(2) In PPA. A suspension of 0.32 g (1.0 mmol) of *N*-(2-biphenylyl)-*N*-hydroxy-4-toluenesulfonamide (**1c**) in 40 g of PPA was stirred at 105 °C for 30 min and poured into 200 mL of cold water to give 0.18 g of a green solid. The solid was extracted with 25 mL of acetone which was evaporated under reduced pressure to give 0.14 g (46%) of *N*-(4-toluenesulfonyl)carbazole (**2c**) as a white solid, mp 128.5–130 °C (lit.[16] mp 133 °C).

Reaction of *N*-Benzoylcarbazole (2b) in PPA. A suspension of 1.0 g (3.7 mmol) of *N*-benzoylcarbazole (**2b**) in 20 g of PPA was stirred at 95 °C for 30 min and poured into 150 mL cold water to give 0.85 g of a green solid. Analysis by preparative TLC ($CHCl_3$) identified the major products, in increasing R_f value, as follows: 3,6-dibenzoylcarbazole (**6**), 31%, mp 252–254 °C (lit.[17] mp 258 °C); 28% of a monosubstituted carbazole, IR 1660 cm^{-1} (CO); carbazole (**2a**), 29%, mp 233–235 °C (lit.[18] mp 238 °C); small amounts (5–7%) of minor products.

Acknowledgment. We thank the University of Connecticut Foundation for financial assistance (to G.T.B.).

Registry No. 1a, 16169-17-8; **1b**, 82390-31-6; **1c**, 82390-32-7; **2b**, 19264-68-7; **2c**, 3165-71-7; **5**, 21711-71-7; **6**, 78901-33-4.

(16) Tucker, S. H. *J. Chem. Soc.* **1926**, 546.
(17) Plant, S. G. P.; Tomlinson, M. L. *J. Chem. Soc.* **1932**, 2188.
(18) Graebe, C.; Glaser, C. *Justus Liebigs Ann. Chem.* **1872**, *163*, 343.

Reductions of Diterpene Epoxides. A Partial Synthesis of 8β-Hydroxyisopimar-15-ene

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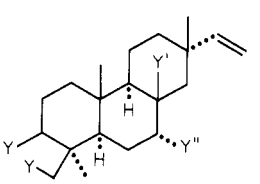
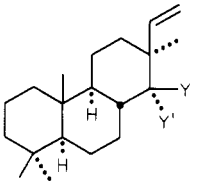
In connection with a study of rearrangements of diterpene epoxides, several pimaradienic monoepoxides had to be prepared. On treatment with *m*-chloroperbenzoic acid,[1] the sandaracopimaradienic substance **1a**[2] was converted into its 8β,14β-epoxide (**1b**),[4,5] and pimaradiene (**2a**)[6,7] was converted into its 8α,14α-epoxide (**2b**).[8] With these epoxides and the 7,8-epoxide pairs **1e** and **1g**, as well as **1f** and **1h**,[10] derived from the isopimaradienic substances virescenol B diacetate (**1c**)[9] and isopimaradiene (**1d**),[7] respectively, it became of interest to investigate their behavior on reduction with a metal and hydrogen source. Whereas previous reductions of such epoxides with lithium in ethylamine[11,12] had led to products in which both the epoxide unit and the vinyl group had been reduced,[13] the following study reveals that lithium–ammonia reduction furnishes alcohols in which the vinyl group remains intact.

Reduction of the 8β,14β-epoxide diacetate **1b** with lithium in liquid ammonia yielded triol **3a**, indicating that

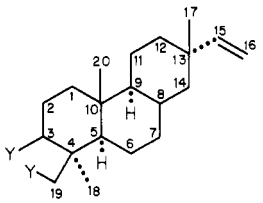


3a, Y = Y′ = OH; Y″ = H
b, Y = OAc; Y′ = OH; Y″ = H
c, Y = Y″ = H; Y′ = OH
d, Y = Y″ = OH; Y′ = H
e, Y = Y′ = H; Y″ = OH

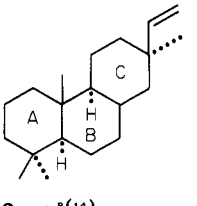


4a, Y = H; Y′ = OH
b, Y = H; Y′ = OAc
c, Y + Y′ = O
d, Y = OH; Y′ = H

it had taken place expectedly at the secondary carbon–oxygen site and had followed the usual steric course of trans diaxial ring opening of an epoxide. Reduction of the 8α,14α-epoxide **2b**, on the other hand, produced two alcohols, **2c** and **4a**. The latter alcohol functioned as a stereochemical point of reference of itself as well as its precursor in view of its ready conversion into ketone **4c** on Jones oxidation, the lack of change of this substance on base-catalyzed equilibration, and its transformation into the starting alcohol (**4a**) and its isomer (**4d**) on reduction with lithium aluminum hydride. The formation of two products in the reduction of the α-epoxide is unusual. Whereas each product is an axial alcohol (with respect to ring C), each substance represents epoxide ring opening at a different carbon–oxygen bond center. This anomaly may be attributable to the greater steric interfernce with chemical activity at C(8), the expected reaction site, than at C(14) and to a lowering of the usual, conformational



1a, Y = OAc; $\Delta^{8(14)}$
b, Y = OAc; 8β,14β-epoxy
c, Y = OAc; $\Delta^{7(8)}$
d, Y = H; $\Delta^{7(8)}$
e, Y = OAc; 7α,8α-epoxy
f, Y = H; 7α,8α-epoxy
g, Y = OAc; 7β,8β-epoxy
h, Y = H; 7β,8β-epoxy



2a, $\Delta^{8(14)}$
b, 8α,14α-epoxy
c, 8α-hydroxy

(1) M. Curini, P. Ceccherelli, R. Pellicciari, and E. Sisani, *Gazz. Chim. Ital.*, **110**, 621 (1980).

(2) This compound was prepared by the photoxygenation–reduction of virescenol B diacetate (**1c**),[3] acetylation of the resultant allylic alcohol, lithium–ammonia reduction of the triacetate, and acetylation of the resultant double-bond isomer of virescenol B (unpublished observations).
(3) P. Ceccherelli, M. Curini, M. Tingoli, and R. Pellicciari, *Gazz. Chim. Ital.*, **108**, 129 (1978); E. Wenkert, M. S. Raju, P. Ceccherelli, M. Curini, M. Tingoli, and R. Pellicciari, *J. Org. Chem.*, **45**, 741 (1980).
(4) For previous preparations of sandaracopimaradienic monoepoxides, see (a) J. W. ApSimon, *Chem. Commun.*, 83 (1970); (b) B. Delmond, M. Taran, and J. Valade, *Tetrahedron Lett.*, 4791 (1978).
(5) In analogy with earlier observations,[4] the oxidation product was expected to be a β-epoxide.
(6) P. Ceccherelli, M. Curini, M. Tingoli, and R. Pellicciari, *J. Chem. Soc., Perkin Trans. 1*, 1924 (1980).
(7) E. Wenkert and Z. Kumazawa, *Chem. Commun.*, 140 (1968).
(8) The α stereochemistry of this substance emerged from its chemical behavior (vide infra). The presence of its β isomer was not investigated.
(9) J. Polonsky, Z. Baskevitch, N. Cagnoli Bellavita, and P. Ceccherelli, *Bull. Soc. Chim. Fr.*, 1912 (1970).
(10) J. W. Blunt, G. S. Boyd, M. P. Hartshorn, and M. H. G. Munro, *Aust. J. Chem.*, **29**, 987 (1976).
(11) A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 3571 (1960); J. Fried, J. W. Brown, and L. Borkenhagen, *Tetrahedron Lett.*, 2499 (1965).
(12) C. R. Enzell and B. R. Thomas, *Tetrahedron Lett.*, 225 (1965).
(13) Vinyl group reductions: ref 4a; P. Ceccherelli, M. Curini, R. Pellicciari, and R. Coccia, unpublished observations.

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dissimilarity of the epoxide's two carbon–oxygen bonds due to the increased conformational flexibility of the cis-decalinic, terminal ring in which the epoxide is attached to one of its bridgehead carbons.

Lithium–ammonia reduction of the rigidly held, ring B epoxides led to single, axial alcohols, the 7α,8α-epoxides **1e** and **1f** yielding the 7α-hydroxy compounds **3d** and **3e**, respectively,[14] and the 7β,8β-epoxides **1g** and **1h** producing the 8β-hydroxy substances **3a** and **3c**, respectively.[12] The **1d** → **1h** → **3c** reaction sequence constitutes a partial synthesis of the heretofore unsynthesized natural product, isopimar-15-en-8β-ol (**3c**).[15]

Experimental Section

Infrared spectra of chloroform solutions were determined on a Beckman Acculab 5 spectrophotometer, and ^{1}H NMR spectra of deuteriochloroform solutions were determined on JEOL INM-C-60 HL and Varian EM-360 spectrometers. Melting points were recorded on a Kofler micro hot stage and are uncorrected. Column chromatography was performed with 0.063–0.200 mm mesh Merck silica gel adsorbant. All organic extracts were dried over anhydrous sodium sulfate.

7,8-Dihydro-8β,14β-epoxyvirescenol B Diacetate (1b). A mixture of 900 mg of 3β,19-diacetoxysandaracopimaradiene (**1a**)[2] and 480 mg of *m*-chloroperbenzoic acid in 30 mL of anhydrous ether was stirred at room temperature, protected from light, for 24 h. It then was treated with 1% sodium bisulfite solution, washed with saturated sodium bicarbonate solution and water, dried ($MgSO_4$), and evaporated. Chromatography of the residue, 870 mg, on alumina (activity IV) and elution with benzene yielded 150 mg of starting material and 420 mg of semisolid epoxide **1b**: ^{1}H NMR δ 1.01, 1.05, 1.10 (s, 3 each, Me), 2.01, 2.01 (s, 3 each, COMe), 2.51 (s, 1, H-14), 4.18, 4.26 (4-line AB, 2, J = 12 Hz, OCH_2), 4.51 (m, 1, OCH).

Anal. Calcd for $C_{24}H_{36}O_5$: C, 71.25; H, 8.97. Found: C, 71.38; H, 8.64.

8,14-Dihydro-8α,14α-epoxypimaradiene (2b). A mixture of 900 mg of pimaradiene (**2a**) and 480 mg of *m*-chloroperbenzoic acid in 30 mL of anhydrous ether was treated and worked up as above, leading to 100 mg of starting diene and 600 mg of semisolid epoxide **2b**: ^{1}H NMR δ 0.90, 0.90, 0.93, 1.11 (s, 3 each, Me), 2.75 (s, 1, H-14).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.45; H, 11.01.

7,8-Dihydro-8β-hydroxyvirescenol B (3a). A solution of 250 mg of epoxide **1b** in 8 mL of tetrahydrofuran was added slowly over a 20-min period to a solution of 35 mg of lithium in 40 mL of liquid ammonia, and the mixture was stirred at −40 °C for 1 h. Bromobenzene, 0.7 mL, was added, the ammonia was evaporated at room temperature under a stream of nitrogen, and 30 mL of 0.5 N sulfuric acid solution was added to the residue. The mixture was extracted with chloroform, and the extract was washed with water, dried, and evaporated under vacuum. Chromatography of the residue, 150 mg, and elution with 25:1 chloroform–methanol gave 120 mg of semisolid triol **3a**: ^{1}H NMR δ 0.95, 1.22, 1.22 (s, 3 each, Me), 3.40 (m, 1, OCH), 3.35 and 4.17 (4-line AB, 2, J = 12 Hz, OCH_2).

Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.60; H, 10.41.

Treatment of 200 mg of epoxide **1g** in 8 mL of tetrahydrofuran with 35 mg of lithium in 40 mL of liquid ammonia and workup as in the reduction of **1b** above yielded 160 mg of crude product, whose chromatography and elution with 25:1 chloroform–methanol yielded 130 mg of triol **3a**.

7,8-Dihydro-8β-hydroxyvirescenol B Diacetate (3b). A solution of 100 mg of triol **3a** and 2 mL of acetic anhydride in 3 mL of pyridine was kept at room temperature for 24 h. After the usual workup the crude product was chromatographed. Elution with 25:1 benzene–ethyl acetate gave 92 mg of semisolid ester **3b**: ^{1}H NMR δ 1.03, 1.03, 1.23 (s, 3 each, Me), 2.06, 2.06 (s, 3 each, COMe), 4.20, 4.43 (4-line AB, 2, J = 12 Hz, OCH_2), 4.60 (m, 1, OCH).

Anal. Calcd for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42. Found: C, 70.70; H, 9.51.

8,14-Dihydro-8α-hydroxypimaradiene (2c) and 8,14-Dihydro-14α-hydroxypimaradiene (4a). Treatment of 500 mg of epoxide **2b** in 16 mL of tetrahydrofuran with 70 mg of lithium in 80 mL of liquid ammonia and workup as in the reduction of **1b** above yielded 400 mg of crude product, whose chromatography and elution with 25:1 benzene–ethyl acetate gave 250 mg of semisolid alcohol **4a**: ^{1}H NMR δ 0.80, 0.83, 0.86, 1.00 (s, 3 each, Me), 3.26 (br s, 1, OCH).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.56; H, 11.92.

Further elution yielded 100 mg of semisolid alcohol **2c**: ^{1}H NMR δ 0.87, 0.90, 1.03, 1.33 (s, 3 each, Me).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.73; H, 11.71.

8,14-Dihydro-14α-acetoxypimaradiene (4b). A solution of 80 mg of of alcohol **4a** and 2 mL of acetic anhydride in 3 mL of pyridine was kept at room temperature for 24 h. After the usual workup, the crude product, 80 mg, was chromatographed. Elution with benzene gave 70 mg of semisolid acetate **4b**: ^{1}H NMR δ 0.80, 0.85, 0.87, 0.90 (s, 3 each, Me), 2.09 (s, 3, COMe), 5.17 (d, 1, J = 2 Hz, OCH).

Anal. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found: C, 79.25; H, 11.12.

8,14-Dihydro-14-oxopimaradiene (4c). A solution of Jones reagent (prepared from a solution of 70 g of chromium trioxide in 500 mL of water and 61 mL of concentrated sulfuric acid) was added slowly to a stirring solution of 200 mg of alcohol **4a** in 15 mL of acetone at room temperature until a brown color persisted for 10 min. The mixture was diluted with water and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue, 180 mg, and elution with 25:1 hexane–ether gave 160 mg of semisolid ketone **4c**: IR 1700 (s, C=O) cm^{-1}; ^{1}H NMR δ 0.83, 0.86, 0.93, 1.10 (s, 3 each, Me), 2.56 (m, 1, COCH).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.15; H, 11.29.

A solution of 50 mg of ketone **4c** and 1 mL of aqueous 1 N potassium hydroxide solution in 4 mL of ethanol was refluxed under nitrogen for 3 h. The cooled mixture was acidified with 2 N hydrochloric acid and extracted with chloroform. The extract was washed with water, dried, and passed through a short silica gel column yielding 45 mg of starting ketone, identical by spectra and TLC behavior with **4c** above.[16]

8,14-Dihydro-14β-hydroxypimaradiene (4d). A solution of 150 mg of ketone **4c** in 5 mL of tetrahydrofuran was added dropwise to a stirring suspension of 50 mg of lithium aluminum hydride in 10 mL of tetrahydrofuran, and the stirring was continued at room temperature for 1 h. After the usual workup and chromatography of the crude products, 140 mg, and elution with 12:1 benzene–ethyl acetate, there was obtained 30 mg of alcohol **4a** (vide supra) and 95 mg of semisolid alcohol **4d**: ^{1}H NMR δ 0.86, 0.86, 0.86, 1.08 (s, 3 each, Me), 2.83 (d, 1, J = 9 Hz, OCH).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.73; H, 11.71.

7,8-Dihydro-7α-hydroxyvirescenol B (3d). Treatment of 750 mg of epoxide **1e** in 20 mL of tetrahdyrofuran with 100 mg of lithium in 100 mL of liquid ammonia and workup as in the reduction of **1b** above yielded 550 mg of crude product, whose chromatography and elution with 25:1 chloroform–methanol gave 500 mg of solid. Crystallization of the latter from ether yielded triol **3d**: mp 200–203 °C; ^{1}H NMR δ 0.78, 1.02, 1.20 (s, 3 each, Me), 3.32 (m, 1, H-3), 3.37, 4.20 (4-line AB, 2, J = 11 Hz, OCH_2), 3.80 (m, 1, H-7).

Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.22; H, 10.89.

7,8-Dihydro-7α-hydroxyisopimaradiene (3e). Treatment of 200 mg of epoxide **1f** in 8 mL of tetrahydrofuran with 35 mg

(14) The C(8) stereochemistry of the products was not investigated. The 8β-H configuration is based on analogy with earlier observations.[12]

(15) R. E. Corbett and R. A. J. Smith, *J. Chem. Soc. C*, 300 (1967); B. R. Thomas, unpublished observations.

(16) Cf. E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Am. Chem. Soc.*, **86**, 2218 (1964); J. W. ApSimon, P. V. Demarco, and J. Lemke, *Can. J. Chem.*, **43**, 2793 (1965).

of lithium in 40 mL of liquid ammonia and workup as in the reduction of **1b** above yielded 180 mg of crude product, whose chromatography and elution with 20:1 benzene–ethyl acetate afforded 90 mg of starting epoxide and 56 mg of semisolid alcohol **3e**: ^{1}H NMR δ 0.86, 0.87, 0.88, 0.96 (s, 3 each, Me), 3.72 (m, 1, OCH).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.76; H, 11.71.

8β-Hydroxyisopimar-15-ene (3c). Treatment of 250 mg of epoxide **1h** in 8 mL of tetrahydrofuran with 35 mg of lithium in 40 mL of liquid ammonia and workup as in the reduction of **1b** above gave 180 mg of crude product, whose chromatography and elution with benzene led to 80 mg of starting epoxide and 60 mg of solid. Crystallization of the latter from aqueous acetone yielded alcohol **3c**: mp, mmp 40–41 °C (lit.[15] mp 40–41 °C); TLC and IR and ^{1}H NMR spectra were identical with those of an authentic sample.

Acknowledgment. The work in Perugia was supported by the C.N.R. (Rome). The authors are indebted to Dr. B. R. Thomas for a sample of natural 8β-hydroxyisopimar-15-ene.

Registry No. 1a, 82521-47-9; **1b**, 82521-48-0; **1c**, 11051-39-1; **1d**, 1686-66-4; **1e**, 77949-30-5; **1f**, 60389-93-7; **1g**, 77983-65-4; **1h**, 60410-34-6; **2a**, 1686-61-9; **2b**, 82521-49-1; **2c**, 82521-50-4; **3a**, 82521-51-5; **3b**, 82536-72-9; **3c**, 14699-32-2; **3d**, 82521-52-6; **3e**, 82521-53-7; **4a**, 82521-54-8; **4b**, 82521-55-9; **4c**, 82521-56-0; **4d**, 82521-57-1.

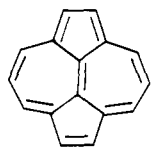
Communications

Azupyrene. Thermal Isomerization. Nitration by Silver Nitrite

Summary: Azupyrene (dicyclopenta[*ef*,*kl*]heptalene) undergoes thermal isomerization to pyrene and nitration in the 3-position by silver nitrite.

Sir: The thermal isomerization of azulene to naphthalene has been studied by several investigators and a recent paper has demonstrated that two competing mechanisms are involved.[1] It was thought, therefore, of interest to examine the stability of azupyrene (**1**) at elevated temperatures.

Heating azupyrene at 500–510 °C under N_2 at 10^{-4} torr for 1 h effected conversion (40% yield) to pyrene (**2**). The



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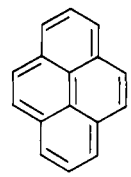

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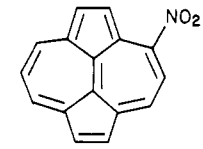
product was characterized by comparison with an authentic sample with respect to (i) its relatively rapid (compared to azupyrene) passage through a silica gel gas chromatograph column, (ii) its mass spectrum fragmentation pattern (main peaks at *m*/*e* (relative intensity) 202.1 (M^+, 100), 200.2 (24), 101 (33.3), 100 (28)), which was first identified as that of pyrene by computer matching with the spectra of 555 compounds of the same molecular weight, and (iii) its characteristic fluorescence spectrum.[2]

Treatment of 1,3-dibromoazulene and 5,7-dichlorocyclopenta[*c*]thiapyran with $AgNO_2$ gives replacement of one of the halogen atoms by a nitro group and evidence for an ionic mechanism for this process was obtained.[3] In that a 1-haloazupyrene could be envisioned to react in an analogous manner, the behavior of crude 1-chloroazupyrene[4] with $AgNO_2$ was examined. The product contained both chlorine and nitro substituents and this remarkable result was confirmed with azupyrene. Reaction of this hydrocarbon with $AgNO_2$ in aqueous THF under reflux (2 h) afforded a 20% (88% net) yield of 3-nitroazupyrene (**3**) as reddish-brown crystals, mp 154–156 °C,



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and metallic silver.[5] To our knowledge this is the first example of the direct substitution of a nitro group for a hydrogen on an aromatic hydrocarbon by nitrite ion. The formation of elemental silver accounts for the necessary reduction process and we suggest initial formation of a silver–azupyrene complex.

Further studies on the above transformations are planned.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation.

Registry No. 1, 193-85-1; 2, 129-00-0; 3, 82510-91-6; $AgNO_2$, 7783-99-5.

(1) Alder, R. W.; Whiteside, R. W.; Whitaker, G.; Wilshire, C. *J. Am. Chem. Soc.* **1979**, *101*, 629. See also: Scott, L. T.; Agopian, G. K. *Ibid.* **1977**, *99*, 4506.

(2) Parker, C. A.; Hatchard, C. G. *Trans. Faraday Soc.* **1963**, *59*, 284. We thank Professor James Callis for recording this spectrum.

(3) Anderson, A. G., Jr.; Harrison, W. F. *J. Am. Chem. Soc.* **1964**, *86*, 708.

(4) Masada, G. M. Ph.D. Thesis, University of Washington, Seattle, WA, 1972.

(5) Characterization of **3**: UV and visible (*n*-hexane), λ_{max} 242 ($10^4\epsilon$ 2.28), 249 (sh, 2.21), 266 (3.13), 307 (1.08), 325 (sh, 9.42), 340 (1.30), 409 ($10^3\epsilon$ 9.42), 439 (4.49), 474 (1.88), 487 (1.27) 511 ($10^2\epsilon$ 6.85), 522 (5.14); ^{1}H NMR ($CDCl_3$) δ 7.67 (t, 1, H-9), 8.52 (m, 4, H-1, H-2, H-6, H-7), 8.63 (d, 1, H-8), 8.79 (d, 1, H-10), 9.74 (m, 2, H-4, H-5); mass spectrum, *m*/*e* (relative intensity) 247 (M^+, 80), 248 (M + 1, 15); exact mass calcd for $C_{16}H_9NO_2$ 247.2535, found 247.2521. The NMR values are distinctly different from and inconsistent with those for 1-(trifluoroacetyl)azupyrene (cf. Anderson, A. G., Jr., Masada, G. M.; Kao, G. L. *J. Org. Chem.* **1980**, *45*, 1312) and 4-nitroazupyrene (cf. Kao, L. G. Ph.D. Thesis, University of Washington, Seattle, WA, 1981).

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