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The preparation of 3b,4a,7b,8a-tetrahydro-4*H*,8*H*-pyreno[4,5-*b*:9,10-*b'*]bisazirine and of 1a,6b,7a,12b-tetrahydro-1*H*,7*H*-dibenz[3,4:7,8]anthra[1,2-*b*:5,6-*b'*]bisazirine is described. The corresponding diepoxides were reacted with sodium azide in aqueous acetone and the mixtures of *trans*-azido alcohols, so formed, were cyclized by tri-*n*-butylphosphine.

J. Heterocyclic Chem., **18**, 1473 (1981).

The recent observation (1) that the mutagenic potencies of the K-region imines of phenanthrene (2), benzo[1,2-*c*:3,4-*c'*]dithiophene (3), benz[*a*]anthracene (4), 3-methylcholanthrene (5) benzo[*a*]pyrene (4), and dibenz[*a,h*]anthracene (4) are ~14 times higher than those of the corresponding arene oxides, urged us to investigate the syntheses of bisazirine derivatives of some carcinogenic and noncarcinogenic hydrocarbons.

In this Note we report the preparation of the first well characterized unsubstituted polycyclic arene bisimines (6).

Pyrene was converted into 3b,4a,7b,8a-tetrahydropyreno[4,5-*b*:9,10-*b'*]bisoxirene (1) via the respective dioxonide and [1,1'-biphenyl]-2,2',6,6'-tetracarboxaldehyde (7-8). Reaction of the diepoxide with a 100 fold of sodium azide in aqueous acetone at pH 7.7 yielded 78% of 2 and 3 in ratio 1:1.2 (calculated from the 300 MHz pmr spectrum). Treatment of the mixture of *trans*-azido alcohols with tri-*n*-butylphosphine in hexane gave

3b,4a,7b,8a-tetrahydro-4*H*,8*H*-pyreno[4,5-*b*:9,10-*b'*]bisazirine(4) in 88% yield. The solid bisimine was shown to be thermally stable, but underwent gradual ring cleavage >230° to give a mixture of aminopyrenes.

Likewise, 1a,6b,7a,12b-tetrahydrodibenz[3,4:7,8]anthra[1,2-*b*:5,6-*b'*]bisoxirene (5) from benz[*a,h*]anthracene via [1,1',4',1''-terphenyl]-2,2',2'',5'-tetracarboxaldehyde (8) was converted in 68% yield into a mixture of *trans*-azido alcohols 6 and 7 (ratio of isomers 1:4). The 300 MHz pmr indicated that practically none of the asymmetrical compound 8 was formed. The mixture of azido-alcohols was then heated with tri-*n*-butylphosphine to give the expected bisimine 9 in 83% yield.

EXPERIMENTAL

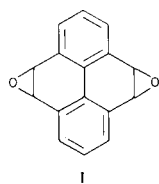
Reaction of 3b,4a,7b,8a-Tetrahydropyreno[4,5-*b*:9,10-*b'*]bisoxirene (1) with Sodium Azide.

A solution of 19.2 g of sodium azide in 150 ml of water and 300 ml of acetone was stirred with 0.7 ml of concentrated sulfuric acid. After 15 minutes 0.72 g of powdered 1(7-8) was added and stirring was continued at reflux for 24 hours. The acetone was removed under reduced pressure at room temperature; the precipitate was washed with water and recrystallized from dioxane-heptane to give 0.77 g (78%) of *trans*-azido-alcohols 2 and 3 (ratio 1:1.2); mp 164-165°; ir (nujol): 330 (OH) 2110 cm⁻¹ (N₃); 300 MHz pmr (deuteriochloroform): δ 2.466 (br s, 2H, OH), 4.691 (d, 1.1H, J = 7.5 Hz, CHN₃), 4.722 (d, 0.9H, J = 7.5 Hz, CHN₃), 4.817 (d, 0.9 H, J = 7.5 Hz, CHOH), 4.839 (d, 1.1H, J = 7.5 Hz, CHOH), 7.397-7.578 (m, 6H, ArH); ms (70 eV, 150°): m/e (relative intensity) 320 (M⁺; 39), 278 (6), 264 (6), 263 (11), 250 (12), 236 (22), 235 (100), 234 (13), 233 (12), 221 (12), 220 (41), 219 (26), 218 (16), 217 (15), 208 (12), 207 (29), 206 (50), 205 (86), 204 (25), 203 (13), 202 (10), 192 (17), 191 (36), 190 (51), 189 (12), 181 (6), 180 (17), 179 (13), 178 (16), 177 (20), 176 (16), 1656 (6), 165 (27), 164 (22), 163 (19), 153 (12), 152 (31), 151 (28), 150 (12).

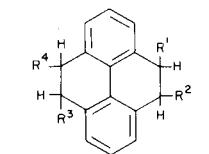
Anal. Calcd. for C₁₆H₁₂N₆O₂: C, 60.00; H, 3.78. Found: C, 60.00; H, 3.87.

3b,7b,8a-Tetrahydro-4*H*,8*H*-pyreno[4,5-*b*:9,10-*b'*]bisazirine (4).

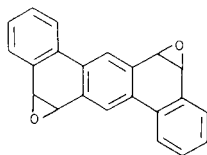
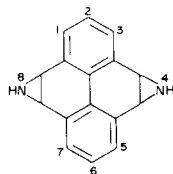
To a precooled solution (5°) of 0.77 g of the above mixture of 2 and 3 in 750 ml of *n*-hexane, there was added under nitrogen atmosphere, 4 ml of tri-*n*-butylphosphine. The mixture was stirred initially at 5° for 25 minutes, then at 25° for 15 minutes, and finally at 70° for 3.5 hours. Most of the hexane was removed *in vacuo*. The residue was filtered and washed thoroughly with hexane and recrystallized five times from ethyl acetate to give 0.49 g (88%) of pale yellow crystals that decompose (without melting) >230°; 300 MHz pmr (deuteriochloroform): δ 3.566 (s, 4H, H_{3b}, H_{4a}, H_{7b}, H_{8a}); 3.623 (br, 2H, H₄, H₈), 7.312 (t, 2H, J = 7.4 Hz,



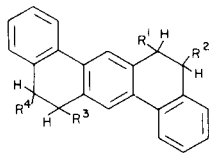
1



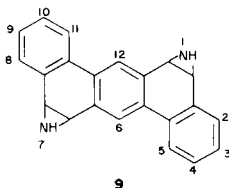
2 R¹ = R³ = N₃, R² = R⁴ = OH
3 R¹ = R⁴ = N₃, R² = R³ = OH



5



6 R¹ = R³ = N₃, R² = R⁴ = OH
7 R¹ = R³ = OH, R² = R⁴ = N₃
8 R¹ = R⁴ = N₃, R² = R³ = OH



9

H₂, H₆), 7.517 (d, 4H, J = 7.4 Hz, H₁, H₃, H₅, H₇); ms (70 eV, 100°): m/e (relative intensity) 232 (M⁺, 22), 218 (9), 217 (7), 204 (6), 189 (47), 176 (11), 162 (25), 161 (21), 147 (26), 134 (29), 133 (7), 120 (45), 105 (10), 92 (100), 78 (58).

Anal. Calcd. for C₁₆H₁₂N₂: C, 82.73; H, 5.17; N, 12.06. Found: C, 82.91; H, 5.38; N, 11.75.

Reaction of 1a,6b,7a,12b-Tetrahydridibenz[3,4:7,8]anthra[1,2-b:5,6-b']-bixoxirene (5) with Sodium Azide.

A solution of 39 g of sodium azide in 300 ml of water, 600 ml of acetone and one ml of concentrated sulfuric acid was stirred for 15 minutes. Under exclusion of air and light, there was added 1.27 g of 5 (8) and the stirring was continued for 16 hours under reflux. The acetone was removed *in vacuo* and the residue filtered and recrystallized twice from chloroform-heptane to give 1.11 g (68%) of azido-alcohols 6 and 7, mp 176-178° dec, darkens >120°; ir (nujol) 3300 (OH), 2105 cm⁻¹ (N₃); 300 MHz pmr (deuteriochloroform): δ 2.286 (br s, 2H, OH), 4.663 (d, 0.4H, J = 7.5 Hz, CHN₃), 4.705 (d, 1.6H, J = 7.3 Hz, CHN₃), 4.797 (d, 1.6H, J = 7.3 Hz, CHOH), 4.815 (d, 0.4H, J = 7.5 Hz, CHOH), 7.301-7.609 (m, 10H, ArH); ms (70 eV, 145°): m/e (relative intensity) 396 (M⁺, 13), 395 (45), 354 (11), 340 (26), 339 (26), 340 (24), 325 (39), 324 (26), 312 (25), 311 (100), 310 (37), 309 (41), 296 (72), 295 (39), 294 (25), 283 (24), 282 (69), 281 (88), 280 (54), 268 (36), 267 (59), 266 (59), 265 (23), 253 (27), 252 (39), 239 (29), 147 (24), 141 (38), 133 (32), 127 (23), 126 (28), 119 (25).

Anal. Calcd for C₂₂H₁₆N₆O₂: C, 66.66; H, 4.07. Found: C, 66.42; H, 4.05.

1a,6b,7a,12b-Tetrahydro-1H,7H-dibenz[3,4:7,8]anthra[1,2-b:5,6-b']bisazirine (9).

A precooled suspension (0°) of 0.70 g of azido-alcohols 6 and 7 in 1250 ml of *n*-hexane was treated with 2.45 ml of tri-*n*-butylphosphine under exclusion of air and moisture. The mixture was heated gradually (30 minutes) to reflux and kept at this temperature for 24 hours. The hexane was evaporated and the residue recrystallized four times from chloroform-hexane to give 0.45 g (83%) of 9 as light tan crystals that did not melt below 260°; 300 MHz pmr (deuteriochloroform): δ 1.600 (br, 2H, H₁, H₇), 3.642 and 3.677 (ABq, 4H, J_{AB} = 5.5 Hz, H_{1a}, H_{6a}, H_{7a}, H_{12a}),

7.346 (dd, 2H, J_{4,3} = 7.3 Hz, J_{4,5} = 8.1 Hz, H₄, H₁₀), 7.429 (dd, 2H, J_{3,2} = 6.9 Hz, J_{3,4} = 7.3 Hz, H₃, H₉), 7.620 (d, 2H, J_{2,3} = 6.9 Hz, H₂, H₈), 8.139 (d, 2H, J_{5,4} = 8.1 Hz, H₅, H₁₁), 8.259 (s, 2H, H₆, H₁₂); ms (70 eV, 170°) m/e (relative intensity) 308 (M⁺, 22), 293 (7), 281 (4), 280 (5), 265 (4), 221 (6), 189 (27), 176 (6), 162 (15), 161 (14), 147 (25), 134 (19), 133 (7), 126 (4), 120 (31), 106 (5), 105 (8), 92 (100), 78 (66).

Anal. Calcd. for C₂₂H₁₆N₂: C, 85.69; H, 5.22; N, 9.08. Found: C, 85.41; H, 5.20; N, 8.76.

Acknowledgement.

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