rus analogue of 3,4-dihydrobenzvalene or as a P_4 tetrahedron open at one edge and bridged by a P_2R_2 unit. The considerable stability of 3 toward air may be ascribed to the good steric shielding of the phosphorus framework by the pentamethylcyclopentadienyl ligands.

The syntheses of **2** and **3** from **1** are further examples of the preparative utility of the labile phosphorus–carbon bond in pentamethylcyclopentadienyl-substituted phosphorus compounds.[9c, 11] Clearly, the new cyclophosphanes **2** and **3** with their functionalized P_6R_x frameworks have promising synthetic potential.[11d]

Experimental Procedure

2: A solution of **1** (3.40 g, 6.82 mmol) in 35 mL of benzene was refluxed for 20 h. The solvent was then removed under vacuum from the clear, orange reaction solution until the viscous residue (ca. 3.5 g) began to form bubbles. Shortly after addition of 7 mL of *n*-hexane, the deep orange oil solidified to a yellow crystalline mass. After removal of the supernatant liquid, **2** was recrystallized from *n*-hexane. Yield: 2.05 g (66%) **2** · n-C_6H_{14}; correct elemental analysis. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.9–2.2 (complex multiplet; C_5Me_5, n-C_6H_{14}). ^{13}C NMR (75 MHz, C_6D_6): δ = 11.0–23.0 (Me), 57.4–59.7 (P-C), 134.8, 135.5, 136.0, 136.4, 139.7, 141.0, 141.6, 141.7 (sp^2-C). ^{31}P NMR (121 MHz, C_6D_6): δ = 78 (2P), 60 (1P), −121 (2P), −129 (1P). MS (*m/z*; rel. int.): $P_6(C_5Me_5)_3^{\oplus}$ (591; 18), $P_6(C_5Me_5)_2^{\oplus}$ (456; 2), $P_3(C_5Me_5)_2^{\oplus}$ (363; 4), $P_6(C_5Me_5)^{\oplus}$ (321; 34), $C_5Me_5^{\oplus}$ (135; 100).

3: **2** · n-C_6H_{14} (5.50 g, 6.77 mmol) was refluxed in 70 mL of xylene for 45 min. After removal of the solvent, the orange residue was treated with 20 mL of *n*-hexane. The precipitated pale yellow powder (ca. 2.5 g) was filtered off and recrystallized several times from *n*-hexane. Yield: 1.42 g (46%) **3**; correct elemental analysis. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.3–2.1, ^{13}C NMR (75 MHz, C_6D_6): δ = 10.9–21.7 (Me), 57.4 (P-C), 136.8, 137.7, 139.5, 140.2 (sp^2-C). ^{31}P NMR (121 MHz, C_6D_6): δ = 105, 70, −237 (intensities 1:1:1). MS (*m/z*; rel. int.): $M^{\oplus}$ (456; 9), $P_6(C_5Me_5)^{\oplus}$ (321; 44), $C_5Me_5^{\oplus}$ (135; 100).

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CAS Registry numbers: **1**, 114029-17-3; **2**, 113924-88-2; **3**, 120295-56-9.

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[5] The thermolysis of **1** in xylene instead of benzene leads directly to **4**. The bis(pentamethylcyclopentadienyl) formed according to Equation (a) can be detected in the reaction solution in each case.

[6] The approximate contributions of the coupling constants were determined by analysis of the spectrum according to the rules for first-order spectra. Refinement of the parameters with the computer program PANIC (version 840419.0; Bruker) led to complete agreement of the calculated with the recorded NMR spectrum. AA'BB'X_2-type spectrum: contributions of the coupling constants in Hz (numbering of the centers as in Fig. 1): ^1J(P(1), P(2)) = ^1J(P(1a),P(2a)) = 387, ^1J(P(2),P(3, 3a)) = ^1J(P(2a),P(3, 3a)) = 217, ^1J(P(1), P(1a)) = 386, ^2J(P(1), P(2a)) = ^2J(P(1a), P(2)) = 8, ^2J(P(1), P(3, 3a)) = ^2J(P(1a), P(3, 3a)) = 0.5, ^2J(P(2), P(2a)) = 56.

[7] **3** forms monoclinic crystals: $C2/c$, a = 1104.4, b = 1308.2, c = 1684.2 pm, β = 106.4°, V = 2334.4 × 10^6 pm^3, Z = 4, ρ_{calcd} = 1.30 g cm^{-3}; solution of the structure by direct methods (SHELXTL), R = 0.052 for 1939 unique reflections with $F_o > 3.92\,\sigma(F_o)$, Syntex P2$_1$ four-circle diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-53719, the names of the authors, and the journal citation.

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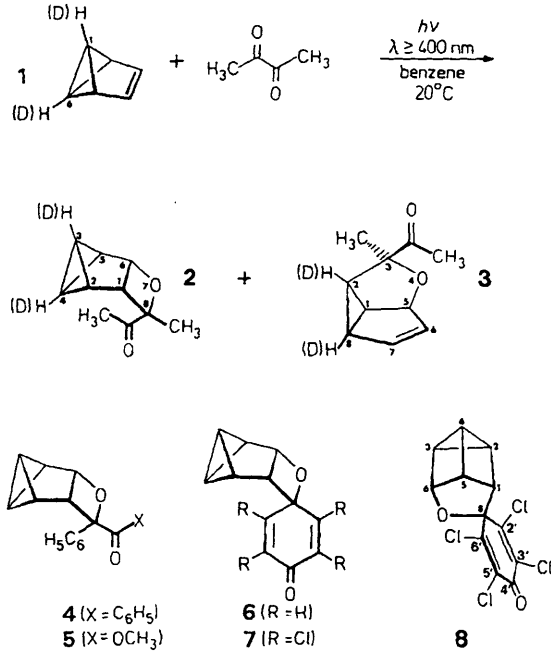
Photocycloadditions of Benzvalene**

By *Manfred Christl** and *Max Braun*

In 1975, *Katz* and *Turro* et al.[1] reported that the sensitized photolysis of benzvalene **1** can lead to two rearrangements. Transformation to benzene occurs with sensitizers with a triplet energy $E_T > 65$ kcal mol^{-1}, whereas automerization (1,3-C migration) is induced by those with $E_T <$ 63 kcal mol^{-1}. Although the sensitizers used were mainly ketones, which are typical substrates for the Paterno–Büchi reaction,[2] the authors mentioned no products with oxetane structure. In view of the high reactivity of benzvalene toward a wide variety of electrophiles,[3] we wanted to know whether, besides the isomerizations noted above, photochemical cycloadditions of **1** take place.

Irradiation[4] of **1**[5] in the presence of acetone and benzophenone (E_T = 78 and 69 kcal mol^{-1}, respectively[2a]) resulted in the formation of benzene. However, with biacetyl (E_T = 56 kcal mol^{-1} [2a]), benzil (54 kcal mol^{-1} [2a]), methyl phenylglyoxylate (61.9 kcal mol^{-1},[6a] irradiation at −30 °C), 1,4-benzoquinone (50 kcal mol^{-1} [2a]), and chloranil (56.4 kcal mol^{-1},[6b] irradiation at −30 °C), the oxetanes **2** (19%), **4** (22%), **5** (38%), **6** (25%), and **7** (51%), respectively, were obtained.[7] In the experiment with biacetyl, we observed, in addition to **2**, the oxadihydrosemibullvalene **3** (**2**:**3** ≈ 30:1), which is also accessible, together with a small amount of its diastereomer, in 48% yield by treatment of **2** with $AgBF_4$ in $CDCl_3$ at 20 °C.[7] The experiment with chloranil afforded pure **7** only at −30 °C; at 20 °C, besides **7**, the rearrangement product **8**[7] (**7**:**8** = 4:1) was formed. For selected physical data for **2**–**8**, see Table 1.



[*] Prof. Dr. M. Christl, Dipl.-Chem. M. Braun
Institut für Organische Chemie der Universität
Am Hubland, D-8700 Würzburg (FRG)

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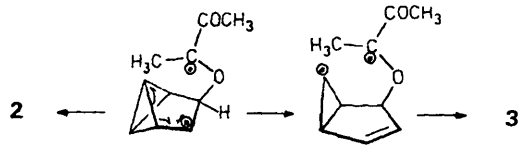
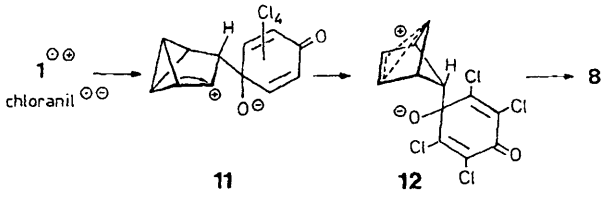
The formation of **3** confirms the multistep mechanism of the Paterno–Büchi reaction.[2] Compound **1** and biacetyl in its triplet state presumably give the diradical **9**, which can then either cyclize to **2** or undergo a cyclopropylmethyl–homoallyl rearrangement,[3a] to afford **10**, provided that, of the two C–C bonds in question in **9**, the bond *cis* to the biacetyl moiety breaks. Diradical **10** would then collapse to **3**. In agreement with this mechanism, [1,6-D_2]benzvalene yields the dideuterated products [3,4-D_2]-**2** and [2,8-D_2]-**3**.



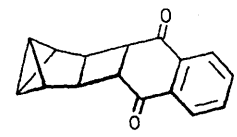
9 **10**

The finding that the labels in **2** are limited to positions 3 and 4[8] rules out the automerization of **1** by the excited sensitizer biacetyl. We arrived at the same conclusion by recovering unused [D_2]-**1** and allowing it to react with 2,4,6-trimethylbenzonitrile oxide. In the resulting dihydroisoxazole,[9] we found the deuterium atoms also restricted to the bicyclobutane bridgehead positions.[8] Interestingly, *Katz* and *Turro* et al.[1] included biacetyl in their table of sensitizers but did not enter a quantum yield for the automerization of **1**. The latter was given as ca. 0.2 for benzil as sensitizer. We have now confirmed that excited benzil effects the automerization of **1**. Adduct [D_2]-**4** was obtained from [1,6-D_2]-**1** with the ratio of the labels in positions 1(6), 2(5), and 3(4) being 1:3:45.[8] Analysis of the 2,4,6-trimethylbenzonitrile oxide adduct revealed that the labels in unused [D_2]-**1** were more evenly distributed, namely in a ratio of 1:2:4 in the positions corresponding to those in **4**.[8] Irradiation of 1,4-benzoquinone and 2-benzoylthiophene (see below) in the presence of [1,6-D_2]-**1** did not lead to a 1,3-C migration in [1,6-D_2]-**1**. Whether benzvalene **1** undergoes automerization in the presence of ketones in the triplet state (E_T < 63 kcal mol^{-1}), therefore, is a question of relative reaction rates. With biacetyl, 1,4-benzoquinone, and 2-benzoylthiophene, the cycloaddition occurs appreciably faster than the energy transfer required for automerization of **1**; the two rates are similar in the case of benzil.

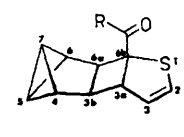
The structure of the product **8** indicates that it is not formed via a diradical analogous to **9**. A radical ion pair is known to be formed upon irradiation of chloranil in the presence of a donor;[10a] for **1** as donor, this was shown by CIDNP signals of **1** and benzene.[10b] Thus, **8** is presumably formed via the radical ion pair, which collapses to zwitterion



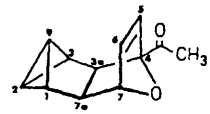
11 **12**



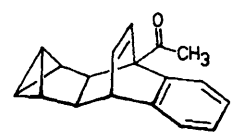
13



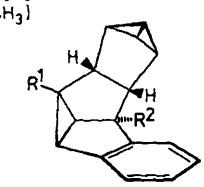
14 (R=C_6H_5)
15 (R=CH_3)



16



17



18 (R^1=$COCH_3$, R^2=H)
19 (R^1=H, R^2=$COCH_3$)

Table 1. Selected physical data for **2**–**8** and **13**–**19**; the boiling point always refers to the temperature measured in the kugelrohr distillation apparatus; the assignment of the bands in the NMR spectra is based on NOE effects and ^{1}H–^{13}C correlations.

2: b.p. 30–50 °C/0.05 torr. IR (CCl_4): $\tilde{\nu}$ = 1713 cm^{-1} (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (s; 8-CH_3), 2.12 (dtt, J(3,4) = 8.8, J(2,4) = J(4,5) = 1.8, J(1,4) = J(4,6) = 1.0 Hz; 4-H), 2.17 (br.dt, J(2,3) = J(3,5) = 1.7 Hz, 3-H), 2.25 (s; CO-CH_3), 2.31 (br.dq, J(2,5) = 4.5, J(1,2) = 1.7 Hz; 2-H), 2.54 (dq, J(5,6) = 1.8 Hz; 5-H), 2.69 (ddd, J(1,6) = 6.0 Hz; 1-H), 4.71 (br.dd; 6-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.2 (C-4), 8.8 (C-3), 24.8 and 25.2 (2 CH_3), 35.8 (C-2), 40.5 (C-5), 49.8 (C-1), 80.1 (C-6), 87.2 (C-8), 213.6 (C=O)

3: b.p. 30–50 °C/0.05 torr. IR (CCl_4): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40 (s; 3-CH_3), 2.05 (dddd, J(2,8) = 6.6, J(1,8) = 6.0, J(7,8) = 2.4, J(6,8) = 0.6 Hz; 8-H), 2.17 (s; CO-CH_3), 2.27 (ddd, J(1,2) = 7.7, J(2,6) = 0.6 Hz; 2-H), 2.96 (dddd, J(1,5) = 4.9, J(1,6) = 0.5 Hz; 1-H), 5.19 (ddd, J(5,6) = 2.0, J(5,7) = 0.6 Hz; 5-H), 5.46 (ddq, J(6,7) = 5.4 Hz; 6-H), 5.84 (ddd; 7-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.8 and 26.5 (2 CH_3), 31.7, 36.6 and 46.0 (C-1, C-2, C-8), 87.0 (C-5), 90.2 (C-3), 130.0 and 135.9 (C-6, C-7), 215.1 (C=O)

4: m.p. 85–86 °C. IR (KBr): $\tilde{\nu}$ = 1670 cm^{-1} (C=O)

5: m.p. 62–63 °C. IR (KBr): $\tilde{\nu}$ = 1735 cm^{-1} (C=O)

6: m.p. 72–73 °C. IR (KBr): $\tilde{\nu}$ = 1667, 1661 (C=O), 1627, 1602 cm^{-1} (C=C)

7: m.p. 140–142 °C. IR (KBr): $\tilde{\nu}$ = 1678 (C=O), 1600, 1568 cm^{-1} (C=C)

8: m.p. 163–165 °C. IR (KBr): $\tilde{\nu}$ = 1680 (C=O), 1607, 1574 cm^{-1} (C=C). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.19 (dddd, J(2,5) = 4.7, J(2,3) = 4.5, J(2,4) = 3.2, J(1,2) = 2.6 Hz; 2-H), 1.70 (tdd, J(3,5) = 4.5, J(3,4) = 3.2, J(3,6) = 2.2 Hz; 3-H), 1.98 (td, J(4,5) = 1.0 Hz; 4-H), 2.14 (dd, J(1,5) = 4.5 Hz; 1-H), 2.60 (quint. d, J(5,6) = 4.7 Hz; 5-H), 4.58 (dd; 6-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.5 and 17.3 (C-2, C-3), 22.3 (C-4), 48.6 (C-5), 59.7 (C-1), 82.4 (C-6), 87.3 (C-8), 128.8 and 131.1 (C-3', C-5'),153.4 and 153.7 (C-2', C-6'), 169.9 (C-4')

13: m.p. 155–156 °C. IR (KBr): $\tilde{\nu}$ = 1665 (C=O), 1592, 1585 cm^{-1} (C=C)

14: m.p. 108–110 °C. IR (KBr): $\tilde{\nu}$ = 1679 (C=O), 1594, 1578 cm^{-1} (C=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (br.s, 5-H, 7-H), 1.94 (dq, J(4,6) = 4.3, J(6.6a) = J(5,6) = J(6,7) = 1.7 Hz; 6-H), 2.29 (dq, J(4,5) = J(3b, 4) = J(4,7) = 1.7 Hz; 4-H), 2.38 (ddd, J(3b,6a) = 7.3, J(3a,3b) = 3.8 Hz; 3b-H), 3.11 (br.d; 6a-H), 3.86 (≈ tt, J(3,3a) = 3.5, J(2,3a) ≈ J(3a,6a) ≈ 1.1 Hz; 3a-H), 5.63 (dd, J(2,3) = 5.9 Hz; 3-H), 6.09 (dd; 2-H), 7.47 (*m*-H), 7.54 (*p*-H), 7.91 (*o*-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.9 (C-7), 6.6 (C-5), 37.3 (C-6), 38.3 (C-4), 45.9 (C-3b), 52.7 (C-3a), 55.8 (C-6a), 63.0 (C-6b), 123.7 (C-3), 124.9 (C-2), 128.6 (*m*-C), 128.9 (*o*-C), 133.0 (*p*-C), 135.1 (*ipso*-C), 195.5 (C=O)

15: b.p. 50–80 °C/0.01 torr. IR (neat): $\tilde{\nu}$ = 1705 cm^{-1} (C=O).

16: b.p. 80 °C/0.01 torr. IR (CCl_4): $\tilde{\nu}$ = 1711 cm^{-1} (C=O). ^{1}H NMR (440 MHz, C_6D_6): δ = 1.35 (dtd, J(1,3) = 4.5, J(1,2) = J(1,9) = 1.8, J(1,7a) = 1.0 Hz; 1-H), 1.63 (dtt, J(2,9) = 8.3, J(3,9) = 1.8, J(3a,9) = J(7a,9) = 1.2 Hz; 9-H), 1.68 (dt, J(2,3) = 1.8 Hz; 2-H), 1.84 (≈ dq, J(3,3a) = 1.1 Hz; 3-H), 2.07 (s; CH_3), 2.53 (dt, J(3a,7a) = 8.1 Hz; 3a-H), 2.58 (ddt, J(7,7a) = 4.6 Hz; 7a-H), 4.39 (dd, J(6,7) = 1.7 Hz; 7-H), 5.81 (dd, J(5,6) = 5.7 Hz; 6-H), 6.20 (d; 5-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 5.6 and 9.3 (C-2, C-9), 25.9 (CH_3), 33.3 and 33.8 (C-1, C-3), 49.8 (C-7a), 51.9 (C-3a), 80.4 (C-7), 94.4 (C-4), 132.6 and 134.2 (C-5, C-6), 207.6 (C=O)

17: b.p. 140 °C/0.01 torr. IR (CCl_4): $\tilde{\nu}$ = 1711 cm^{-1} (C=O)

18: m.p. 128–130 °C. IR (KBr): $\tilde{\nu}$ = 1676 cm^{-1} (C=O)

19: oil. IR (CCl_4): $\tilde{\nu}$ = 1708 cm^{-1} (C=O)

11. A Wagner–Meerwein rearrangement in the cationic moiety of **11** involving migration of the bicyclobutane bridgehead carbon atom *trans* to the anionic moiety[3] would then have to occur to give **12**, which would subsequently yield **8**.

In contrast to the reaction with 1,4-benzoquinone, irradiation[4] of **1**[5] with 1,4-naphthoquinone (E_T = 57 kcal mol^{-1}[6c]) at −30 °C gave the cyclobutane **13**[7] (17%). Motivated by the work of *Cantrell*,[11] we also employed 2-benzoylthiophene (62.6 kcal mol^{-1}[11]) at room temperature as well as 2-acetylthiophene (64.5 kcal mol^{-1}[11]) and 2-acetylfuran (64.9 kcal mol^{-1}[11]) at −30 °C and obtained the [2 + 2] cycloadducts **14** (21%), and **15** (27%) as well as the [4 + 2] cycloadduct **16** (19%) together with its diastereomer (6%).[7] At −30 °C, excited 1-acetylnaphthalene (56.4 kcal mol^{-1}[6a]) and **1**[5] gave initially the [4 + 2] cycloadduct **17** (25%). Upon further irradiation, however, **17** was converted at a similar rate into **18** (41%) and **19** (9%)[7] (di-π-methane rearrangement). Selected physical data for **13**–**19** are given in Table 1.

We obtained no cycloadduct from **1** and cyclopent-2-en-1-one (E_T = 74 kcal mol^{-1}[2a]). In conclusion, **1**, too, can undergo photochemical cycloadditions, provided that the reaction partner has a triplet energy E_T < 65 kcal mol^{-1}.

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CAS Registry numbers: **1**, 659-85-8; **2**, 120229-54-1; **3** isomer 1, 120229-55-2; **3** isomer 2, 120328-37-2; **4**, 120229-56-3; **5**, 120229-57-4; **6**, 120229-58-5; **7**, 120262-48-8; **8**, 120229-59-6; **13**, 120229-60-9; **14**, 120229-61-0; **15**, 120229-62-1; **16** isomer 1, 120229-63-2; **16** isomer 2, 120328-38-3; **17**, 120229-64-3; **18**, 120262-49-9; **19**, 120220-65-4; $(MeCO)_2$, 431-03-8; $(PhCO)_2$, 134-81-6; methylphenylglyoxylate, 15206-55-0; 1,4-benzoquinone, 106-51-4; chloranil, 118-75-2, 1,4-naphthoquinone, 130-15-4; 2-benzoylthiophene, 135-00-2; 2-acetylthiophene, 88-15-3; 2-acetylfuran, 1192-62-7; 1-acetylnaphthalene, 941-98-0.

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[2] a) N. J. Turro: *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, 1978; b) W. M. Horspool (Ed.): *Synthetic Organic Photochemistry*, Plenum Press, New York 1984.
[3] a) M. Christl, *Angew. Chem. 93* (1981) 515; *Angew. Chem. Int. Ed. Engl. 20* (1981) 529, and references cited therein; b) M. Christl, E. Brunn, F. Lanzendörfer, *J. Am. Chem. Soc. 106* (1984) 373.
[4] Light sources: medium-pressure Hg lamp (Hanovia, 450 W) in a Pyrex immersion well; radiation with λ < 400 nm was filtered out for colored substrates. 1,4-Naphthoquinone and 1-acetylnaphthalene were irradiated in a Rayonet® RPR 100 photoreactor with 350-nm and 300-nm light, respectively.
[5] We used **1** as a solution in hexane, which was diluted with the same or up to a fivefold quantity of benzene (experiments at room temperature) or toluene (experiments at −30 °C). The solutions, which were saturated with nitrogen before photolysis, were ca. 0.10 M in **1** and 0.05 M in the carbonyl compound.
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[7] The isolation was carried out by flash chromatography with petroleum ether/ethyl acetate on SiO_2 (**4**–**8**, **13**–**15**) or on basic Al_2O_3, activity III (**17**–**19**), and by preparative gas chromatography with Carbowax 20M on Volaspher® A 2 (**2**, **3**) or silicon SE 30 on Chromosorb® W (**16** and diastereomer). Elemental analyses as well as mass, IR, and NMR spectra support the proposed structures. Except for **13**, the configurations were determined from the characteristic magnitudes of the coupling constants or from NOE effects.
[8] Analysis by ^{2}H NMR spectroscopy.
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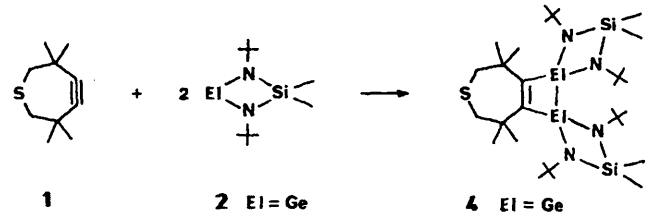
Synthesis and Structure of Digerma- and Distannacyclobutenes**

By *Adolf Krebs,** *Andrea Jacobsen-Bauer, Erhard Haupt, Michael Veith,** and *Volker Huch*

The first germirenes (germacyclopropenes) were synthesized by reaction of 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne **1** with suitable precursors of dialkylgermylenes (dialkylgermanediyls);[1] **1** combines high reactivity of the C–C triple bond with steric shielding of the resulting addition product, thereby often making possible the synthesis of systems otherwise accessible only with difficulty.[2] Since, until recently, no addition reactions of stannylenes to C–C triple bonds had been described,[3] we allowed **1** to react with the stabilized diaminogermylene **2**[4] as well as the diaminostannylene **3**[4] and obtained, in addition to the digermacyclobutene **4**, the first distannacyclobutene **5**. Compounds **4** and **5** are both dispiro compounds.

Addition of **1** to the red solution of **3** in various solvents (benzene, THF, *n*-hexane, diethyl ether) resulted in immediate precipitation of a yellow solid, whose ^{1}H and ^{13}C NMR spectroscopic data in concentrated solution indicate the formation of the 1:2 adduct **5**. In dilute solution, however, only the ^{1}H NMR signals of the starting materials were observed; in the ^{13}C NMR spectrum of **5**, the signal for the sp-hybridized C atom of **1** was absent. Proof for the presence of an Sn–Sn bond was provided by the ^{119}Sn NMR spectrum, which showed a signal at δ = + 155 (rel. to $Sn(CH_3)_4$; $J(^{119}Sn, ^{117}Sn)$ = 3723 Hz). Compound **4** was synthesized in a similar way from **1** and **2**.



1 **2** El = Ge, **3** El = Sn → **4** El = Ge, **5** El = Sn

The results of the X-ray structure analyses of **4** and **5** are given in Figure 1. They confirm the structure derived for **5** in solution. In both cases, there is a central four-membered ring containing two sp^2-hybridized carbon atoms and two four-fold coordinated germanium or tin atoms, respectively. Whereas in **5** the nearly planar peripheral diazasilastanna four-membered rings are perpendicular to the completely planar central distannacyclobutene (**5** has a C_2 axis in the crystal, the thiacycloheptene unit being disordered; only one of the two variants is shown in Fig. 1), the diazasilagerma four-membered rings in **4**, which are also planar, are twisted

[*] Prof. Dr. A. Krebs, Dipl.-Chem. A. Jacobsen-Bauer
Institut für Organische Chemie der Universität
Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (FRG)
Dr. E. Haupt
Institut für Anorganische und Angewandte Chemie der Universität Hamburg
Prof. Dr. M. Veith, Dr. V. Huch
Institut für Anorganische Chemie der Universität
Im Stadtwald, D-6600 Saarbrücken 11 (FRG)

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