

Thermolysis of Oxazolin-5-ones, 12<sup>1)</sup>

## Formation of a Cage Compound by Thermolysis of 2-(4-Chlorophenyl)-2-(3,3-dimethylallyl)-4-phenyl-5(2*H*)-oxazolone

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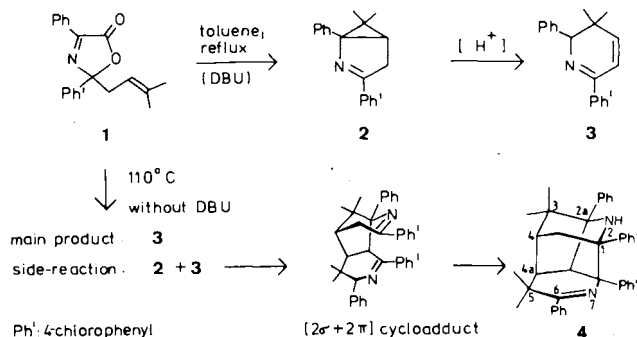
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During thermolysis of title compound **1**, the unusual cage compound **4** is formed (along with 2,3-dihydropyridine **3**); the structure of **4** was determined by X-ray structure analysis. The formation of **4** can be explained by dimerization of the intermediates **2** and **3**.

Thermolysis of 2-(4-chlorophenyl)-2-(3,3-dimethylallyl)-4-phenyl-5(2*H*)-oxazolone (**1**) in the presence of a strong base (e.g. 1,5-diazabicyclo[5.4.0]undec-5-ene) as proton scavenger affords 3-(4-chlorophenyl)-6,6-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**2**) as sole product in 80% yield<sup>2)</sup>. **2** is formed by means of an intramolecular 1,1-cycloaddition from an intermediary nitrilide<sup>2,3)</sup>.

When the reaction is carried out in melt or in solution without the addition of base, the formation of an insoluble compound **4** is observed in 23% yield. The main product is 6-(4-chlorophenyl)-2,3-dihydro-3,3-dimethyl-2-phenyl-pyridine (**3**), which had been obtained before on treatment of azabicyclohexene **2** with acids<sup>2)</sup> (Scheme 1).

### Scheme 1



The high-resolution mass spectrum of **4** gave a molecular composition of C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>Cl<sub>2</sub> which points to a dimerization product of **2** or **3**. Because the information obtained from the NMR spectra was insufficient to elucidate the structure of the dimer, this problem was solved by means of a single-crystal X-ray analysis.

As shown by Fig. 1, computed from the final atomic coordinates listed in Table 1, the structure of **4** incorporates a piperidine and a tetrahydropyridine ring, which are connected by three bonds thus forming a cage molecule. The flaps of two envelope-shaped and *cis*-

fused five-membered rings [the dihedral angle of their best planes is 68.0(1)<sup>°</sup>] are cross-linked thus closing two additional six-membered rings: a cyclohexane and a piperidine ring, which both assume chair conformations. The cyclohexane ring bears a tetrahydropyridine ring in 1,3-*diaxial* position. This fifth ring is of half-chair conformation due to the localized C=N bond [126.9(5) pm]. The phenyl substituent of this ring has a *pseudo-equatorial* orientation. The two 4-chlorophenyl moieties are bound to the cyclohexane ring *cis-equatorially*. The best planes of these phenyl rings make a dihedral angle of 65.3(1)<sup>°</sup>. The fourth phenyl substituent is linked to the *cis*-junction of the five-membered rings. It assumes a *pseudo-equatorial* position relative to the piperidine ring.

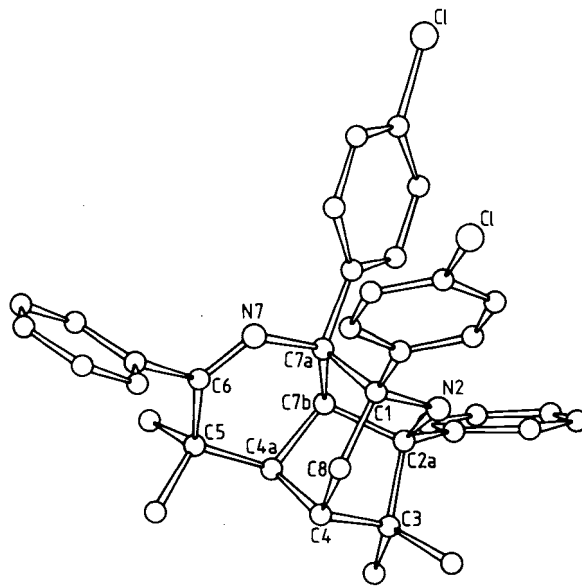


Fig. 1. Perspective view of the molecule **4** and numbering of atoms belonging to the cage skeleton (the hydrogen atoms are deliberately omitted)

The formation of **4** can be explained by reaction of the protonated dihydropyridine **3** with azabicyclohexene **2**, which yields a formal [2σ + 2π]-cycloadduct<sup>4)</sup>. The third bond between the two tetrahydropyridine rings may then be formed by intramolecular addition of a 2-azaallyl anion to the imino group present in the other ring. Certainly, other pathways for the formation of **4** can be envisioned, and the detailed mechanism awaits further investigations.

Table 1. Final fractional coordinates and temperature parameters of **4** with their e.s.d.'s in parentheses [ $B_{eq} = 4/3$  of the trace ( $BG$ ) where  $G$  is the metric tensor]

Atom	x/a	y/b	z/c	B(eq)
C(1)	0.69811(7)	1.19380(5)	0.18913(5)	3.52(6)
C(1)	0.78420(8)	0.60999(6)	0.75959(5)	4.35(8)
N(2)	0.7146(1)	0.6680(1)	0.2562(1)	2.4(1)
N(7)	0.3425(1)	0.8998(1)	0.3305(1)	2.2(1)
C(1)	0.5898(2)	0.6834(1)	0.3338(1)	2.2(2)
C(2a)	0.6446(2)	0.6902(1)	0.1563(1)	2.4(2)
C(3)	0.6113(2)	0.5812(1)	0.1704(1)	2.7(2)
C(4)	0.4723(2)	0.6026(1)	0.2461(1)	2.5(2)
C(4a)	0.3748(2)	0.7271(1)	0.1823(1)	2.2(2)
C(5)	0.2201(2)	0.7844(1)	0.2296(1)	2.3(2)
C(6)	0.2308(2)	0.8250(1)	0.3164(1)	2.3(2)
C(7a)	0.4820(2)	0.8101(1)	0.2675(1)	2.1(1)
C(7b)	0.4836(2)	0.7875(1)	0.1634(1)	2.2(1)
C(8)	0.5131(2)	0.5976(1)	0.3524(1)	2.7(2)
C(9)	0.7383(2)	0.4661(1)	0.2175(2)	3.8(2)
C(10)	0.5793(2)	0.5813(2)	0.0637(1)	3.1(2)
C(11)	0.5442(2)	0.7918(1)	0.2501(1)	2.1(1)
C(12)	0.6327(2)	0.9353(1)	0.1603(1)	2.4(2)
C(13)	0.6835(2)	1.0221(1)	0.1436(1)	2.7(2)
C(14)	0.6423(2)	1.0790(1)	0.2159(1)	2.6(2)
C(15)	0.5575(2)	1.0467(1)	0.3074(1)	2.5(2)
C(16)	0.5102(2)	0.9587(1)	0.3238(1)	2.4(2)
C(17)	0.6394(2)	0.6690(1)	0.4388(1)	2.4(2)
C(18)	0.7872(2)	0.7875(2)	0.4574(1)	3.8(2)
C(19)	0.8330(2)	0.6132(2)	0.5547(1)	3.4(2)
C(20)	0.7297(2)	0.6344(1)	0.6355(1)	2.9(2)
C(21)	0.5810(2)	0.6734(1)	0.6198(1)	2.9(2)
C(22)	0.5371(2)	0.6904(1)	0.5224(1)	2.8(2)
C(23)	0.1820(2)	0.8498(1)	0.3954(1)	2.3(2)
C(24)	0.1866(2)	0.7680(2)	0.4970(2)	3.8(2)
C(25)	-0.0856(2)	0.7897(2)	0.5738(2)	4.4(3)
C(26)	-0.1238(2)	0.8919(2)	0.5498(2)	3.9(3)
C(27)	-0.1297(2)	0.9735(2)	0.4504(2)	4.3(3)
C(28)	-0.0185(2)	0.9530(2)	0.3730(1)	3.7(2)
C(29)	0.7471(2)	0.7200(1)	0.0597(1)	2.4(2)
C(30)	0.6961(2)	0.7963(2)	-0.0404(1)	3.1(2)
C(31)	0.7920(2)	0.8285(2)	-0.1271(1)	3.7(2)
C(32)	0.9418(2)	0.7689(2)	-0.1154(1)	3.7(2)
C(33)	0.9953(2)	0.6924(2)	-0.0174(2)	4.8(3)
C(34)	0.8998(2)	0.6681(2)	0.0697(1)	3.4(2)
C(35)	0.1288(2)	0.8914(2)	0.1402(1)	3.5(2)
C(36)	0.1382(2)	0.7803(2)	0.2722(2)	2.9(2)

( $CDCl_3$ ) of the residue obtained by evaporation of the ether solutions showed the typical signals of **3**, which was not further characterized. 0.1 g of **4** was recrystallized from 25 ml of acetone to give colorless crystals, m. p. 262–263 °C, suitable for X-ray analysis. —  $^1H$ -NMR ( $CDCl_3$ ):  $\delta = 0.80, 1.18, 1.27, 1.36$  (each s, 12H), 1.80–2.30 (m, 5H), 3.29 (d,  $J = 7$  Hz, 1H), 6.71 (d,  $J = 9$  Hz, 2H), 6.93 (d,  $J = 9$  Hz, 2H), 7.00–7.20 (m, 4H), 7.27–7.69 (m, 10H). — MS (70 eV, DI, 180 °C):  $m/z$  (%) = 592/590 (75/100) [ $M^+$ ], 298/296 (32/97) [ $C_{19}H_{19}ClN$ ], 282/280 (28/80) [ $C_{18}H_{15}ClN$ ], 131, 91.

$C_{38}H_{36}Cl_2N_2$  (591.6)

Calcd. C 77.15 H 6.13 N 4.74

Found C 76.53 H 6.07 N 4.65

*X-ray Diffraction Analysis of 4*:  $C_{38}H_{36}Cl_2N_2$ , molecular mass 591.6; crystal dimensions 0.07, 0.20, 0.40 mm. **4** crystallizes in the triclinic space group  $P\bar{1}$  with the lattice parameters  $a = 995.2(1)$ ,  $b = 1350.1(3)$ ,  $c = 1354.9(1)$  pm;  $\alpha = 66.96(1)$ ,  $\beta = 78.28(1)$ ,  $\gamma = 65.41(1)^\circ$ ;  $V = 1521.6(4) \cdot 10^6$  pm $^3$ ;  $d_c = 1.29$  gcm $^{-3}$ ;  $Z = 2$ . An Enraf-Nonius CAD-4 diffractometer was used with monochromatic  $CuK\alpha$  radiation;  $\omega$ - $2\theta$ -Scan in the range of  $3.0^\circ < 2\theta < 150^\circ$ , at 296(1) K. Out of 5372 unique reflections, 4144 with  $F^2 > 3.0\sigma(F^2)$  were taken as observed. Empirical absorption correction ( $\mu = 21.6$  cm $^{-1}$ ) was applied by the use of the DIFABS program<sup>5)</sup>. Relative transmission coefficients ranged from 0.713 to 1.367. The structure was solved by direct methods (MULTAN 82). H atoms were entered in calculated positions. Anisotropic full-matrix least-squares treatment of the non-hydrogen atoms resulted in  $R = 0.046$  ( $R_w = 0.047$ ,  $R_{int} = 0.066$ ) for 379 parameters refined. Max.  $\Delta/\sigma = 0.038$ ; highest peak in the final difference map  $0.24(4) \cdot 10^{-6}$  e/pm $^3$ . Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53146, the names of the authors, and the journal citation.

#### CAS Registry Numbers

1: 62045-65-2 / 3: 64329-75-5 / 4: 115119-01-2

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## Experimental

*1,7a-Bis(4-chlorophenyl)-3,3,5,5-tetramethyl-2a,6-diphenyl-2,2a,3,4,4a,5,7a,7b-octahydro-1H-2,7-diaza-1,4-methanocyclopenta[cd]indene (4)*: 1.0 g of **1** was heated at 110 °C for 10 h. After cooling to room temp., 15 ml of diethyl ether was added, and the precipitate was filtered and washed with diethyl ether to yield 0.2 g (23%) of **4**, m. p. 259–261 °C (dec.). The  $^1H$ -NMR spectrum

<sup>1)</sup> Part 11: S. Jendrzewski, W. Steglich, *Chem. Ber.* **114** (1981) 1337.

<sup>2)</sup> N. Engel, J. Fischer, W. Steglich, *J. Chem. Res. (S)* **1977**, 162.

<sup>3)</sup> J. Fischer, W. Steglich, *Angew. Chem.* **91** (1979) 168; *Angew. Chem., Int. Ed. Engl.* **18** (1979) 167.

<sup>4)</sup> K. Hasenrück, H.-D. Martin, B. Mayer, T. Urbanek, T. Zinres, R. Walsh, H.-D. Beckhaus, *Chem. Ber.* **120** (1987) 177.

<sup>5)</sup> N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.

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