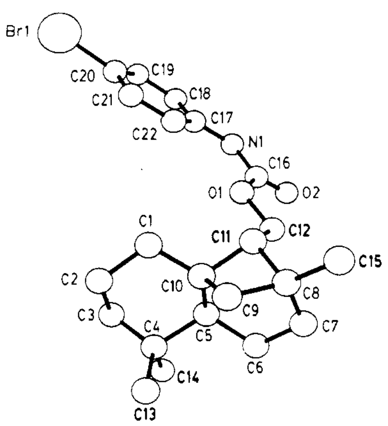


Figure 1.

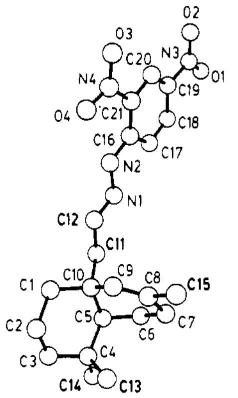
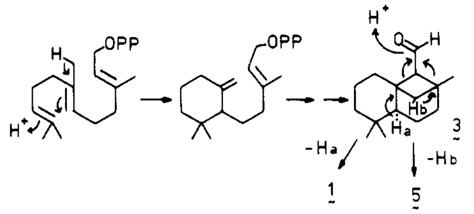


Figure 2.

Scheme I



variable 1° ω scan and graphite-monochromated Cu K$\bar{\alpha}$ radiation (1.54178 Å). After correction for Lorentz, polarization, and background effects, 2365 (75%) were judged observed $((|F_0| \gtrsim 3\sigma(F_0))$. A phasing model was found by standard heavy atom methods, and least-squares refinements with anisotropic heavy atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.078 for the observed reflections.[2] Both molecules in the asymmetric unit had the same stereostructure, and a computer-generated perspective drawing is given in Figure 1. Additional details can be found in the supplementary material section.

Isoacanthodoral (5), the second minor component, yielded the (p-bromophenyl)urethane derivative 6 as an oil: $[\alpha]_D$ −39° (hexane); MS, M$^+$, m/z 421, 419, $C_{22}H_{30}BrNO_2$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.01 (s, 3 H), 1.61 (br s, 3 H), 1.48 (ddd, 1 H, J = 13.0, 6.7, 8.9 Hz), 2.10 (ddd, 1 H, J = 13.0, 6.4, 9.0 Hz), 4.18 (m, 2 H), 5.06 (br s, 1 H), 6.50 (br s, 1 H), 7.27 (d, 2 H), 7.40 (d, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) (only terpenoid carbons are listed) δ 19.3, 20.0, 23.3, 26.5, 29.0, 32.3, 34.1, 37.5, 38.0, 40.4, 42.5, 45.6, 63.3, 131.0, 134.2.

In light of the already determined structures of nanaimoal (1) and acanthodoral (3), and spectral data, we proposed structure 6 for the urethane derivative of 5. This was confirmed via a single-crystal X-ray diffraction analysis on the 2,4-dinitrophenylhydrazone 7.[3] Crystals of 7 also belonged to space group $P2_1$ with a = 6.027 (1) Å, b = 31.613 (8) Å, c = 8.910 Å, and β = 80.89 (1)°. The asymmetric unit consisted of two molecules of composition $C_{21}H_{32}O_4N_4$. Diffraction data were collected by the method described above and 1713 (59%) were judged observed. Solution by direct methods was routine and least-squares refinements have converged to a standard crystallographic residual of 0.048.[2] A computer-generated perspective drawing of one of the identical molecules of 7 forming the asymmetric unit is given in Figure 2, and the supplementary material should be consulted for further details.

Acanthodoral (3) and isoacanthodoral (5) both have new sesquiterpenoid carbon skeletons for which we propose the names acanthodorane and isoacanthodorane. A proposed biogenesis for all three *A. nanaimoensis* sesquiterpenoids is shown in Scheme I.

Acknowledgment. We thank Mike Le Blanc and the staff of the Blamfield Marine Station for assistance in collecting *A. nanaimoensis*. Financial assistance from NSERC in the form of a grant to R.J.A. and a postgraduate scholarship to S.W.A. is acknowledged. The work at Cornell was supported by NIH CA24487 and NSF INT 8117327.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles for 4 and 7 (14 pages). Ordering information is given on any current masthead page.

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[2] All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessigner, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Center, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

[3] 2,4-Dinitrophenylhydrazone 7: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.03 (s, 3 H), 1.66 (s, 3 H), 1.95 (m, 3 H), 2.24 (dd, J = 6.0, 14.0 Hz, 1 H), 2.79 (dd, J = 6.0, 14.0 Hz, 1 H), 5.11 (br s, 1 H), 7.42 (dd, J = 6.0, 6.0 Hz, 1 H), 7.88 (d, J = 9.4 Hz, 1 H), 8.25 (dd, J = 2.5, 9.4 Hz, 1 H), 9.08 (d, J = 2.5 Hz, 1 H), 10.9 (br s, 1 H), 1.1–1.8 (m, 8 H).

Aminyl Oxides (Nitroxides). 36.[1] Formation of 3,7-Dioxa-2,6-diazabicyclo[3.3.0]octanes by Dimerization of Vinyl Aminyl Oxides (Vinyl Nitroxides)

Summary: Oxidation of N-aryl-N-(2-aroyl-2-arylethyl)hydroxylamines 5 yields dimers of the vinyl aminyl oxides

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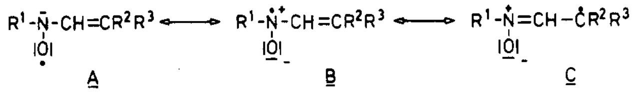
[1] Aminyl oxides (nitroxides). 35, see; Aurich, H. G.; Baum, G.; Massa, W.; Mogendorf, K.-D.; Schmidt, M. *Chem. Ber.*, in press

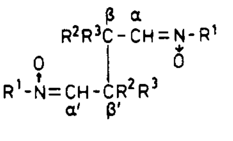
0022-3263/84/1949-2654$01.50/0

7 for which structure **9** was derived. Dimerization of **7** seems to take place by initial C–O bond formation to afford intermediates **3** which are converted to **9** by an intramolecular 1,3-dipolar cycloaddition.

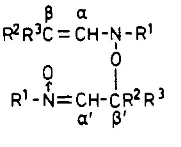
Sir: Vinyl aminyl oxides **1** may be described by the mesomeric formulas A–C. Dimerization of **1** is expected to



1



2

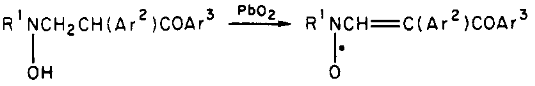


3

give either compounds **2** or **3**, since formation of a carbon–carbon bond or a carbon–oxygen bond seems to be energetically most favorable. To date only the β,β′-bonded dimers **2** have been observed.[2,3]

In contrast, a benzoyl group at the β-position of **1** effects dimerization in a specific manner. The *N-tert*-butyl-substituted radical **6**, generated by oxidation of **4**, dimerizes to give **8**.[1] It is assumed that this reaction also begins with β,β′ bond formation followed by an intramolecular (3 + 3 + 2) cycloaddition involving one nitrone group and two carbonyl groups (formation of bonds O–γC, O–γ′C, and O–αC). Dimer **8** dissociates in solution at elevated temperatures to give radical **6**.

Herein we report that *N*-aryl-substituted (β-benzoylvinyl) aminyl oxides **7**[3] react in a completely different way. When hydroxylamines **5a–d**[4] were oxidized in chloroform



$$\underset{\text{OH}}{\text{R}^1\text{N}}\text{CH}_2\text{CH}(\text{Ar}^2)\text{COAr}^3 \xrightarrow{\text{PbO}_2} \underset{\text{O}^\bullet}{\text{R}^1\text{N}}\text{CH}{=}\text{C}(\text{Ar}^2)\text{COAr}^3$$

4, R^1 = *t*-Bu; $Ar^2 = Ar^3$ = Ph

5a–d, R^1 = Ar

6, R^1 = *t*-Bu; $Ar^2 = Ar^3$ = Ph

7a–d, R^1 = Ar

	R^1	Ar^2	Ar^3
a	Ph	Ph	Ph
b	Ph	Ph	*p*-Tol
c	Ph	*p*-Tol	Ph
d	*p*-Tol	Ph	Ph

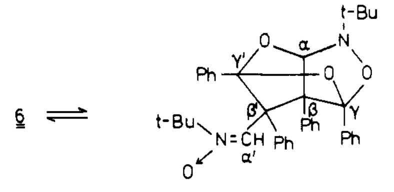
(20 mmol in 300 mL) with lead dioxide (1 h at 0 °C, subsequently 15 h at room temperature), dimers of the radicals **7a–d** were isolated in 30–93% yield. During oxidation **7a–d** could be detected by ESR (a^N = 8.1 G for **7a–d**) in the reaction mixture.

Contrary to **8** the dimers of **7a–d** do not dissociate at elevated temperatures. Their spectral data [^{13}C NMR α-C 74.7–75.0 (d, *J* = 150–151 Hz), β-C 94.6–94.8, γ-C 196.5–197.5 ppm; ^{1}H NMR 6.4–6.55 ppm (α-CH);[5] IR ν (CO) 1660–1680 cm^{-1}] indicate that neither structure **8** (aryl instead of *tert*-butyl) pertains nor structure **2** (R^1–R^3 = aryl) as originally assumed for the dimer of **7a**[3]. On the basis of these data structure **9** can be assigned to the dimers of **7**; however, they would also be compatible with structure **10** or **11**.

Table I. 3,7-Dioxa-2,6-diazabicyclo[3.3.0]octanes 9[a]

	Ar^1	Ar^2	Ar^3	mp	% yield
9a	C_6H_5	C_6H_5	C_6H_5	199–200[b]	93
9a-[α,α′-^{13}C]				200–201[b]	80
9b	C_6H_5	C_6H_5	$C_6H_4CH_3$-*p*	228–229[c]	76
9c	C_6H_5	$C_6H_4CH_3$-*p*	C_6H_5	216[b]	30
9d	$C_6H_4CH_3$-*p*	C_6H_5	C_6H_5	209–211[c]	66

[a] Satisfactory analytical data (±0.4% for C, H, N) were found for all new compounds listed in the table. [b] From methylenchloride/*n*-hexane. [c] From toluene/*n*-hexane.



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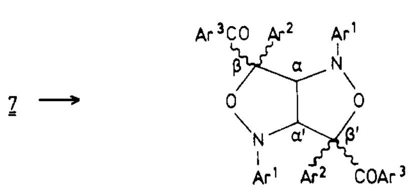
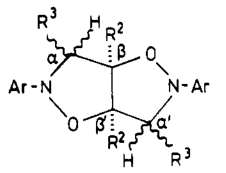
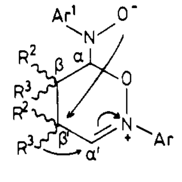


9



10: R^2 = Ar R^3 = COAr

11: R^2 = COAr R^3 = Ar



12

Compounds **9** can arise by initial formation of a carbon–oxygen bond (β′-O) to afford intermediates **3** (R^1 = R^2 = Ar, R^3 = ArCO) which subsequently undergo intramolecular 1,3-dipolar cycloaddition involving the nitrone and the olefinic group[6] (α,α′ and β,O bonding). On the other hand, **10** or **11** can be formed from β,β′-bonded dimers **2** by ring closure giving **12**, as has been assumed for reactions of other dinitrones,[3,7] followed by a sequence of rearrangements accompanied by migration of the two aroyl groups ArCO or the two aryl groups Ar, respectively. However, structures **10** and **11** can be excluded by aid of ^{13}C-labeling at the α-position. For this purpose desoxybenzoin was treated with ^{13}C-labeled formaldehyde[8] to yield the labeled methylene desoxybenzoin.[9] Addition of phenyl hydroxylamine then affords **5a** (α-^{13}C, R^1 = Ar^2 = Ar^3 = Ph) oxidation of which gave the dimer labeled at both α-positions via radical **7a**. The ^{13}C NMR spectrum of the labeled compound shows the splitting of the β-carbon signal expected for compound **9a** as well as for **10a**

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(2) Aurich, H. G.; Hahn, K.; Stork, K. *Chem. Ber.* **1979**, *112*, 2776.

(3) Aurich, H. G. *Can. J. Chem.* **1982**, *60*, 1414.

(4) **5a–d** were prepared from methylene desoxybenzoin or the corresponding *p*-methyl-substituted compounds and phenyl hydroxylamine or *p*-tolylhydroxylamine, respectively, according to the procedure described by Thesing, J.; Müller, A.; Michel, G. *Chem. Ber.* **1955**, *88*, 1027. See also: De Sarlo, F.; Renzi, G. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1113.

(5) The low-field shift of this signal is caused by the phenyl groups at the nitrogen atom and at the β-carbon atom.

(6) For reviews, see: (a) Padwa, A. *Angew. Chem., Int Ed. Engl.* **1976**, *15*, 123. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (c) Black, D. S. C.; Crozier, R. F.; Davis, V. C. *Synthesis* **1975**, *7*, 205.

(7) De Sarlo, F.; Brandi, A.; Guarna, A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1395.

(8) An aqueous solution of ^{13}C-formaldehyde (90% enrichment) was purchased from Amersham and Buchler.

(9) According to the procedure described by Fiesselmann, H.; Ribka, J. *Chem. Ber.* **1956**, *89*, 27.

Table II. Characteristic Peaks of Mass Spectra (27 eV) for 9a–c[a]

	M^+ (rel, intensity)	i	ii	iii
9a	628 (43)	418 (21)	313 (53)	208 (100)
9a-[α,α'-^{13}C]	630 (38)	420 (37)	315 (91)	210 (100)
9b	656 (13)	432 (18)	313 (100)	208 (40)
9c	656 (27)	432 (28)	327 (36)	208 (100)

[a] i, $[M - Ar^2CO - Ar^3CO]^+$. ii, $[M - Ar^2CO - 2(Ar^3CO)]^+$, high resolution for **9a** 313.1351, $C_{21}H_{17}N_2O$ requires 313.1346. iii, $[(Ar^1NCH)_2]^+$, high resolution for **9a** 208.0974, $C_{14}H_{12}N_2$ requires 208.0987.

or **11a** and also the coupling between the α- and α′-carbon atoms, which is not compatible with structures **10a** and **11a** ($J_{\alpha\beta} = 33.7$ Hz, $J_{\alpha\beta'} = 0.8$ Hz, $J_{\alpha\alpha'} = 43.4$ Hz).[10] Additional evidence in favor of structure **9** comes from the fact that neither splitting of the signal of the carbonyl C atom due to structure **10** nor of the signal of the phenyl 1-C atom due to **11** is observed (Table I).

Furthermore, the structure of dimers **9** has been confirmed by their mass spectra (Table II). The fragmentation patterns, in particular the $(Ar^1NCH)_2$ fragments, are only in accord with structure **9**. Thus the reaction of the *N*-aryl-substituted vinyl aminyl oxides **7** constitutes the first example of carbon–oxygen bond formation in the dimerization of vinyl aminyl oxides and gives rise to formation of a new class of hetero bicyclic compounds, the 3,7-dioxa-2,6-diazacyclo[3.3.0]octanes **9**.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research.

Supplementary Material Available: A listing of the ^{13}C NMR, ^1H NMR, ESR, and mass spectral data (4 pages). Ordering information is given on any current masthead page.

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Received April 13, 1984

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[10] The coupling constants were confirmed by simulation of the splitting pattern. We thank Priv.-Doz. Dr. S. Berger for recording the spectrum of the labeled compound and for performing the simulation.

Additions and Corrections

Vol. 48, 1983

Manfred K. Eberhardt* and Anselmo Fuentes-Aponte. Formation of OH Radicals from Radical Cations of Some Substituted Benzenes in Aqueous Solutions at 80 °C and at Room Temperature. Effect of Oxygen[1].

Page 3446. Table II, entry 6, under *o*-nitrophenol 14.0, under *p*-nitrophenol 7.0.

George R. Newkome,* Garry E. Kiefer, Wallace E. Puckett, and Thomas Vreeland. α-Methyl Functionalization of Electron-Poor Heterocycles: 2,9-Bis(chloromethyl)-1,10-phenanthroline. Synthesis of a [3.3]Cyclophane Containing the 1,10-Phenanthrolino Moiety.

Page 5113. For the conversion of **5** to **6**, add "2)MeOH" beneath the arrow. Compound **7** should be a dihydroxy compound rather than the dichloride shown.

Vol. 49, 1984

Donald C. Berndt,* Nop Utrapiromsuk, and Douglas E. Conran. Substituent Effects and Mechanism in the Micellar Hydrolysis of Hydroxamic Acids.

Page 108, eq 7: value for α for eq 7 should be 0.287.

Cornelis J. Elsevier, Hendrik J. T. Bos, Peter Vermeer,* Anthony L. Spek,* and Jan Kroon. Synthesis and Structure of Side Chain Haloallenes in the Steroid Series.

Page 381. The *R* value of 0.076 in the "Crystallographic Data and X-ray Structure Analysis of **2b**" section should read 0.067 instead of 0.076.

Page 381. **Supplementary Material Available**: Table of final coordinates and equivalent isotropic thermal parameters for molecules A and B (1 page). Ordering information is given on any current masthead page.