

Darzens Reactions with Quinonoid Systems. Part 1. Spiro[oxiran-2,9'-phenanthrenes] from Phenanthrenequinone, and Phenanthro-oxazoles from Phenanthrenequinone Imine or Phenanthrenequinone Mono-oxime

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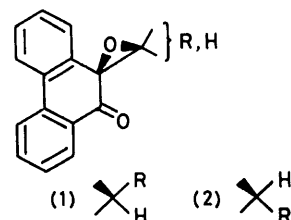
Phenanthrenequinone reacts with substituted benzyl and phenacyl halides in the presence of base to give derivatives of spiro[oxiran-2,9'-phenanthrene]. Phenanthrenequinone imine and mono-oxime, under similar conditions, give phenanthro-oxazoles.

PROLONGED reaction of phenanthrenequinone with *p*-nitrobenzyl chloride¹ in the presence of base gives the spiro[oxiran-2,9'-phenanthrene] (1; R = C₆H₄·NO₂-*p*). We have found that a shorter reaction time produces a product which we consider to be the corresponding *S*-isomer (2; R = C₆H₄NO₂-*p*). Presumably the latter isomerized to the *R*-form (1) during prolonged treatment with base.

With *o*-nitrobenzyl chloride only one product was isolated; by analogy we believe this to be the *S*-isomer (2; R = C₆H₄NO₂-*o*).

Similar reactions with phenacyl chloride or *p*-bromophenacyl bromide gave in each case two products in amounts depending on the time of heating. Heating for 1 h gave the spiro-compounds (2; R = COPh) and (2;

R = CO·C₆H₄Br-*p*), respectively, whereas after 14 h the corresponding enol forms were obtained. Each of the latter shows only one C=O band and hydroxy-absorption in the i.r. In addition the keto-compound



(2; R = CO·C₆H₄Br-*p*) shows an oxiran proton n.m.r. signal at δ 4.2, which is absent from spectrum of the enol form. The latter showed instead a signal for an enolic

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¹ E. Bergmann and J. Harvey, *Ber.*, 1929, **62**, 893.

TABLE 1
Products from Darzens reactions with phenanthrenequinone

| Compound (2; R = C ₆ H ₄ NO ₂ - <i>p</i>) ^b | Reaction time (h) | M.p. (°C) | Yield (%) | Found (%) | | | Formula | Required % | | | ν _{max.} / cm ⁻¹ | λ _{max.} / nm (ε _{max}) |
|---|----------------------|-----------|--------------|-----------|------|---------------|--|------------|------|---------------|---|---|
| | | | | C | H | N | | C | H | N | | |
| | 1 | 137—138 | 74.6 | 73.3 | 3.95 | 4.4 | C ₂₁ H ₁₃ NO ₄ | 73.45 | 3.79 | 4.1 | 1 684, 1 572, 826 | 256 (56 000), 310 (10 000), 323 (13 000), 365 (1 900), 383 (1 700), |
| (1; R = C ₆ H ₄ NO ₂ - <i>p</i>) ^a | 14 | 153 | 79.4 | 73.9 | 3.9 | 4.15 | C ₂₁ H ₁₃ NO ₄ | 73.45 | 3.79 | 4.1 | 1 667, 1 527, 826 | 256 (70 000), 310 (16 000), 323 (17 000), 365 (2 200), 382 (2 100), |
| (2; R = C ₆ H ₄ NO ₂ - <i>o</i>) ^a | 1 or 14 | 190—191 | 35.0 | 73.4 | 4.0 | 4.15 | C ₂₁ H ₁₃ NO ₄ | 73.45 | 3.79 | 4.1 | 1 695, 1 534, 797 | 245 (53 000) |
| (2; R = COPh) ^a | 1 | 161—162 | 31.8 | 81.05 | 4.25 | | C ₂₂ H ₁₄ O ₃ | 81.0 | 4.3 | | 1 689, 794 | 247 (45 000) |
| (2; R = COPh) (enol form) ^c | 14 | 195—197 | 41.8 | 80.45 | 4.25 | | C ₂₂ H ₁₄ O ₃ | 81.0 | 4.3 | | 3 326, 1 695, 1 643, 799 | 246 (65 000), 360 (7 800), 377 (81,000) |
| (2; R = CO·C ₆ H ₄ Br- <i>p</i>) ^d | 1 | 169—170 | 71.0 | 65.95 | 3.2 | (Br 19.05) | C ₂₂ H ₁₃ BrO ₃ | 65.2 | 3.2 | (Br 19.75) | 1 681, 779 | 247 (51 000) |
| (2; R = CO·C ₆ H ₄ Br- <i>p</i>) enol form ^d | 14 | 215 | 79.0 | 65.55 | 3.15 | (19.65) | C ₂₂ H ₁₃ BrO ₃ | 65.2 | 3.2 | (19.75) | 3 226, 1 689, 1 626, 769 | 246 (71 000), 360 (8 700), 377 (9 100) |

^a From ethanol. ^b From glacial acetic acid. ^c From 2 : 1 v/v glacial acetic acid-water. ^d From methanol.

TABLE 2
Products from Darzens reactions with phenanthrenequinone imine

| Compound (3; R = C ₆ H ₄ NO ₂ - <i>p</i>) ^b | Reaction time (h) | M.p. (°C) | Yield (%) | Found (%) | | | Formula | Required (%) | | | ν _{max.} / cm ⁻¹ | λ _{max.} / nm (ε _{max}) |
|---|----------------------|-----------|--------------|-----------|------|------|---|--------------|------|------|---|---|
| | | | | C | H | N | | C | H | N | | |
| | 14 | 280—281 | 72.7 | 74.1 | 3.6 | 8.2 | C ₂₁ H ₁₂ N ₂ O ₃ | 74.1 | 3.55 | 8.25 | 1 511 | 250 (163 200), 377 (58 140) |
| (3; R = C ₆ H ₄ NO ₂ - <i>o</i>) ^a | 14 | 170—172 | 56.1 | 74.35 | 3.7 | 8.7 | C ₂₁ H ₁₂ N ₂ O ₃ | 74.1 | 3.55 | 8.25 | 1 534 | 252 (157 250), 355 (23 800) |
| (3; R = COPh) ^a | 14 | 201—203 | 39.5 | 82.3 | 4.05 | | C ₂₂ H ₁₃ NO ₂ | 81.75 | 4.0 | | 1 661 | 244 (109 800), 252 (129 200), 366 (31 500) |
| (3; R = CO·C ₆ H ₄ Br- <i>p</i>) ^b | 14 | 240—241 | 74.5 | 65.55 | 3.0 | 3.65 | C ₂₂ H ₁₂ BrNO ₂ * | 65.65 | 3.0 | 3.5 | 1 656 | 244 (67 770), 252 (73 940), 272 (28 700), 370 (21 250) |

^a From ethanol. ^b From glacial acetic acid.

* Found: Br, 20.0. C₂₂H₁₂BrNO₂ requires Br, 19.9%.

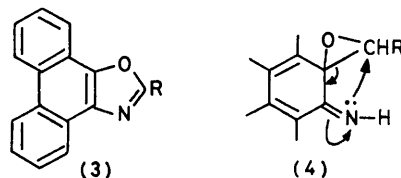
proton at δ 6.48, similar to that observed with cyclic α-diketones.²

Phenanthrenequinone imine reacts with *o*- and *p*-nitrobenzyl chloride, phenacyl chloride, and *p*-bromophenacyl bromide to give the 2-substituted phenanthro-oxazoles (3; R = C₆H₄NO₂-*o*), (3; R = C₆H₄NO₂-*p*), (3; R = COPh), and (3; R = CO·C₆H₄Br-*p*), respectively. Presumably the oxiran (4) formed initially cyclises as shown to give the dihydrophenanthro-oxazole which then undergoes aerial oxidation.

o- and *p*-Nitrobenzyl chloride also react with phenanthrenequinone mono-oxime to give the oxazoles (3; R = C₆H₄NO₂-*o*) and (3; R = C₆H₄NO₂-*p*), respectively. These last compounds were also prepared from phenanthrenequinone imine and *o*- or *p*-nitrobenzaldehyde in the presence of triethylamine.³ The oxazole

(3; R = C₆H₄NO₂-*p*) was also prepared by the photo-reaction of phenanthrenequinone imine with *p*-nitrobenzaldehyde followed by pyrolysis.⁴

Phenanthrenequinone di-imine⁵ tetra-acetate did not react with *o*- or *p*-nitrobenzyl chloride.



EXPERIMENTAL

I.r. spectra were recorded for KBr discs, u.v. spectra for solutions in ethanol, and n.m.r. spectra (100 MHz) for solutions in deuteriated chloroform or acetonitrile.

⁴ A. Schönberg and W. I. Awad, *J. Chem. Soc.*, 1945, 197.

⁵ E. A. Steck and A. R. Day, *J. Amer. Chem. Soc.*, 1943, **65**, 452.

² R. M. Silverstein, and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' Wiley, New York, 1967, p. 144.
³ W. C. Stein and A. R. Day, *J. Amer. Chem. Soc.*, 1942, **64**, 2567.

Reactions of Phenanthrenequinone with Benzyl or Phenacyl Halides.—A mixture of phenanthrenequinone (1.3 g), *o*- or *p*-nitrobenzyl chloride (2.2 g), potassium carbonate (1.0 g), and ethanol (30 ml) was boiled under reflux and then cooled. The precipitate was collected, washed with hot water, and crystallized. Similar reactions were performed with phenacyl chloride (1.9 g) and *p*-bromophenacyl bromide (3.5 g) to give the products described in Table 1.

The products from related reactions with phenanthrenequinone imine ⁶ and mono-oxime ⁷ are described in Table 2.

2-(4-Nitrophenyl)phenanthro[9,10-d]oxazole.—(a) A mixture of phenanthrenequinone imine (0.7 g), *p*-nitrobenzaldehyde (0.5 g), and triethylamine (0.3 g) in ethanol (25 ml) was boiled for 30 min, cooled, and filtered. The residual solid crystallized from glacial acetic acid to give the *phenanthro-oxazole* (0.7 g), m.p. 280—281 °C (Found: N, 8.45. C₂₁H₁₂N₂O₃ requires N, 8.25%).

(b) A mixture of phenanthrenequinone imine (0.7 g), *p*-nitrobenzaldehyde (0.5 g), and benzene (60 ml) in a

Pyrex Schlenk tube under nitrogen was exposed to September Iraqi sunlight for 1 day. The crystalline product crystallized from benzene to give *2,3-dihydro-2-hydroxy-2-(4-nitrophenyl)phenanthro[9,10-d]oxazole* (62.4%), m.p. 250—252 °C (Found: C, 70.45; H, 3.9; N, 7.9. C₂₁H₁₄N₂O₄ requires C, 70.4; H, 3.9; N, 7.8%), ν_{\max} . 3 311 (NH) and 3 049 cm⁻¹ (OH), λ_{\max} . 251 nm (ϵ 43 000). This was heated under vacuum at 270 °C; the product crystallized from glacial acetic acid to give the phenanthro-oxazole, m.p. 280—282°.

2-(2-Nitrophenyl)phenanthro[9,10-d]oxazole.—Prepared from *o*-nitrobenzaldehyde as in (a) above, this *oxazole* crystallized from ethanol; m.p. 170—172°; yield 56.1% (Found: C, 74.0; H, 3.45; N, 8.35. C₂₁H₁₂N₂O₃ requires C, 74.1; H, 3.55; N, 8.25%).

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⁶ J. Schmidt and E. Junghans, *Ber.*, 1904, **37**, 3558.

⁷ J. Meisenheimer, *Annalen*, 1907, **355**, 307.