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Generation and Fate of 1-Dewar-pyridin-3-olates and -2-olates. Synthesis of 1-Dewar-pyridin-3-ones ☆

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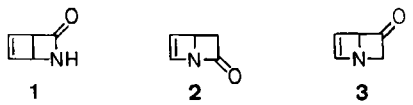
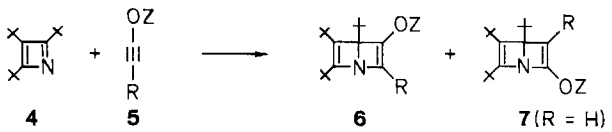
3-Oxy-1-azabicyclo[2.2.0]hexa-2,5-dienes ("3-oxy-1-Dewar-pyridines") **6a–d**, on cleavage of the enol ether or enol ester function, yield either 1-azabicyclo[2.2.0]hex-2-en-5-ones ("1-Dewar-pyridin-3-ones") **9** or 2-azabicyclo[3.1.0]hex-2-en-4-ones **11**, depending on the substituents and reaction conditions. Ester cleavage of 2-(benzoyloxy)-1-Dewar-pyridine **7a** with methyllithium does not furnish a 1-Dewar-2-pyridinone, but a dimer thereof, namely the tricyclic compound **14**.

Out of the three possible Dewar-pyridinones **1–3**, only **1** and derivatives thereof have been synthesized by several routes[1–3]. The most direct route to the molecular framework of **1**, photochemical isomerization of a 2-pyridinone, does not furnish a 1-Dewar-pyridin-2-one **2**; similarly, isomerization of 3-hydroxypyridines to 1-Dewar-pyridin-3-ones **3** has not been reported.



1 **2** **3**

In a recent communication[4], we have reported that cycloaddition of alkynyl esters and ethers **5** to 2,3,4-tri-*tert*-butylazete (**4**) yields 3-oxy-1-Dewar-pyridines **6** exclusively when disubstituted alkynes are used, whereas terminal alkynes (**5**, R = H) lead to a mixture of **6** and the regioisomeric 2-oxy-1-Dewar-pyridine **7**.



4 **5** **6** **7** (R = H)

Z = COPh, SiR_3, Tos, Et

The enol derivatives **6** and **7** appear to be ideal precursors of Dewar-pyridinones of type **2** and **3**, resp. In the following, we show that this strategy indeed leads to the molecular framework of **3**, but not of **2**. Furthermore, we report that under certain conditions intermediarily formed 1-Dewar-pyridin-3-olates undergo an unexpected and unprecedented rearrangement which ultimately yields 2-azabicyclo[3.1.0]-hex-2-en-4-ones.

Results

The results obtained with **6a–d** are summarized in Scheme 1 and Table 1. Ester cleavage of alkenyl benzoate **6a** either by hydroxide or by methyllithium affords only the 1-Dewar-3-pyridinone derivative **9a**. The identity of this novel heterocycle is established by the following spectroscopic data: The $\tilde{\nu}$(C=O) vibration at 1775 cm^{-1} indicates a cyclobutanone substructure. Although higher wave numbers of carbonyl stretching vibrations (1805–1820 cm^{-1}) have been reported for monocyclic 3-azetidinones[5,6], the value for **9a** agrees quite well with that of the alicyclic analogue (**9a**, C–CO_2tBu instead of N: 1765 cm^{-1} [7]). In the ^{13}C-NMR spectrum, chemical shifts of C-2 and C-3 are nearly the same as those of C-6 and C-5 in the precursor **6a**, thus indicating that the azetine moiety has remained intact. The adjacent carbonyl group causes a low-field shift of 18.0 ppm for C-4 with respect to **6a**. The C-6 methylene group, deshielded by two electronegative neighbors, appears in the expected region both in the ^{13}C-NMR (δ = 67.7) and in the ^{1}H-NMR spectrum (δ_A = 3.75, δ_B = 3.91, $|\,^2J\,|$ = 16.8 Hz).

Acidic hydrolysis of the (*tert*-butyldimethylsilyl) enol ether **6b** provides the substituted 1-Dewar-3-pyridinone **9b**. Its NMR and IR spectra closely resemble those of **9a**, taking into account the influence of the additional 6-phenyl substituent. Most importantly, δ(C-6) is now found at 80.5 and δ(6-H) at 5.18. Furthermore, the ^{1}H-NMR signals of the *t*Bu groups appear at δ = 0.70, 1.22, 1.26. The significant high-field shift of one of the *t*Bu signals as compared to **9a** (δ = 1.12, 1.20, 1.21) is explained by the *endo*-6-phenyl substitution, which brings the *t*Bu group at C-2 in the shielding region of the aromatic ring. A similar observation has been made for 4,5,6-tri-*tert*-butyl-*endo*-2-phenyl-1-aza-3-oxabicyclo[2.2.0]hex-5-ene[8]. The alternative assignment – an *exo*-6-phenyl ring which would shield the 4-*t*Bu group – is ruled out based on consideration of a molecular model; in this case, the two substituents, although in a 1,3-*cis*-relationship, point into opposite directions.

Not unexpectedly, the (triisopropylsilyl) enol ether **6c** cannot be cleaved with aqueous acid[9]. However, desilylation

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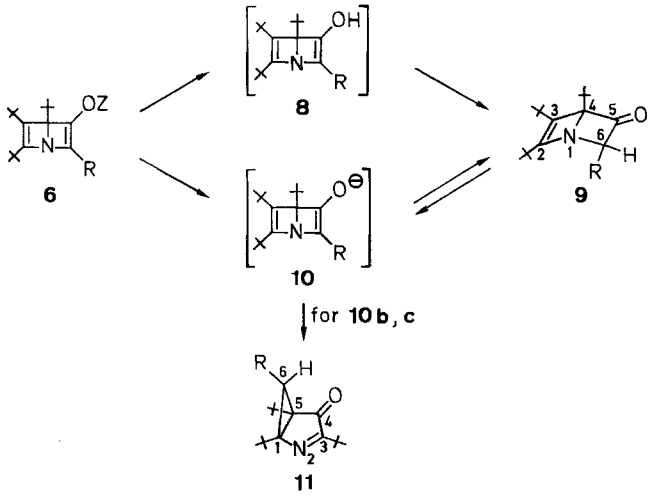
succeeds with caesium fluoride. Surprisingly, not the expected 1-Dewar-3-pyridinone **9b**, but the 2-azabicyclo-[3.1.0]hex-2-en-4-one **11b** is isolated, the structure of which has been established by an X-ray structure analysis (Figure 1). Similarly, alkaline cleavage of alkenyl sulfonate **6d** leads to **11c**, the ^{13}C-NMR spectrum of which is almost identical to that of **11b**, except for δ(C-6) and the additional *t*Bu group (Table 2). The unusually high chemical shifts of the cyclopropyl carbon atoms in **11b** and **11c** are due to a considerable part to the great influence of a *t*Bu substituent ($\Delta\delta(\alpha) \approx +25$ ppm[10]) and, for C-6, to the deshielding β effect of the hetero π substituents at the three-membered ring.

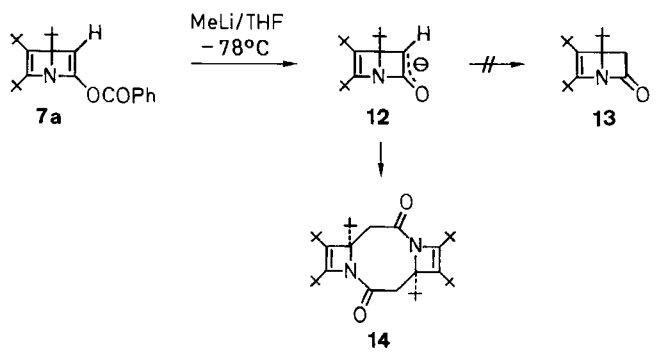
Scheme 1. For reaction conditions, see Table 1



6	R	Z
a	H	COPh
b	Ph	$SiMe_2tBu$
c	Ph	$SiiPr_3$
d	*t*Bu	$SO_2-C_6H_4-(4)-CH_3$

8-11	R
a	H
b	Ph
c	*t*Bu

Scheme 2



Ester cleavage of 2-(benzoyloxy)-1-Dewar-pyridine derivative **7a** with methyllithium does not furnish the expected 1-Dewar-pyridin-2-one **13** (Scheme 2). Instead, a product is isolated which, according to the mass spectrum, is a dimer of **13** and which has a strong IR absorption at 1648 cm^{-1} located in the typical range of carboxamides. An X-ray structure analysis has established structure **14** (Figure 2) and thus confirmed the spectroscopic findings. The two four-membered rings fused to the central perhydro-1,5-diazocine ring are *syn* to each other. Whereas the molecules has no twofold rotation axis in the crystalline state, a (time-averaged) symmetrical structure is indicated by the number of signals of the NMR spectra in solution. Formation of **14** is assumed to originate in a ring-opening reaction of the bicyclic enolate (or α-deprotonated carboxamide) **12**, leading to the anion of a (2-azetin-4-yl) ketene which then dimerizes.

Table 1. Cleavage of enol derivatives **6**

Enol Derivative	Reaction Conditions	Product	Yield [%]
6a	KOH (3 N), CH_3OH	9a	62
	MeLi, THF, -78 °C	9a	60
6b	HCl, H_2O, acetone	9b	58
6c	HCl, H_2O, acetone	no reaction	
	CsF, CH_3CN, CH_2Cl_2	11b	51
6d	KOH (3 N), CH_3OH, Δ *T*	11c	72

Table 2. ^{13}C-NMR data (100.6 MHz, $CDCl_3$, δ, *J* in Hz) for heterocycles **9** and **11**

	9a	9b	11b	11c
C-1	-	-	71.5	71.4
C-2	166.3	164.8	-	-
C-3	136.2	136.3	170.9	170.5
C-4	105.5	102.8	202.5	202.5
C-5	206.7	207.6	54.7	56.2
C-6	67.7	80.5	59.5	72.0
^1J(C,H)	*144.4*	*140.3*	*155.9*	*162.8*
CMe_3	31.8, 33.5, 33.9	32.3, 32.3, 33.9	33.3, 34.6, 34.8	33.0, 34.2, 34.3, 34.7
CMe_3	26.0, 29.2, 31.2	26.3, 29.5, 31.0	27.3, 31.3, 31.5	26.9, 31.2, 31.6, 32.5

The different outcome of the acidic hydrolysis of **6b** (to **9b**) and the fluoride-induced desilylation of **6c** (to **11b**) suggests that in the former case enol **8b** is formed primarily which then tautomerizes to ketone **9b**. In the latter case, enolate **10b** is generated which subsequently rearranges to furnish **11b**. In fact, when enolate **10b** is formed from **9b** (NaOMe/MeOH), compound **11b** is obtained again in 57% yield. However, an analogous treatment of **9a** does not furnish any **11a**; only unspecified decomposition takes place to a small extent.

The mechanism of the skeletal rearrangement of enolates **10b,c** is as yet a matter of speculation. Two tentative pathways are depicted in Scheme 3.

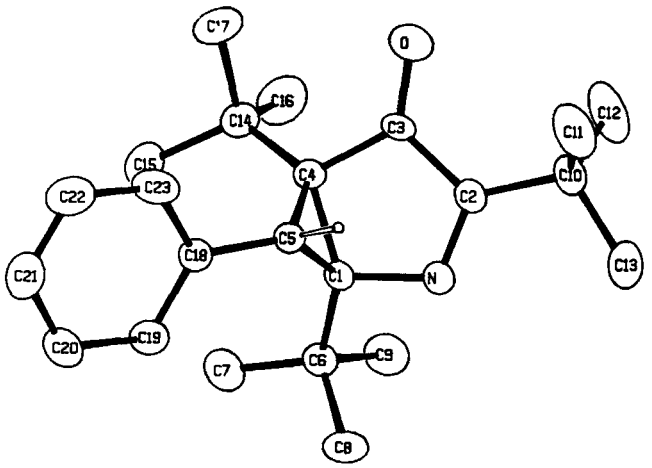


Figure 1. ORTEP plot of **11b**. Ellipsoids of thermal vibration represent a 33% probability. See Table 4 for selected bond lengths and angles. The five-membered ring is planar (deviations of individual atoms from the least-squares plane are ≤ 0.017 Å). The five-membered and three-membered rings include an angle of 101.7°

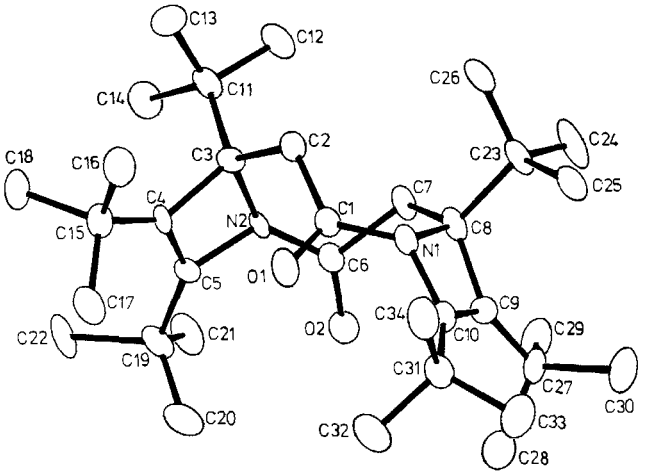
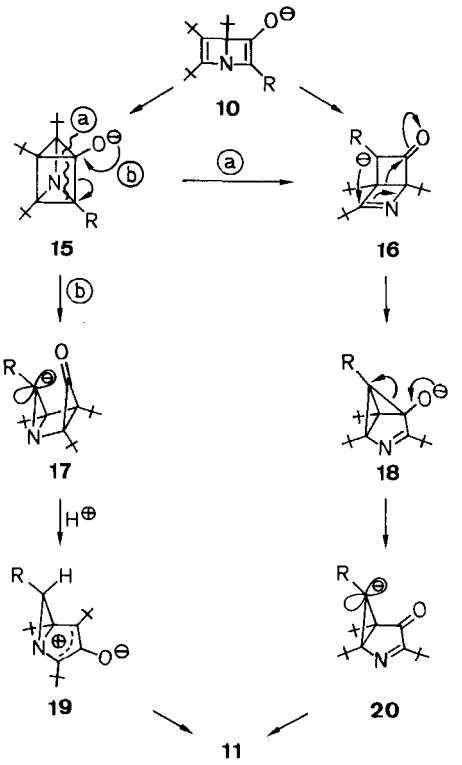


Figure 2. ORTEP plot of **14**. Ellipsoids of thermal vibration represent a 33% probability. Torsion angles [°] in the perhydro-1,5-diazocine ring: C1–C2–C3–N2, −42.7; C2–C3–N2–C6, −12.2; C3–N2–C6–C7, −42.2; N2–C6–C7–C8, 115.6; C6–C7–C8–N1, −43.2; C7–C8–N1–C1, −13.3; C8–N1–C1–C2, −38.4; N1–C1–C2–C3, 113.3

Valence isomerization of 1-Dewar-pyridines to azaprismanes has been observed before under photochemical, but never under thermal conditions[11]. We have found, that 3-oxy-1-Dewar-pyridines **6a** (2-Me instead of 2-H), **6b**, and **6d** do not isomerize in boiling toluene, and that upon irradiation at $\lambda = 300$ nm only unspecified decomposition takes place. Nevertheless, formation of azaprisman-olate **15** from **10** could be feasible as a Homo-Michael-type reaction. Retro-aldol-like reaction of **15** would lead to **17**, which is expected to be protonated immediately and to undergo a spontaneous isomerization of cyclopropanone to 2-oxallyl cation. Compounds of type **19** with CH instead of N are known to undergo a rapid [1,4] rearrangement with inversion of configuration at the migrating center[12]. In our case, this would indeed lead to **11** with an *exo*-6 substituent.

An alternative reaction pathway includes **16**, which could be formed by a [2 + 2] cycloreversion from azaprismane

Scheme 3



15 or perhaps directly from **10**. Rearrangement of **16** as indicated, ring-opening of the resulting cyclopropanolate **18**, and protonation of **20** would again lead to **11**.

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Experimental

NMR: $CDCl_3$ as solvent, TMS as internal standard; Varian EM 390 (^{1}H, 90 MHz), Bruker AM 400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz). – IR: Perkin-Elmer 397. – Elemental analyses: Perkin-Elmer EA 2400. – X-ray diffraction: Enraf-Nonius CAD4. – Melting points are corrected. – Column chromatography: Merck Lobar columns (LiChroprep SI 60, 40–63 μm, size A and B). – The synthesis of **6a–d** has been reported[4].

2,3,4-Tri-tert-butyl-1-azabicyclo[2.2.0]hex-2-en-5-one (**9a**)

Method A: Compound **6a** (0.278 g, 0.76 mmol) is dissolved in a 3 N solution of KOH in methanol (2 ml). After stirring for 1 h (precipitation of potassium benzoate starts after a few minutes), H_2O (5 ml) is added, and the mixture is extracted with ether (2 × 10 ml). The united organic extracts are washed with H_2O (5 ml), dried ($MgSO_4$), and purified by column chromatography (petroleum ether/ether, 5:1) to give **9a** (0.125 g, 62%) as a colorless oil. – IR (film): $\tilde{\nu} = 1775$ cm^{-1} (C=O), 1612 (C=C). – ^{1}H NMR (400 MHz): $\delta = 1.12$, 1.20, 1.21 (each s, 9H, *t*Bu), 3.75 and 3.91 (AB system, $|\,^2J\,| = 16.8$, CH_2).

$C_{17}H_{29}NO$ (263.4)
Calcd. C 77.51 H 11.10 N 5.32
Found C 77.1 H 11.1 N 5.2

Method B: A solution of methyllithium in ether (1.6 M, 0.6 ml) is added at −78°C to **6a** (0.345 g, 0.94 mmol) in THF (10 ml). After 1 h at this temp., the reaction is quenched with NH_4Cl in water (10%, 1 ml), the mixture is brought to room temp., concentrated at 12 Torr to a volume of 3 ml, and extracted with petroleum ether (3 × 10 ml). The combined organic layers are dried ($MgSO_4$) and purified as described above (method A) to give **9a** (0.138 g, 56%).

2,3,4-Tri-tert-butyl-endo-6-phenyl-1-azabicyclo[2.2.0]hex-2-en-5-one (**9b**): To a solution of **6b** (0.289 g, 0.64 mmol) in acetone (5 ml) is added hydrochloric acid (0.001 M, 0.5 ml). After stirring for 8 h, a solution of Na_2CO_3 in water (10%, 2 ml) is added. Extraction with ether (2 × 10 ml), drying ($MgSO_4$), and evaporation of the solvent at 12 Torr leaves a yellow oil to which petroleum ether (1.5 ml) is added at −30°C. The yellowish solid thus formed is isolated and washed with cold petroleum ether until it is nearly colorless: 0.124 g (58%) of **9b**, m.p. 94°C. — IR (KBr): $\tilde{\nu}$ = 1770 cm^{-1} (C=O), 1605 (C=C). — ^1H NMR (90 MHz): δ = 0.70, 1.22, 1.26 (each s, 9H, *t*Bu), 5.18 (s, 1H, 6-H), 7.10−7.40 (m, 5H).

$C_{23}H_{33}NO$ (339.5)
Calcd. C 81.37 H 9.80 N 4.13
Found C 80.9 H 9.7 N 4.3

1,3,5-Tri-tert-butyl-exo-6-phenyl-2-azabicyclo[3.1.0]hex-2-en-4-one (**11b**)

a) *From* **6c**: To a solution of **6c** (0.536 g, 1.08 mmol) in CH_2Cl_2 (5 ml) is added caesium fluoride (0.167 g, 1.10 mmol) in CH_3CN (2.5 ml). After stirring for 24 h, H_2O (5 ml) is added. Extraction with ether (2 × 10 ml), drying ($MgSO_4$), and column chromatography (petroleum ether/ether, 10:1) yields a yellow oil, which is dissolved in petroleum ether. At −78°C, yellow crystals of **11b** (0.188 g, 51%) are obtained, m.p. 91°C. — IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} (C=O), 1635 cm^{-1} (C=N). — ^1H NMR (90 MHz): δ = 1.23, 1.28, 1.32 (each s, 9H, *t*Bu), 2.20 (s, 1H, 6-H), 7.06−7.60 (m, 5H).

$C_{23}H_{33}NO$ (339.5)
Calcd. C 81.37 H 9.80 N 4.13
Found C 81.3 H 9.9 N 4.0

b) *From* **9b**: To a solution of **9b** (0.124 g, 0.37 mmol) in methanol (2 ml) is added a 1 M solution of sodium methoxide in methanol (0.04 ml). After 2 h, the yellow solution is filtered over silica gel [20 g, elution with ether (5 ml)], then separated by column chromatography (petroleum ether/ether, 10:1) to give **11b** (0.071 g, 57%), m.p. 91°C.

1,3,5,exo-6-Tetra-tert-butyl-2-azabicyclo[3.1.0]hex-2-en-4-one (**11c**): To a solution of KOH in methanol (3 N, 5 ml) is added **6d** (0.460 g, 0.97 mmol). The suspension is heated at reflux for 3 h, and after cooling the resulting yellow solution is extracted with pentane (3 × 10 ml). The combined organic layers are washed with H_2O (5 ml) and dried ($MgSO_4$). Purification by column chromatography (petroleum ether/ether, 5:1) and Kugelrohr distillation at 100°C (oven temp.)/0.3 mbar yields **11c** (0.220 g, 72%) as a yellow oil. — IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (C=O), 1630 (C=N). — ^1H NMR (90 MHz): δ = 0.40 (s, 1H, 6-H), 1.10 (s, 18H, 2 × *t*Bu), 1.24 (s, 18H, 2 × *t*Bu).

$C_{21}H_{37}NO$ (319.5)
Calcd. C 78.94 H 11.67 N 4.38
Found C 79.1 H 11.2 N 4.2

(1α,4α,7α,10α)-4,5,6,10,11,12-Hexa-tert-butyl-1,7-diazatricyclo-[8.2.0.0^{4,7}]dodeca-5,11-diene-2,8-dione (**14**): To a solution of **7a** (0.228 g, 0.62 mmol) in THF (10 ml), methyllithium in ether (1.6 M, 0.4 ml) is added at −78°C. After 1 h at this temp., the reaction is quenched with aqueous NH_4Cl (10% solution, 1 ml). Workup as described for the synthesis of **9a** (method B) and recrystallization from ether yields **14** (0.086 g, 56%) as colorless crystals, m.p. 306°C. — IR (KBr): $\tilde{\nu}$ = 1648 cm^{-1}. — ^1H NMR (400 MHz): δ = 1.17, 1.35, 1.40 (each s, 18H, *t*Bu), 2.85/2.97 (AB system, $|\,^2J\,|$ = 13.7 Hz). — ^{13}C NMR: δ = 28.9/31.3/32.7 (each q, CMe_3), 32.9/34.4/38.5 (each s, CMe_3), 35.8 [t, $COCH_2$, ^1J(C,H) = 127.5], 85.5 (N−C_{sp^3}), 139.3 (NC=*C*), 154.0 (N*C*=C), 165.2 (C=O). — MS (70 eV): *m/z* (%) = 527 (100) [M^+].

$C_{34}H_{58}N_2O_2$ (526.9)
Calcd. C 77.51 H 11.10 N 5.32
Found C 76.2 H 11.0 N 5.1

X-Ray Crystal Structure Analysis of **11b**[13]: *Crystal data:* $C_{23}H_{33}NO$, molecular mass 339.5, triclinic, space group $P\bar{1}$, *a* = 8.820(2), *b* = 10.195(4), *c* = 13.023(4) Å, α = 104.14(3), β = 90.37(2), γ = 114.10(2)°, *Z* = 2, d_{calc} = 1.10 g cm^{-3}. — *Data collection:* Crystal size 0.60 × 0.45 × 0.15 mm, monochromatized Mo-K_α radiation, 2353 independent reflections in the range 2.0 ≤ Θ ≤ 21.5°, ω/2Θ scan, scan width (1.25 + 0.35 tan Θ)°. — *Structure solution and refinement:* Structure solution by direct methods (SHELXS), refinement[14] by a full-matrix least-squares method. H

Table 3. Positional and thermal parameters for **11b** in the crystalline state. Standard deviations are in parentheses

Atom	x/a	y/b	z/c	U_{eq}
O	0.5530(6)	0.4836(5)	0.7932(5)	0.089(2)
N	0.2212(5)	0.5366(5)	0.7031(4)	0.041(2)
C1	0.1233(6)	0.3886(6)	0.7216(4)	0.032(2)
C2	0.3792(7)	0.5777(6)	0.7250(5)	0.041(2)
C3	0.4124(6)	0.4667(6)	0.7622(5)	0.041(2)
C4	0.2495(6)	0.3411(6)	0.7653(5)	0.036(2)
C5	0.1463(6)	0.4095(6)	0.8413(4)	0.035(2)
C6	-0.0330(7)	0.3086(6)	0.6380(4)	0.040(2)
C7	-0.1475(8)	0.1502(8)	0.6343(6)	0.060(3)
C8	-0.1309(7)	0.4052(8)	0.6581(5)	0.059(2)
C9	0.0275(8)	0.3070(8)	0.5285(5)	0.062(3)
C10	0.5116(7)	0.7220(7)	0.7132(5)	0.049(2)
C11	0.5970(10)	0.8200(8)	0.8217(7)	0.078(3)
C12	0.6329(10)	0.6893(9)	0.6416(7)	0.087(3)
C13	0.4285(10)	0.8037(8)	0.6655(7)	0.089(3)
C14	0.2562(7)	0.1919(6)	0.7537(5)	0.048(2)
C15	0.0950(9)	0.0617(7)	0.7637(7)	0.079(3)
C16	0.3123(10)	0.1480(8)	0.6476(7)	0.082(3)
C17	0.3856(9)	0.2062(8)	0.8424(7)	0.083(3)
C18	0.0346(7)	0.3321(6)	0.9130(4)	0.038(2)
C19	-0.1362(7)	0.2799(7)	0.9025(5)	0.047(2)
C20	-0.2298(8)	0.2150(7)	0.9758(5)	0.058(2)
C21	-0.1506(9)	0.2090(8)	1.0637(5)	0.067(2)
C22	0.0179(9)	0.2667(9)	1.0795(5)	0.080(3)
C23	0.1097(8)	0.3310(8)	1.0058(5)	0.068(3)

Table 4. Selected bond lengths and angles of **11b**. Standard deviations are in parentheses

Bond lengths [Å]			
C(1)-N	1.483(7)	C(1)-C(4)	1.538(7)
N -C(2)	1.288(7)	C(1)-C(5)	1.521(7)
C(2)-C(3)	1.462(8)	C(4)-C(5)	1.577(7)
C(3)-O	1.230(6)	C(1)-C(6)	1.543(7)
C(3)-C(4)	1.493(7)	C(4)-C(14)	1.517(8)
Bond angles [°]			
C(1)-N -C(2)	110.8(4)	C(3)-C(4)-C(5)	107.3(5)
N- C(2)-C(3)	111.5(5)	C(1)-C(4)-C(5)	58.4(3)
C(2)-C(3)-C(4)	108.8(4)	N -C(1)-C(5)	106.7(4)
C(3)-C(4)-C(1)	101.8(4)	C(4)-C(1)-C(5)	62.1(3)
C(4)-C(1)-N	106.9(4)	C(1)-C(5)-C(4)	59.5(3)

atoms were localized in a ΔF map, but only 21 out of 33 were refined (with B fixed). With 1696 reflections [$I > 3\sigma(I)$] and 358 variables refinement converged at $R = 0.077$, $R_w = (\Sigma\Delta^2 F/\Sigma F_o^2)^{1/2} = 0.085$ (shift/error ratio $\leqslant 0.88$, residual electron density $\leqslant 0.60$). Positional and thermal parameters of non-hydrogen atoms are given in Table 3, selected bond distances and angles in Table 4.

Table 5. Positional and thermal parameters for **14** in the crystalline state. Standard deviations are in parentheses

Atom	x/a	y/b	z/c	U_{eq}
O1	-0.0533(7)	0.0304(3)	0.7775(2)	0.049(2)
O2	0.2886(6)	0.1786(4)	0.7362(2)	0.048(2)
N1	0.0421(7)	0.1222(4)	0.8461(3)	0.031(2)
N2	0.0602(6)	0.2035(4)	0.6973(2)	0.025(2)
C1	-0.0481(9)	0.1029(5)	0.7979(3)	0.031(2)
C2	-0.1460(9)	0.1685(5)	0.7706(3)	0.035(2)
C3	-0.1058(8)	0.1941(5)	0.7041(3)	0.031(2)
C4	-0.0909(8)	0.1206(5)	0.6582(3)	0.028(2)
C5	0.0533(8)	0.1376(5)	0.6504(3)	0.031(2)
C6	0.1643(8)	0.2066(5)	0.7407(3)	0.028(2)
C7	0.1328(9)	0.2596(5)	0.7982(3)	0.036(2)
C8	0.1262(9)	0.2023(5)	0.8560(3)	0.037(2)
C9	0.2583(4)	0.1465(6)	0.8706(3)	0.034(2)
C10	0.1731(9)	0.0787(5)	0.8657(3)	0.035(2)
C11	-0.1872(10)	0.2703(5)	0.6815(3)	0.042(2)
C12	-0.1549(11)	0.3496(6)	0.7195(4)	0.055(3)
C13	-0.3577(10)	0.2563(6)	0.6805(4)	0.054(3)
C14	-0.1434(11)	0.2927(6)	0.6151(4)	0.055(3)
C15	-0.1928(10)	0.0540(5)	0.6364(4)	0.043(3)
C16	-0.3250(10)	0.0395(6)	0.6799(4)	0.051(3)
C17	-0.1134(11)	-0.0302(5)	0.6320(4)	0.054(3)
C18	-0.2655(11)	0.0749(6)	0.5728(4)	0.054(3)
C19	0.1803(10)	0.1196(5)	0.6067(4)	0.045(3)
C20	0.2706(11)	0.0478(6)	0.6286(4)	0.062(3)
C21	0.2728(10)	0.1980(6)	0.5987(4)	0.054(3)
C22	0.1114(11)	0.1001(7)	0.5415(4)	0.063(3)
C23	0.0624(10)	0.2522(5)	0.9130(3)	0.045(3)
C24	0.1498(13)	0.3300(6)	0.9269(4)	0.072(3)
C25	0.0660(10)	0.1952(6)	0.9701(3)	0.052(3)
C26	-0.1007(11)	0.2758(6)	0.9019(4)	0.058(3)
C27	0.4199(9)	0.1619(6)	0.8829(3)	0.044(3)
C28	0.5103(10)	0.0965(7)	0.8501(4)	0.063(3)
C29	0.4699(10)	0.2466(7)	0.8570(4)	0.057(3)
C30	0.4612(11)	0.1631(7)	0.9516(4)	0.064(3)
C31	0.1738(10)	-0.0154(5)	0.8820(4)	0.044(3)
C32	0.2206(13)	-0.0675(6)	0.8264(5)	0.067(3)
C33	0.2780(12)	-0.0331(6)	0.9359(4)	0.065(3)
C34	0.0188(11)	-0.0406(6)	0.9012(4)	0.054(3)

X-Ray Crystal Structure Analysis of **14**[13]: *Crystal data:* $C_{34}H_{58}N_2O_2$, molecular mass 526.9, monoclinic, space group $P2_1/n$, $a = 9.068(3)$, $b = 15.917(5)$, $c = 21.879(6)$ Å, $\beta = 91.00(4)°$, $Z = 4$, $d_{calc} = 1.11$ g cm^{-3}. — *Data collection:* Crystal size 0.70 × 0.70 × 0.35 mm, monochromatized Mo-K_α radiation, 3372 independent reflections in the range $2.0 \leqslant \Theta \leqslant 21.0°$, $\omega/2\Theta$ scan, scan width $(1.30 + 0.35\tan\Theta)°$. — *Structure solution and refinement*[14]: Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method. Methylene H atoms were localized in a ΔF map, all *t*Bu H atoms were calculated in fully staggered positions; all H atoms were included in the structure factor calculations, but not refined. With 2363 reflections [$I > 3\sigma(I)$] and 343 variables, refinement converged at $R = 0.091$, $R_w = (\Sigma\Delta^2 F/\Sigma_o^2)^{1/2} = 0.102$ (shift/error ratio $\leqslant 0.08$, residual electron density $\leqslant 0.43$). For positional and thermal parameters see Table 5.

CAS Registry Numbers

6a: 132911-05-8 / **6b**: 132911-06-9 / **6c**: 132911-07-0 / **6d**: 132911-08-1 / **7a**: 132911-09-2 / **9a**: 132911-00-3 / **9b**: 132911-01-4 / **11b**: 132911-02-5 / **11c**: 132911-03-6 / **14**: 132911-04-7

☆ Dedicated to Professor *Jürgen Sauer* on the occasion of his 60th birthday.

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[13] Further crystal structure data have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Inquiries should be accompanied by the depository number CSD-55085, the names of the authors and the reference to this publication.

[14] The program system *Structure Determination Package* (Enraf-Nonius, Delft, The Netherlands) was used.

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