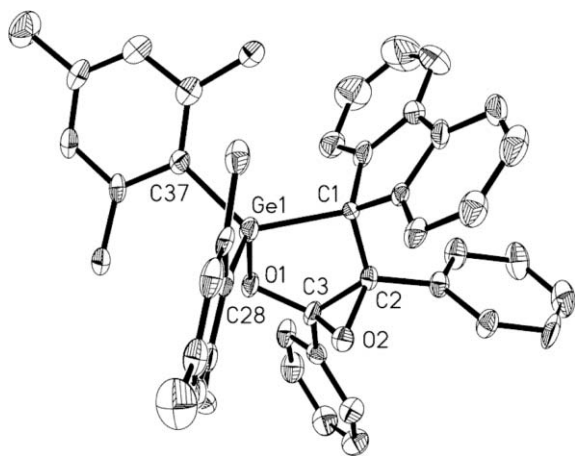


Fig. 1 Molecular structure of **2a** (thermal ellipsoids at the 50% probability level); H atoms are omitted for clarity; selected bond lengths (Å), angles (°) and torsion angle (°). Ge(1)–C(1) 2.034(5), Ge(1)–O(1) 1.824(4), C(1)–C(2) 1.553(7), C(2)–C(3) 1.461(7), C(3)–O(1) 1.388(6), C(2)–O(2) 1.441(6), C(3)–O(2) 1.431(6), Ge(1)–C(37) 1.968(15), Ge(1)–C(28) 1.961(5), C(1)–Ge(1)–O(1) 90.22(18), C(1)–C(2)–C(3) 115.1(4), Ge(1)–C(1)–C(2) 98.3(3), C(2)–C(3)–O(1) 116.2(5), C(3)–O(1)–Ge(1) 109.1(3), C(1)–C(2)–C(3)–O(1) –0.42; between plane C(2)–O(2)–C(3) and mean plane C(1)–C(2)–C(3)–O(1): 75.5.

Only one couple of enantiomers was obtained for compounds **2**, with the aryl groups of the epoxide moiety in a *trans* disposition, as proved by the X-ray analysis of **2a**. The great steric hindrance in **2a** is confirmed by the lengthening of the intracyclic Ge–C(1) distance (2.034(5) Å) compared to the Ge–C(Mes) bonds (1.968(15) and 1.961(5) Å), which lie in the normal range (1.93–1.98 Å).¹¹ The Ge–O bond (1.824(4) Å) is also elongated compared with the standard Ge–O distance (1.73–1.79 Å). By contrast, the C(2)–C(3) bond

length (1.461(7) Å) is within the standard range (1.45–1.49 Å) for such a bond in epoxides.¹²

Such a type of reaction leading to epoxides **2** has never been observed previously with heteroalkenes; to the best of our knowledge, the only similar case of epoxidation from an α -diketone occurred between the central diketone moiety of MeO₂C–COCO–CO₂Me and the C=C double bond of ethoxyethylene.¹³

Conclusion

In conclusion, dimesitylfluorenylidene germane gives a surprising diastereoselective epoxidation reaction, probably due to its particular structure involving a fluorenylidene group, and thus appears to be a very useful building block in organogermanium and heterocyclic chemistry. Research is now focused on the ring opening of these α -germylated epoxides and on the enantioselective synthesis of such epoxides by using prochiral germenes.

Experimental

Synthesis of germene **1**

Germene **1** was prepared as previously described¹⁴ by the addition of 1 molar equivalent of *tert*-butyllithium (1.7 M in pentane) to a solution of the fluorogermane Mes₂Ge(F)CHR₂ (1.00 g, 2.02 mmol) in Et₂O (20 mL) cooled to –78 °C. **1** was produced quantitatively by warming to room temperature. All reactions were performed on the crude reaction mixture containing LiF without isolation of **1**. The yields of compounds **2** were calculated in relation to the starting Mes₂Ge(F)CHR₂.

Reaction of **1** with benzil: synthesis of **2a**

A solution of benzil (0.44 g, 2.1 mmol) in Et₂O (10 mL) was added by syringe to the crude solution of **1** cooled to –30 °C. The initially orange reaction mixture turned light yellow on warming to room temperature. After removal of LiF by filtration, Et₂O was evaporated under vacuum and replaced by pentane (20 mL); a fractional crystallization at –20 °C afforded 1.08 g (78%) of white crystals of **2a** (mp 232 °C).

δ_{H} (250.13 MHz): 2.21 and 2.31 (2 s, 2 × 3H, *p*-Me of Mes), 1.50–3.20 (extremely broad s (width at half-height 250 Hz), 12H, *o*-Me of Mes), 6.33 (d, ³J_{HH} = 7.6 Hz, 2H) and 6.58 (t, ³J_{HH} = 7.6 Hz, 2H) (arom. H of CR₂), 6.82 and 6.85 (2 broad s; 2 × 2H, arom. H of Mes), 7.10–7.46 (m, 11H, arom. H of Ph and 1H of CR₂), 7.57, 7.62 and 7.72 (3d, ³J_{HH} = 7.6 Hz, 3 × 1H, arom. H of CR₂).

δ_{C} (75.47 MHz): 20.93 and 21.06 (*p*-Me of Mes), 23.26 and 22.64 (*o*-Me of Mes), 61.06 (CR₂), 78.45 (R₂CCO), 91.91 (GeOCO), 119.95 and 119.97 (C4C5 of CR₂), 125.48, 125.53, 126.64, 126.83, 126.87, 126.98, 127.10 and 128.05 (*p*-C of Ph and C1–8 of CR₂), 126.03, 127.37, 127.60 and 128.62 (*o*- and *m*-C of Ph), 128.88 (*m*-C of Mes), 132.67, 132.92, 133.49, 134.98, 139.22, 139.31, 140.98, 141.49, 143.69 and 145.11 (arom. C).

MS (DCI/NH₃): 687 (M + 1, 40), 359 (M + 1 – Mes₂GeO, 100).
Anal. calcd for C₄₅H₄₀GeO₂ (685.401) C, 78.86; H, 5.88%.
Found: C, 79.02; H, 6.10%.

Crystal data for 2a

C₄₅H₄₀GeO₂, *M* = 685.36, triclinic, *a* = 10.828(4), *b* = 11.700(4), *c* = 15.348(5) Å, α = 75.228(8), β = 74.785(8), γ = 73.428(7)°, *V* = 1763.8(10) Å³, *T* = 173(2)K, space group *P*1̄, *Z* = 2, 7319 reflections measured, 4524 unique (*R*_{int} = 0.0299). The final *R*₁ (for *I* > 2σ(*I*)) was 0.0558 and *wR*₂ (all data) was 0.418 with *R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o| and *wR*₂ = (Σ*w*(*F*_o² - *F*_c²)²/Σ*w*(*F*_o²)²)^{0.5}.

Data for the structure represented in this paper were collected at low temperature by using an oil coated shock cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods¹⁵ and all non-hydrogen atoms were refined anisotropically by using the least-squares method on *F*².¹⁶

Selected NMR data

2b δ_C (75.47 MHz): 60.84 (CR₂), 77.90 (R₂CCO), 91.62 (GeOCO), 160.48 (d, ²*J*_{CF} = 98.1 Hz, CF), 164.75 (d, ²*J*_{CF} = 98.9 Hz, CF).

2c δ_H (250.13 MHz): 3.26 and 3.60 (2 s, 2 × 3H, OMe); δ_C (75.47 MHz): 54.84 and 55.09 (OMe), 61.02 (CR₂), 78.46 (R₂CCO), 91.90 (GeOCO), 157.56 and 158.93 (COMe).

2d δ_H (250.13 MHz): 3.29 and 3.66 (2 s, 2 × 3H, OMe); δ_C (75.47 MHz): 54.67 and 55.15 (OMe), 61.17 (CR₂), 77.97 (R₂CCO), 91.90 (GeOCO), 157.91 and 159.40 (COMe).

2e δ_C (75.47 MHz): 20.89, 21.02 and 21.25 (*p*-Me of Mes and *p*-Me of C₆H₄Me), 61.19 (CR₂), 78.25 (R₂CCO), 91.93 (GeOCO).

Acknowledgements

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Notes and references

1 For reviews, see: (a) G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419–509; (b) A. G. Brook and M. Brook, *Adv. Organomet. Chem.*, 1996, **39**, 71–158; (c) T. Müller, W. Ziche and N. Auner, in *The Chemistry of Organosilicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, part 2, chap. 16; (d) T. L. Morkin and W. J.

Leigh, *Acc. Chem. Res.*, 2001, **34**, 129–136; (e) T. L. Morkin, T. R. Owens and W. J. Leigh, in *The Chemistry of Organosilicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 2001, vol. 3, chap. 17, 949–1026; (f) L. E. Gusev'nikov, *Coord. Chem. Rev.*, 2003, **244**, 149–240; (g) V. Y. Lee and A. Sekiguchi, *Organometallics*, 2004, **23**, 2822–2834; (h) H. Ottosson and P. G. Steel, *Chem.-Eur. J.*, 2006, **12**, 1576–1585.

- 2 For reviews, see: (a) K. M. Baines and W. G. Stibbs, *Adv. Organomet. Chem.*, 1996, **39**, 275–324; (b) J. Escudié and H. Ranaivonjatovo, *Adv. Organomet. Chem.*, 1999, **44**, 113–174; (c) J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Coord. Chem. Rev.*, 1994, **130**, 427–480; (d) N. Tokitoh and R. Okazaki, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, ed. Z. Rappoport, Wiley and Sons, New York, 2002, vol. 2, chap. 13, 843–901.
- 3 (a) M. Lazraq, C. Couret, J. Escudié, J. Satgé and M. Dräger, *Organometallics*, 1991, **10**, 1771–1778; (b) J. Barrau, G. Rima, M. El Amine and J. Satgé, *Synth. React. Inorg. Met.-Org. Chem.*, 1988, **18**, 317–324; (c) N. J. Mosey, K. M. Baines and T. K. Woo, *J. Am. Chem. Soc.*, 2002, **124**, 13306–13321.
- 4 M. Lazraq, J. Escudié, C. Couret, J. Satgé and M. Soufiaoui, *Organometallics*, 1992, **11**, 555–558.
- 5 S. Ech-Cherif El Kettani, M. Lazraq, H. Ranaivonjatovo, J. Escudié, H. Gornitzka and F. Ouhsaine, *Organometallics*, 2007, **26**, 3729–3734.
- 6 G. Delpon-Lacaze, C. Couret, J. Escudié and J. Satgé, *Main Group Met. Chem.*, 1993, **16**, 419–433.
- 7 N. Wiberg and C.-K. Kim, *Chem. Ber.*, 1986, **119**, 2980–2994.
- 8 In the case of the silene (Me₃Si)₂Si=C(OSiMe₃)R (R = *t*Bu, Ad) produced by photolysis, a [2 + 4] cycloaddition occurred between the Si=C double bond and the two C=O double bonds of benzil; see A. Naka and M. Ishikawa, *J. Organomet. Chem.*, 2003, **685**, 162–167.
- 9 A [2 + 4] cycloaddition leading to a six-membered ring derivative has also been reported between the Ge=P double bond of the phosphagermene Mes*P=GeMes₂ (Mes* = 2,4,6-tri-*tert*-butylphenyl) and the two C=O double bonds of benzil; see A. Kandri Rodi, J.-P. Declercq, A. Dubourg, H. Ranaivonjatovo and J. Escudié, *Organometallics*, 1995, **14**, 1954–1960.
- 10 The transient germavinylidene [Me₃SiN=P(Ph₂)₂]₂C=Ge: possesses both a Ge=C double bond and a germylene function. Reaction with benzil occurs exclusively on the germanium atom by a [1 + 4] cycloaddition, the Ge=C double bond being not involved; see W.-P. Leung, K.-W. Kan, C.-W. So and T. C. W. Mak, *Organometallics*, 2007, **26**, 3802–3806.
- 11 (a) K. M. Baines and W. G. Stibbs, *Coord. Chem. Rev.*, 1995, **145**, 157–200; (b) C. E. Holloway and M. Melnik, *Main Group Met. Chem.*, 2002, **25**, 185–266.
- 12 Cambridge Crystallographic Data Centre, CSD version 5.29 updates (Jan 2008).
- 13 R. Sustmann and M. Felderhoff, *Heterocycles*, 1995, **40**, 1027–1033.
- 14 C. Couret, J. Escudié, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.*, 1987, **109**, 4411–4412.
- 15 G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467–473.
- 16 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.