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.

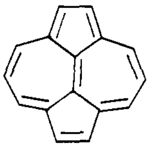
Communications

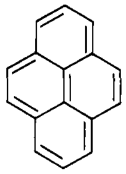
Azupyrene. Thermal Isomerization. Nitration by Silver Nitrite

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

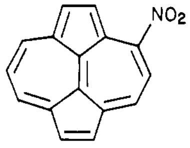
Sir: The thermal isomerization of azulene to naphthalene has been studied by several investigators and a recent paper has demonstrated that two competing mechanisms are involved.[1] It was thought, therefore, of interest to examine the stability of azupyrene (**1**) at elevated temperatures.

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


1


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, 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.



3

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.

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[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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