reaction was carried out in methylene chloride solution at 100 °C in a sealed tube. The NMR spectrum indicated that the adduct consisted of an equimolar mixture of exo and endo isomers. The isomers could not be separated by TLC.

It is of interest that 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) is the product one would obtain from the Diels–Alder reaction of anthracene with dinitroacetylene. Dinitroacetylene has not been reported, although *tert*-butylnitroacetylene[11] and phenylnitroacetylene[12] have been described recently.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. The 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene was prepared by using previously described procedures,[2] and 1,2-dimethoxyethane was distilled from sodium benzophenone ketyl. Reactions of polynitro compounds were carried out behind safety shielding.

11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2). A bent tube containing 0.1–0.15 g of 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (1) was fitted to a 50-mL round-bottom flask that was partially immersed in a 250–260 °C oil bath. The flask was evacuated to 0.5 mmHg, and the solid was added rapidly by rotating the tube. A yellow solid condensed quickly on the unheated portion of the flask and in the vacuum exit; essentially no residue remained in the heated area. The flask was cooled and the product was taken up in methylene chloride. A total of 0.94 g (2.0 mmol) of the tetranitro compound was pyrolized in this way in increments. Solvent was removed from the combined solutions, and the residue was washed with hexane. The crude product, which was found to contain 15% starting material, was repyrolyzed by the above procedure. the product was recrystallized from benzene–hexane and dried for 2 h at 56 °C (0.05 mmHg) to give 0.37 g (62%) of yellow solid: mp 162–164 °C dec; IR (CH_2Cl_2) 1540, 1460, 1350 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (m, 8 H, aromatic), 5.60 (s, 2 H, bridgehead CH).

Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 65.31; H, 3.43, N, 9.52. Found: C, 65.13; H, 3.81; N, 9.32.

Reaction of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2) with Sodium Iodide. A solution of 0.56 g (0.38 mmol) of sodium iodide in 2 mL of dry 1,2-dimethoxyethane was added to a solution of 0.070 g (0.19 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene in 1 mL of 1,2-dimethoxyethane, and the resulting dark red mixture was stirred for 1 h. The precipitated product was isolated by filtration, washed with 1,2-dimethoxyethane and with methylene chloride, and air dried to give 0.030 g (48%) of the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (3) as a complex with 0.5 mol/mol of 1,2-dimethoxyethane which was identical with an authentic sample.[2]

11-(Butylthio)-12-nitro-9,10-dihydro-9,10-ethenoanthracene. A solution of 0.10 g (0.34 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) in 4 mL of methanol and 2 mL of tetrahydrofuran was cooled to −25 °C, and a solution of 0.34 mmol of sodium *n*-butylmercaptide in 2 mL of methanol was added over a 5-min period with stirring. The reaction mixture was stirred for 15 min at −20 °C and was then warmed to 0 °C over a 30-min period. The solvent was removed in vacuo, and the residue was chromatographed over 10 g of silica gel (1:1 methylene chloride–hexane). The yellow fractions were combined, and the solvent was evaporated. Recrystallization of the residue from cyclohexane gave 0.050 g (43%) of bright yellow prisms: mp 144–145.5 °C; IR (CH_2Cl_2) 1540, 1460, 1320, 1300 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.3 (m, 8 H, Ar), 5.93 (s, 1 H, bridgehead CH), 5.47 (s, 1 H, bridgehead CH), 3.10 (t, 2 H, CH_2S), 1.62 (m, 4 H, CH_2CH_2), 0.98 (m, 3 H, CH_3).

Anal. Calcd for $C_{20}H_{19}NSO_2$: C, 71.19; H, 5.68; N, 4.15; S, 9.50. Found: C, 71.15; H, 5.66; N, 4.09; S, 9.39.

11-(Benzylamino)-12-nitro-9,10-dihydro-9,10-ethenoanthracene. A solution of 0.10 g (0.34 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) and 0.040 g (0.37 mmol) of benzylamine in 4.0 mL of dry tetrahydrofuran was allowed to stand 28 h at room temperature. The solvent was evaporated, and the residue was washed with ether–THF to give 0.075 g (63%) of crystalline product. An analytical sample was recrystallized f rom ether–THF: mp 243–244.5 °C dec; IR (CH_2Cl_2) 1610, 1460, 1410, 1370, 1350 cm^{-1}; NMR ($CDCl_3$) δ 10.5 (m, 1 H, NH), 6.8–7.4 (m, 13 H, Ar), 5.88 (s, 1 H, bridgehead), 5.20 (s, 1 H, bridgehead), 4.78 (d, 2 H, J = 6 Hz, benzyl CH_2).

Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12, N, 7.90. Found: C, 78.15; H, 5.05; N, 7.85.

Reaction of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2) with Cyclopentadiene. A solution of 0.25 mL of cyclopentadiene and 0.060 g (0.20 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene in 2 mL of methylene chloride was heated in a sealed tube for 1 h at 100 °C. Column chromatography (10 g of silica gel, hexane–methylene chloride) and recrystallization of the colorless middle fractions from benzene–hexane gave 0.025 g (17%) of the Diels–Alder adduct of cyclopentadiene and 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene: colorless needles; mp 167–168 °C. An analytical sample was dried for 3 h at 56 °C (0.05 mm): IR (CH_2Cl_2) 1545, 1360 cm^{-1}; NMR ($CDCl_3$) indicated a 1:1 mixture of exo and endo isomers, δ 7.17 (m, 16 H, Ar), 6.40 (m, 2 H, CH=CH), 5.27 (m, 2 H, CH=CH), 5.00 (s, 2 H, ArCHAr), 4.83 (s, 2 H, ArCHAr), 3.60 (m, 2 H, CH), 3.30 (m, 2 H, CH), 3.00, 1.88, 1.20, and 0.066 (4 d, J = 11 Hz, 1 H each, CH_2).

Anal. Calcd for $C_{21}H_{16}H_2O_4$: C, 69.99; H, 4.48; N, 7.77. Found: C, 69.89; H, 4.47; N, 7.62.

Registry No. 1, 73804-83-8; 2, 79069-90-2; 3·Na, 73804-87-2; 11-(1-butylthio)-12-nitro-9,10-dihydro-9,10-ethenoanthracene, 79083-87-7; sodium *n*-butylmercaptide, 4779-86-6; 11-(benzylamino)-12-nitro-9,10-dihydro-9,10-ethenoanthracene, 79069-91-3; benzylamine, 100-46-9; cyclopentadiene/11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene Diels–Alder adduct (endo), 79069-92-4; cyclopentadiene/11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene Diels–Alder adduct (exo), 79120-27-7.

(11) Motte, J. C.; Viehe, H. G. *Chimia* **1975**, *29*, 515.
(12) Yamabe, K.; Yasutake, A. *Sasebo Kogyo Koto Senmon Gakko Kenkyu Hokoku* **1979**, *16*, 63; *Chem. Abstr.* **1980**, *93*, 185856.

Stereodynamics in Benzamidoximes. A Reassignment

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In a previous work concerning the study of the stereochemistry of benzamidoximes by NMR we observed,[2] inter alia, nonequivalence for the ortho methyl groups in compounds 1 and 2 at room temperatures in Me_2SO. As at higher temperature the NMR signals of these substituents broadened and coalesced into a single peak at ca. 110 °C, the free energies of activations for the related exchange process calculated from the total line-shape study were 21.5 and 19.9 kcal/mol for 1 and 2, respectively. The internal motions which could in principle be responsible for the exchange process were thought to be the restricted rotation about the C—N single bond or the inversion of configu-

(1) (a) University of Ferrara. (b) University of Bologna. (c) Institute of CNR.
(2) Dondoni, A.; Lunazzi, L.; Giorgianni, P.; Macciantelli, D. *J. Org. Chem.* **1975**, *40*, 2979.

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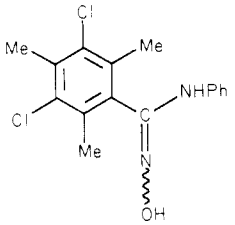

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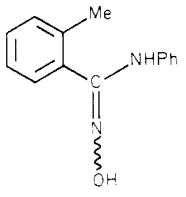
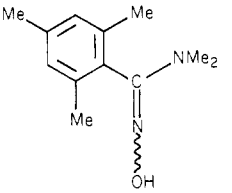


2

ration about the C=N double bond. The former phenomenon seemed more likely than the latter since the thermal *E,Z* isomerization in oximino compounds was currently considered a very high energy process as substantiated by the activation energy of 32 kcal/mol determined for a typical case:[3] this value considerably exceeds the 20 kcal/mol observed for **1** and **2**. However, doubts were advanced in view of the possibility that the presence of the heteroatom could lower the *E,Z* barrier to the change, as exceptionally observed for other oximino compounds.[4] This doubt has been reinforced by the recent work by Dignam and Hegarty,[5] who in fact reported the rate constants for the *E,Z* isomerization of a series of amidoximes from which activation energies as low as 21–25 kcal/mol can be calculated.

(3) Vassian, E. G.; Murmann, R. K. *J. Org. Chem.* **1962**, *27*, 4309.
(4) McCarty, C. G. In "The Chemistry of the Carbon–Nitrogen Double Bond"; Patai, S., Ed.; Interscience: New York, 1969; p 363.
(5) Dignam, K. J.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1437.

In order to clarify this point we have studied the ^{13}C NMR spectrum of amidoxime **3** in CD_2Cl_2 as a function



3

of temperature; this compound belongs to the same series of benzamidoximes **1** and **2** and has been properly built up to allow unambiguous assignments of the stereodynamic processes. Since at room temperature we observed one signal for each set of equivalent methyls, this indicates that the C—N rotation is fast and that we are dealing with one of the two configurational isomers *E* or *Z* or, less likely, that the *E,Z* isomerization is very fast. On lowering the temperature, we could detect two signals of equal intensities for the NMe_2 methyl, whereas the ortho methyls of the mesityl group remained equivalent. This clearly proves that the C—NMe_2 rotation has been locked; the energy barrier calculated from the line-shape analysis was 11.2 kcal/mol, a much lower value than that obtained for the internal motion in **1** and **2**. Consequently, we are now convinced that *E,Z* isomerization, rather than rotation about the C—N bond, was the phenomenon observed also in benzamidoximes **1** and **2**.

Registry No. **1**, 27886-91-5; **2**, 78965-29-4; **3**, 6157-67-1.

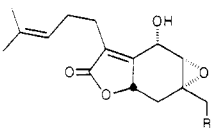
Communications

A Common Strategy for Construction of the Paniculides (A–C): Total Synthesis of Paniculide A

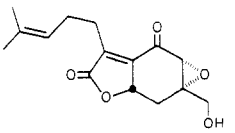
Summary: We disclose here the first total synthesis of (±)-paniculide A.

Sir: The paniculides A–C, highly oxygenated sesquiterpenes, were isolated in 1968 by Overton and co-workers[1] from callus cultures of *Andrographis paniculata*, during the course of phytochemical studies[2] both with intact plants[3] and the derived tissue cultures. While these novel sesquiterpenes have been known for well over a decade, their structures have yet to be confirmed either by X-ray analysis or by total synthesis; currently they rest on elemental composition data in conjunction with spectral properties, most notably high-field NMR data.[1] Indeed, to the best of our knowledge there exists only one report directed at construction of the basic carbocyclic skeleton; this is the work of Jacobi.[4]

In this communication we report the *first* total synthesis of (±)-paniculide A (**1**). We note in advance that our strategy is short, highly efficient, and stereocontrolled; furthermore, it serves for the *first time* to confirm the structural assignments of the paniculides.



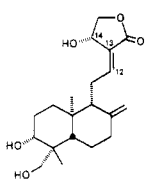
1, Paniculide A (R = H)
2, Paniculide B (R = OH)



3, Paniculide C

At the outset, we set as an overall goal the development of a common synthetic strategy that would in turn afford paniculides A, B, and C.[5] Ideal in this regard appeared to be bicyclic ketones **4a** and **4b**, both presumably readily available after modest functional group manipulation of

(1) A. J. Allison, D. N. Butcher, J. D. Connolly, and K. H. Overton, *Chem. Commun.*, 1493 (1968).
(2) D. N. Butcher and J. D. Connolly, *J. Exp. Bot.*, **22**, 314 (1971).
(3) Recently, we have successfully completed a single-crystal X-ray analysis of andrographolide, the major diterpenoid metabolite of the parent plant; unpublished results of B. H. Toder and P. J. Carroll. The structure including stereochemistry was found to be i:



i

(4) P. A. Jacobi and T. Craig, *J. Am. Chem. Soc.*, **100**, 7748 (1978); also see P. A. Jacobi, D. G. Walker, and I. M. A. Odeh, *J. Org. Chem.*, **46**, 2065 (1981).
(5) Paniculide C (**3**) has been prepared from paniculide B (**2**) via mild oxidation; see ref 1.

0022-3263/81/1946-4814$01.25/0