Synthesis and Structures of Two Isomeric 4-Diazo-2,3,4,5-tetrahydrofuran-3-ones

by **Sergey A. Malashikhin**[a][b])[1]), **Anthony Linden**[b]), **Heinz Heimgartner***[b]), **Ludmila L. Rodina**[a]), and **Valerij A. Nikolaev***[a])

[a]) Department of Organic Chemistry, Saint-Petersburg State University, University prosp. 26, RU-198504 Saint-Petersburg (e-mail: vnikola@vn6646.spb.edu)

[b]) Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (phone: +41 44 635 4282; fax: +41 44 635 6812; e-mail: heimgart@oci.uzh.ch)

The two regioisomeric 4-diazo-2,3,4,5-tetrahydrofuran-3-ones **6** and **7** were prepared *via* the common intermediate 2,3,4,5-tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one (**8**). Diazo transfer with 2,4,6-triisopropylbenzenesulfonyl azide yielded **6**, whereas **7** was obtained *via* oxidation of the monohydrazone **12**, which was prepared selectively from tetrahydrofuran-3,4-dione **11**. The crystal structures of **6** and **7** have been established by X-ray crystallography.

1. Introduction. – The chemistry of aliphatic diazo compounds has a long tradition [1–4] and continues to attract the interest of chemists [5–8]. For example, diazoalkanes are used as 1,3-dipoles in 1,3-dipolar cycloadditions [9–11], and as precursors of carbenes or carbenoids in thermal, photochemical, and metal-catalyzed decomposition reactions [7][8][12]. Recently, naturally occurring diazo compounds, the kinamycines, gained attention [13], and different research groups published total syntheses of these pharmaceutically active compounds [14–16].

In the case of α-diazo carbonyl compounds, the elimination of N_2 leads *via* an α-ketocarbene or a concerted *Wolff* rearrangement to a ketene, which undergoes further reactions [17–19]. This reaction, which has been studied extensively in recent years, can be carried out photolytically [1][2][19][20], under metal catalysis [21][22], and thermally or under microwave irradiation [23]. No matter how the reaction is performed, the *Wolff* rearrangement is mostly characteristic for cyclic α-diazo ketones.

It was shown earlier that photolysis ($\lambda > 300$ nm) of 2,2,5,5-tetraalkyl-4-diazo-2,3,4,5-tetrahydrofuran-3-one (**1**) in dioxane/H_2O gives 2,2,4,4-tetraalkyloxetane-3-carboxylic acid (**2**) as the product of the *Wolff* rearrangement in almost quantitative yield [24][25] (*Scheme 1*).

Recently, it has been shown for the first time that irradiation of the 2,2,5,5-tetraphenyl-substituted 4-diazotetrahydrofuran-3-one (4-diazo-3-furanidone) **3** in THF/H_2O, along with the expected product of the *Wolff* rearrangment **4** (Nu = OH) gives rise to the adduct of **3** and THF, *i.e.*, **5**, in up to equal amounts with **4** and in overall yields of 85–87% [25] (*Scheme 1*). Compound **5** is formally an insertion product of the terminal N-atom of the diazo group of **3** into the H–C(α) bond of THF.

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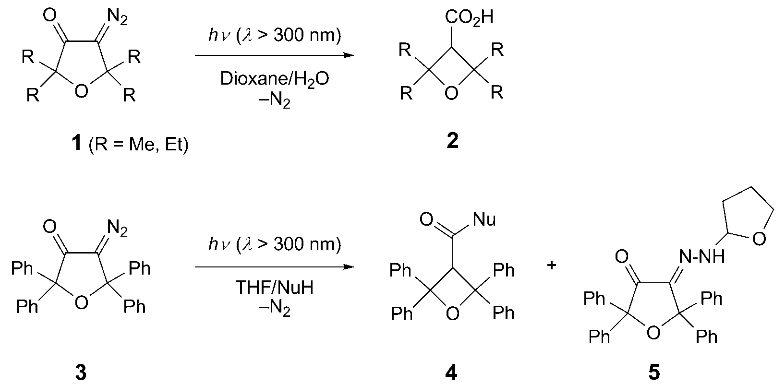
[1]) Part of the Diploma thesis of *S.A.M.*, Saint-Petersburg State University, 2005.

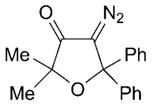
Scheme 1



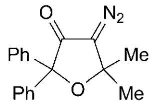
This photoreaction appears to be one of the rare examples of a chemical transformation of the photoexcited diazo ketone without elimination of N_2, *i.e.*, with preservation of the 'dinitrogen' unit in the product. Therefore, this reaction could become a powerful instrument for the identification and study of the nature of primary processes that take place during photolysis of diazo compounds.

Since the above mentioned reaction was observed only in the case of the 2,2,5,5-tetraphenyl derivative **3** and did not occur upon photolysis of corresponding tetraalkyl-substituted analogues **1** [24], it was reasonable to assume that the crucial influence on the outcome of this photoprocess was exerted by the Ph substituents adjacent to the diazo group.

With the aim of evaluating this assumption experimentally, the two regioisomeric diazofuranidones 4-diazo-2,3,4,5-tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one (**6**) and 4-diazo-2,3,4,5-tetrahydro-5,5-dimethyl-2,2-diphenylfuran-3-one (**7**) were synthesized.



6



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2. Results and Discussion. – 2.1. *Synthesis of the Diazofuranidones* **6** *and* **7**. The common intermediate of **6** and **7** is the known 2,3,4,5-tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one (**8**) [26]. It has been prepared starting with 2-methylbut-3-yn-2-ol (**9**), which, by subsequent treatment with EtMgBr in Et_2O, benzophenone, and a solution of NH_4Cl in H_2O, gave 4-methyl-1,1-diphenylpent-2-yne-1,4-diol (**10**) in 78% yield [27] (*Scheme 2*). Heating of **10** in $EtOH/H_2O$ in the presence of H_2SO_4 led to the tetrahydrofuran-3-one **8** (81%) [26][2]. The diazotation at C(4) was achieved *via* a

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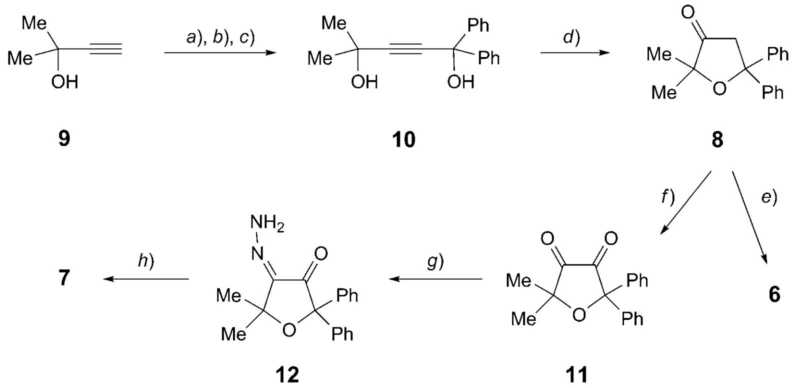
[2] This cyclization has been interpreted to occur *via* an initial acetylene-allene isomerization, followed by an intramolecular *Michael* addition [26].

diazo-transfer reaction in a two-phase system (PTC conditions)[3]: stirring a solution of **8** in benzene/aq. KOH and 2,4,6-triisopropylbenzenesulfonyl azide in the presence of 18-crown-6 and $Bu_4N^+Br^-$ at 40° gave the first isomer **6** as a pale yellow, crystalline material in 66% yield. Characteristic spectroscopic data are the IR absorptions (KBr) at 2093 and 1692 cm^{-1} for $C{=}N_2$ and $C{=}O$, respectively, and the corresponding ^{13}C-NMR signals at 64.4 and 197.0 ppm. Furthermore, the CI-MS (NH_3) shows the $[M+1]^+$ peak at m/z 293 and the base peak (100%) at m/z 265 ($[M+1-N_2]^+$).

Scheme 2



a) EtMgBr, Et_2O. *b*) $Ph_2C{=}O$. *c*) NH_4Cl, H_2O. *d*) H_2SO_4, EtOH, H_2O, Δ. *e*) 2,4,6-Triisopropylbenzenesulfonyl azide, benzene, aq. KOH, Bu_4NBr. *f*) SeO_2, Ac_2O. *g*) $NH_2NH_2 \cdot H_2O$. *h*) HgO, benzene, EtOH, KOH, Δ.

The second isomer **7** was prepared from **8** in a three-step process (*Scheme 2*). Oxidation of **8** with SeO_2 in Ac_2O yielded the diketone **11** (*ca.* 60%, ^1H-NMR). The crude product was dissolved in EtOH, and at 5°, $NH_2NH_2 \cdot H_2O$ was added to give the monohydrazone **12** in 89% yield. Finally, the oxidation of **12** to yield **7** was performed in benzene by treatment with HgO and a catalytic amount of KOH in EtOH at 50°. This isomer, obtained in 86% yield, is again a pale yellow crystalline product. In the IR spectrum (KBr), the indicative absorptions for $C{=}N_2$ and $C{=}O$ appear at 2092 and 1678 cm^{-1}, respectively, and in the ^{13}C-NMR spectrum ($CDCl_3$) at 65.3 and 192.7 ppm, respectively. In the CI-MS (NH_3), the base peak is at m/z 310 ($[M+NH_4]^+$), and other intense peaks appear at m/z 293 ($[M+1]^+$) and 265 ($[M+1-N_2]^+$).

Although these data are in accordance with the expected structures, they offer no unambiguous proof for the regioisomeric structures of the obtained diazo ketones **6** and **7**. For this reason, the structures have been determined by X-ray crystallography.

2.2. *Crystal Structures of* **6** *and* **7**. Suitable crystals for single-crystal X-ray diffraction were grown by crystallization of **6** from Et_2O/MeOH and **7** from hexane/Et_2O at room temperature. The molecular structures of **6** and **7** are shown in the *Figure*.

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[3] The attempted diazotations *via* formylation or trifluoroacetylation at C(4) [1][3] and reaction with 4-methylbenzenesulfonyl azide were unsuccessful.

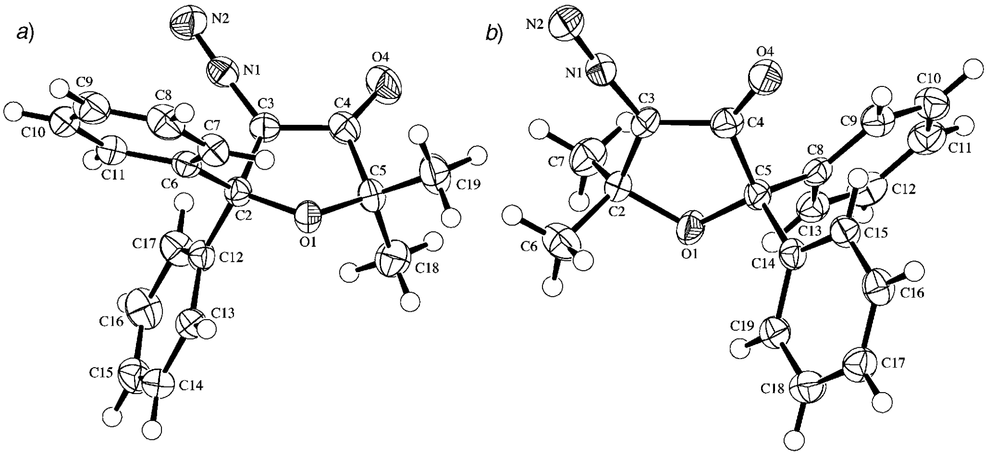

Figure. *ORTEP Plots* [28] *of the molecular structure of* a) **6** *and* b) **7** (arbitrary numbering of atoms; 50% probability ellipsoids)

The molecular structures of the two isomers are very similar. Whereas the five-membered ring of **6** has a shallow envelope conformation with the atom O(1) lying 0.329(1) Å from the plane defined by the other four ring atoms, the five-membered ring of the isomer **7** is almost planar. In both cases, the C(4)=O(4) as well as the diazo group are also lying in the plane defined by C(2)–C(3)–C(4)–C(5). The planes of the Ph groups at C(2) of **6** form angles of 46.37(11)° and 68.47(11)° with the plane defined by C(6)–C(2)–C(12), while the Ph groups at C(5) of **7** form angles of 79.2(2)° and 78.1(2)° with the corresponding plane defined by C(8)–C(5)–C(14). As a result, the intramolecular distances in **7** between the *ortho*-H-atoms H–C(9) and H–C(15), and the carbonyl O(4) are short (2.47 and 2.44 Å, resp.), however, the C–H ··· O angles are quite sharp (121 and 120°, resp.). Furthermore, the other *ortho*-H-atoms H–C(13) and H–C(19) are close to the ring O(1)-atom (2.36 and 2.38 Å, resp., C–H ··· O angles 102°). Thus, it seems that these 'short contacts' between two pairs of *ortho*-H- and two O-atoms, apparently force the tetrahydrofuran ring to adopt a planar conformation.

In the other isomer **6**, the distances between the *ortho*-H-atoms H–C(7) and H–C(13), and the ring O(1)-atom are 2.41 and 2.71 Å, respectively. Keeping in mind that the C=O absorptions of **6** in the IR and ^{13}C-NMR spectra are at 1692 cm^{-1} and 197.0 ppm, respectively, whereas the corresponding signals of **7** appear at 1678 cm^{-1} and 192.7 ppm, it is possible that weak C–H ··· O interactions (so-called 'short contacts') [29] are present in the case of **7**, although it cannot be excluded that the observed conformation results purely from intramolecular steric constraints. The same effect could also be responsible for the selectivity of the hydrazone formation of **11**, in which the C=O group neighboring Me$_2$C(2) reacts exclusively.

In conclusion, the isomeric 4-diazotetrahydrofuran-3-ones **6** and **7** were prepared selectively *via* the common 2,3,4,5-tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one (**8**), and their crystal structures were determined. These isomers will be used to elucidate the reasons of the different photochemical behavior of 2,2,5,5-tetraalkyl- and 2,2,5,5-tetraphenyl-substituted 4-diazotetrahydrofuran-3-ones.

We thank the analytical sections of our institutes for spectra and analyses, and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

1. *General.* All reagents and solvents were of reagent-grade and were used without further purification unless otherwise specified. Column chromatography (CC): flash chromatography, *Merck* silica gel *60* (particle size 0.040 – 0.063 mm) packed in glass columns; for each chromatography, the eluting solvent was optimized by TLC. Anal. TLC: *Macherey-Nagel POLYGRAM SIL N-HR/UV 254* or *ALOX N/UV 254*. M.p.: *Mettler FP-5* or *Büchi B-450* apparatus; uncorrected. IR Spectra: *Perkin-Elmer Spectrum-One* (FT-IR) spectrophotometer; in KBr; absorptions in cm^{-1}. ^{1}H- (300 MHz) and ^{1}H-decoupled ^{13}C-NMR (75.5 MHz) spectra: *Bruker AV-300* instrument; in $CDCl_3$; δ in ppm (TMS = 0 ppm), coupling constants J in Hz. CI-MS (NH_3): *Finnigan MAT-90* instrument. Elemental analyses were performed at the Institute of Organic Chemistry, University of Zürich.

2. *Preparation of Diazofuranidons* **6** *and* **7**. 2.1. *4-Methyl-1,1-diphenylpent-2-yne-1,4-diol* (**10**) was prepared from *2-methylbut-3-yn-2-ol* (**9**) and benzophenone according to [27]. Yield: 78%.

2.2. *2,3,4,5-Tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one* (**8**) was obtained from **10** by treatment with H_2SO_4 in EtOH/H_2O according to [26]. Yield: 81%. ^{1}H-NMR: 1.21 (*s*, 2 Me); 3.32 (*s*, CH_2); 7.20 – 7.28 (*m*, 2 arom. H); 7.29 – 7.32 (*m*, 4 arom. H); 7.39 – 7.42 (*m*, 4 arom. H). ^{13}C-NMR: 25.3 (2 Me); 48.1 (CH_2); 81.4, 82.7 (C(2), C(5)); 126.0, 127.4, 128.3 (10 arom. CH); 146.1 (2 arom. C).

2.3. *4-Diazo-2,3,4,5-tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3-one* (**6**). To a soln. of **8** (0.3 g, 1.4 mmol), 2,4,6-triisopropylbenzenesulfonyl azide [30] (0.4 g, 1.3 mmol), Bu_4NBr (0.12 g, 3.2 mmol), and 18-crown-6 (10 mg) in benzene (20 ml), 20 ml of a 60% aq. KOH soln. were added. After stirring the mixture at 40° for 4 h, it was extracted with Et_2O (3 ×). The combined org. layer was washed with sat. aq. NaCl soln. and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. CC (SiO_2; hexane/Et_2O) provided 0.22 g (66%) of **6**. M.p. 118.7 – 118.9°. IR: 3065*w*, 3046*w*, 2981*s*, 2932*w*, 2866*w*, 2680*w*, 2093v*s* (C=N_2), 1832*w*, 1806*w*, 1692v*s* (C=O), 1599*w*, 1491*m*, 1446*s*, 1376*s*, 1347v*s*, 1227*s*, 1185*m*, 1164*m*, 1153*m*, 1083*w*, 1022*s*, 1005*s*, 945*w*, 932*w*, 921*w*, 907*m*, 894*m*, 760*s*, 727*w*, 702*s*, 676*w*. ^{1}H-NMR: 1.35 (*s*, 2 Me); 7.30 – 7.38 (*m*, 10 arom. H). ^{13}C-NMR: 25.3 (2 Me); 64.4 (C=N_2); 84.2, 85.5 (C(5), C(2)); 128.5, 128.3, 126.4 (10 arom. CH); 143.8 (2 arom. C); 197.0 (C=O). CI-MS: 293 (23, $[M + H]^+$), 265 (100), 237 (22), 215 (6). Anal. calc. for $C_{18}H_{16}N_2O_2$ (292.34): C 73.96, H 5.52, N 9.58; found: C 73.94, H 5.53, N 9.58.

2.4. *2,3,4,5-Tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3,4-dione* (**11**). The mixture of **8** (3.3 g, 12.5 mmol) and SeO_2 (1.5 g, 13.5 mmol) in Ac_2O (25 ml) was stirred under reflux for 5 h. The precipitated Se was filtered off, and the soln. was concentrated under reduced pressure. The crimson residue (3.4 g) containing *ca.* 60% of **11** (according to ^{1}H-NMR) was used without further purification.

2.5. *2,3,4,5-Tetrahydro-2,2-dimethyl-5,5-diphenylfuran-3,4-dione 3-Hydrazone* (**12**). The soln. of 9.3 g of the crude **11** in abs. EtOH (35 ml) was cooled to 5°, and 50 ml of $NH_2NH_2 \cdot H_2O$ were added. The precipitate formed was filtered off, washed with H_2O, and dried. Recrystallization from hexane provided 6.1 g (89%) of **12**. Yellow solid. M.p. 113 – 114°. IR (CCl_4): 3450*s*, 3230*w*, 3210*w*, 3020*w*, 2950*m*, 2910*w*, 2830*w*, 1700*w*, 1670v*s* (C=O), 1580v*s*, 1510v*s*, 1480*s*, 1430*s*, 1350*w*, 1270*w*, 1170*w*, 1100*s*, 1010*m*, 910*m*, 730*s*, 680v*s*, 640*m*. ^{1}H-NMR: 1.45 (*s*, 2 Me); 7.21 – 7.36 (*m*, 6 arom. H); 7.47 – 7.53 (*m*, 4 arom. H); 10.06 (*s*, NH_2). ^{13}C-NMR: 29.5 (2 Me); 79.4, 85.8 (C(5), C(2)); 128.6, 128.1, 127.1 (6 arom. CH); 140.1 (C=NNH_2); 142.6 (2 arom. C); 196.0 (C=O). Anal. calc. for $C_{18}H_{18}N_2O_2$ (294.35): C 73.45, H 6.16, N 9.52; found: C 73.35, H 6.06, N 9.58.

2.6. *4-Diazo-2,3,4,5-tetrahydro-5,5-dimethyl-2,2-diphenylfuran-3-one* (**7**). To a soln. of **6** (1 g, 3.4 mmol) in benzene (20 ml), a few drops of sat. KOH soln. in EtOH and 3 g (13.7 mmol) of yellow HgO were added. The suspension was heated to 50° and stirred for 1 h. After filtration, the solvent was removed under reduced pressure, and the solid product was recrystallized from hexane to provide 0.85 g (86%) of **7**. M.p. 62.8 – 63.4°. IR: 3090*w*, 3058*m*, 2978*m*, 2930*w*, 2694*w*, 2092v*s* (C=N_2), 1813*w*, 1678v*s* (C=O), 1596*m*, 1487*m*, 1448*m*, 1382*m*, 1353v*s*, 1302*s*, 1190*m*, 1148*m*, 1101*w*, 1189*w*, 1047*s*, 1031*m*, 986*w*, 905*s*, 847*w*, 821*w*, 757*s*, 749*s*, 706*s*, 692*m*, 651*w*. ^{1}H-NMR: 1.61 (*s*, 2 Me); 7.23 – 7.26, 7.29 – 7.31, 7.47 – 7.51 (3*m*, 10 arom. H). ^{13}C-NMR: 28.9 (2 Me); 65.3 (C=N_2); 78.4 (C(5)); 90.3 (C(2)); 128.2, 127.8, 126.6 (10 arom. CH); 141.7 (2 arom. C); 192.7 (C=O). CI-MS: 310 (100, $[M + NH_4]^+$), 293 (66, $[M + H]^+$), 282

Table. *Crystallographic Data for Compounds* **6** *and* **7**

	6	**7**
Crystallized from	Et_2O/MeOH	hexane/Et_2O
Empirical formula	$C_{18}H_{16}N_2O_2$	$C_{18}H_{16}N_2O_2$
Formula weight	292.34	292.34
Crystal color, habit	yellow, tablet	yellow, prism
Crystal dimensions [mm]	0.10 × 0.25 × 0.25	0.22 × 0.25 × 0.27
Temp. [K]	160(1)	160(1)
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*
Z	8	8
Reflections for cell determination	3924	2951
2θ Range for cell determination [°]	4–55	4–50
Unit cell parameters a [Å]	15.2668(4)	14.0980(5)
b [Å]	12.2452(2)	13.2256(5)
c [Å]	16.4813(4)	15.8558(7)
V [Å^3]	3081.1(1)	2956.4(2)
D_x [g cm^{-3}]	1.260	1.313
μ(MoK_α) [mm^{-1}]	0.0833	0.0868
Scan type	ϕ and ω	ω
$2\theta_{(\max)}$ [°]	55	50
Total reflections measured	48432	29768
Symmetry independent reflections	3504	2601
Reflections with $I > 2\sigma(I)$	2548	1800
Reflections used in refinement	3503	2600
Parameters refined	202	202
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0434	0.0456
$wR(F^2)$ (all data)	0.1122	0.1180
Weighting parameters [a; b][a])	0.0494; 0.3967	0.0536; 0.11
Goodness of fit	1.083	1.051
Secondary extinction coefficient	0.008(1)	0.0064(9)
Final $\Delta_{\max}/\sigma$	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.25; −0.19	0.17; −0.20

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

(9), 265 (85), 237 (18). Anal. calc. for $C_{18}H_{16}N_2O_2$ (292.34): C 73.96, H 5.52, N 9.58; found: C 73.81, H 5.56, N 9.60.

3. *X-Ray Crystal-Structure Determination of* **6** *and* **7** (*Table* and *Fig.*)[4]). All measurements were performed on a *Nonius KappaCCD* diffractometer [31] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [32]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. The structures were solved by direct methods using SIR92 [33], which revealed the positions of all non-H-atoms. The non-H-

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[4]) CCDC-690001–690002 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. In each case, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [34a], and the scattering factors for H-atoms were taken from [35]. Anomalous dispersion effects were included in F_c [36]; the values for f' and f'' were those of [34b]. The values of the mass attenuation coefficients are those of [34c]. All calculations were performed using the SHELXL97 [37] program.

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