Direct Amination of 9-Hydroxy-1-oxophenalene to Produce 9-Amino-1-oxophenalene and Related Compounds

R.C. HADDON*, S. V. CHICHERSTER, S. L. MAYO**

AT & T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974, U.S.A.

In connection with our studies of organo-non-metallic complexes of the 1,9-disubstituted phenalene unit 1 we required access to compounds possessing a total of just two ionizable hydrogen atoms in the A,B groups of 1. The prototypical compound in this series, 9-amino-1-oxophenalene (2), is not known although 9-hydroxy-1-oxophenalene (3) was first prepared in 1941 and a number of derivatives of 1 possessing one or three ionizable hydrogen atoms in the A,B groups have recently become available. We have found that the high-pressure reaction between 9-hydroxy-1-oxophenalene (3) and aqueous ammonia affords the desired 9-amino-1-oxophenalene (2) in high yield and good purity under relatively mild conditions. In addition 2 may be alkylated to produce the 9-amino-1-ethoxyphenalenylium salt which serves as a precursor for the other derivatives in this series with two ionizable hydrogen atoms in the A,B groups of 1.

In connection with our studies of organo-non-metallic complexes of the 1,9-disubstituted phenalene unit 1, we required access to compounds possessing a total of just two ionizable hydrogen atoms in the A,B groups (1). The prototypical compound in this series, 9-amino-1-oxophenalene (2), is not known although 9-hydroxy-1-oxophenalene (3) was first prepared in 1941 and a number of derivatives of 1 possessing one or three ionizable hydrogen atoms in the A,B groups have recently become available.

The related 6-amino-7-oxobenz[d,e]anthracene (4) was first prepared by heating 7-oxobenz[d,e]anthracene (5) with sodium amide in the presence of oxygen while a subsequent synthesis utilized the high-pressure reaction between 6-hydroxy-7-oxobenz[d,e]anthracene (6) and aqueous ammonia at 210-220°C over a period of six hours. While these reactions did not prove particularly satisfactory in our hands, the analogous reaction between 9-hydroxy-1-oxophenalene (3) and aqueous ammonia affords the desired 9-amino-1-oxophenalene (2) in high yield and good purity under relatively mild conditions (125°C, 1 h). This reaction provides a particularly convenient entry into this series of compounds as previous general syntheses of derivatives 1 have first required the generation of a 9-alkoxy-1-oxophenalene via the use of silver oxide and an alkyl iodide to disrupt the hydrogen bond in 3.

The direct amination of 9-hydroxy-1-oxophenalene (3) is not restricted to the reaction with aqueous ammonia. Thus,
aqueous dimethylaniline reacts with 3 under the same conditions as were employed in the preparation of 2. In this way it is possible to prepare 9-alkylamino-1-oxophenalenes (e.g. 11) directly from 3 in high yield and good purity. In the case of high boiling primary amines (b.p. > 130 °C), high-pressure techniques are not required and overnight reflux of 3 in the neat amine effects a virtually quantitative conversion of 12 with n-hexylamine (b.p. 131–132 °C).

Although it seems clear that the amination of 3 depends on a nucleophilic attack by the amine, we found other nucleophiles to be ineffective in this regard. Aqueous sodium sulfide and anhydrous hydrogen sulfide both failed to produce 9-hydroxy-1-thioxophenalene and compound 3 was recovered unchanged. Likewise the action of methanol did not bring about the formation of 9-methoxy-1-oxophenalene. Under particularly forcing conditions this reaction gave rise to dark needles containing copper and nickel—presumably in the form of complexes generated by reaction of 3 with the Monel bomb.

The amination reaction itself must be regarded as unusual as the reaction of 9-hydroxy-1-oxophenalene with aqueous sodium sulfide in an evacuated Monel bomb vented and opened, and the contents poured into boiling heptane; total yield: 7.8 g (85%); m.p. 159–159.9 °C. 9-Amino-1-oxophenalene (2):

A mixture of 9-hydroxy-1-oxophenalene (3; 9.8 g, 0.05 mol) and concentrated ammonium hydroxide solution (200 ml, specific gravity 0.9) is placed in a Monel bomb. The contents are stirred vigorously at an internal temperature of 125 °C for 1 h during which the pressure in the bomb is about 175 psi. The mixture is allowed to cool, the bomb vented, opened, and the contents poured into distilled water (200 ml), and the mixture separated by filtration. The crude yield is virtually quantitative and the material quite pure (m.p. 159 °C). Sublimation gives rise to an orange-yellow solid; yield: 7.8 g (80%); leafless from benzene; m.p. 159.2–159.9 °C. C₅₋₆H₄NO calc. C 79.98 H 4.65 N 7.18 (195.2) found 79.93 4.95 7.14

1H-N.M.R. (CDCl₃/TMS): δ = 6.8–7.9 (m, 7 H); 6.9 ppm (br, s, 1 H).

I.R. (CsI): ν = 3290 (s, br), 3140 (m, br), 3030 (w), 1632 (vs), 1587 (s), 1560 (s), 1525 (s), 1462 (w), 1423 (m), 1346 (s), 1323 (m), 1281 (m), 1235 (m), 1210 (w), 1170 (m), 1146 (w), 1121 (m), 965 (s), 944 (m), 830 (vs), 739 (s), 730 (m), 696 (w), 670 (w), 580 (m), 524 (m), 460 (w), 428 (m), 400 (w), 335 cm⁻¹ (w).

U. V. (CH₂Cl₂); λ_max = 248 (ε = 38,000); 265 (17,000); 277 (16,000); 334 (14,000); 349 (27,000); 405 (6,100); 429 (14,000); 455 nm (18,000).

9-Amino-1-ethoxyphenalenylidene Tetrafluoroborate (7):

Triethyl oxonium tetrafluoroborate (1.9 g, 0.01 mol) is added to a solution of 9-aminomethoxyphenalenylidene (2; 1.95 g, 0.01 mol) in dry 1,2-dichloroethane (50 ml) under argon. The resulting wine-red solution gives rise to a yellow precipitate. After stirring overnight a bright yellow solid is separated by filtration and vacuum dried; yield 2.51 g (81%). This material is suitable for use in subsequent reactions, but can be further purified by recrystallization from ethanol to give yellow needles; m.p. 232 °C.

C₁₃H₁₄BF₄NO calc. C 75.00 H 5.05 N 4.50 (311.1) found 75.75 4.53 4.46

1H-N.M.R. (CDCl₃/TMS): δ = 2.48 (q, 4, 2 H, f = 7 Hz); 4.62 (q, 4, 2 H, J = 7 Hz); 6.9–8.4 (m, 7 H); 8.5 (br, s, 1 H); 8.9 ppm (br, s, 1 H).

U. V. (CH₃CN): λ_max = 265 (ε = 23,600); 284 (19,900); 314 (5,900); 337 (3,600); 350 (3700); 372 (23,600); 410 (7,100); 432 (11,800); 456 nm (12,300).

9-Amino-1-iminophenalene (8):

Ammonia gas is bubbled through a slurry of 9-aminomethoxyphenalenylidene tetrafluoroborate (7; 1.55 g, 0.005 mol) in ethanol (50 ml) until all of the solid has dissolved (~ 2 h) to give a dark green solution. The ethanol is removed by evaporation and the solid extracted with benzene. The benzene solution is washed with water, dried with magnesium sulfate, and taken down on a rotary evaporator. The solid is recrystallized from heptane to give a yellow solid (0.82 g). Recrystallization from heptane gives yellow plates; yield: 0.53 g (55%); m.p. 186 °C (Ref. 3.5; m.p. 188 °C).

C₁₃H₁₂BF₄NO calc. C 76.00 H 5.24 N 4.50 (280.3) found 76.07 5.25 4.46

1H-N.M.R. (CDCl₃/TMS): δ = 3.00 (s, 6 H); 6.6–8.0 ppm (2 H); 6.9–7.3 ppm (6 H); 7.0 ppm (2 H); 7.3 (1 H); 8.0 ppm (1 H); 8.0 ppm (1 H).

U. V. (hexane); λ_max = 240 (ε = 32,900); 284 (19,900); 314 (5,900); 337 (3,600); 350 (7400); 372 (6300); 394 (5300); 428 (6600); 450 (12300); 478 nm (12300).

9-Amino-1-thioxophenalene (9):

33% Ethanolamine (8.03 mol, 4 ml) is added to a slurry of 9-aminomethoxyphenalenylidene tetrafluoroborate (7; 1.55 g, 0.005 mol) in ethanol (50 ml) and the mixture stirred overnight. The resulting yellow solid is separated by filtration and recrystallized from heptane to give brownish-yellow needles (0.40 g). A further quantity of product is obtained by taking the filtrate to dryness and extracting the solid with boiling heptane; total yield: 0.54 g (44%); m.p. 148 °C.

C₁₃H₁₂N₂O calc. C 80.77 H 5.77 N 13.46 (208.3) found 80.77 5.83 13.45

1H-N.M.R. (CDCl₃/TMS): δ = 3.00 (s, 6 H); 6.6–8.0 ppm (2 H); br, 7H, m, 7H).

U. V. (hexane): λ_max = 265 (ε = 39,100); 284 (19,900); 314 (5,900); 337 (3,600); 350 (7400); 372 (6300); 394 (5300); 428 (6600); 450 (12300); 478 nm (12300).

9-Amino-1-thioxophenalene (10):

Sodium 9-hydroxy-1-thioxophenalene tetrafluoroborate (7; 1.55 g, 0.005 mol) in methanol (50 ml) and the mixture stirred overnight. The solvent is removed and the residue extracted with benzene. The resulting solution is washed with water, the organic layer dried with magnesium sulfate, and then taken down on a rotary evaporator. The solid is recrystallized from benzene/heptane to give shiny, dark-red plates; yield: 0.52 g (50%); m.p. 130–131 °C.

C₁₃H₁₀NS calc. C 73.93 H 4.27 N 6.64 (211.3) found 74.01 4.62 6.68

1H-N.M.R. (CDCl₃/TMS): δ = 6.8–8.2 (m, 7 H); 6.0–8.6 ppm (br).
U.V. (hexane): $\lambda_{\text{max}} = 230 (t = 14,600); 250 (16,300); 269 (14,600); 292 (24,400); 330 (5,000); 345 (7,100); 372 (10,200); 390 (26,300); 426 (3,700); 452 (6,000); 495 (10,600); 517 (9,700); 528 nm (11,100).

9-Methylamino-1-oxophenalene (11):
A mixture of 9-hydroxy-1-oxophenalene (3; 0.98 g, 0.005 mol) and aqueous methylamine (10 ml; 40% solution) is placed in a Monel bomb. The contents are stirred vigorously at an internal temperature of 125 °C for 1 h during which the pressure in the bomb is about 150 psi. The mixture is allowed to cool, the bomb vented, opened, and the contents poured into distilled water (50 ml). The aqueous mixture is extracted with benzene, the organic layer is separated, dried with magnesium sulfate, and taken down on a rotary evaporator to give a yellow solid; yield: 0.88 g (83%); m.p. 110-111 °C (Ref. 5, m.p. 112 °C).

9-n-Hexylamino-1-oxo-phenalene (12):
A mixture of 9-hydroxy-1-oxophenalene (3; 0.98 g, 0.005 mol) and hexylamine (10 ml) is refluxed overnight. The excess amine is removed on a rotary evaporator to give a brownish-yellow oil which crystallizes on standing under a stream of nitrogen. Recrystallization from hexane gives yellow plates; yield: 1.2 g (85%); m.p. 72 °C. 

$C_{14}H_{21}NO$

<table>
<thead>
<tr>
<th>Calc.</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.68</td>
<td>7.58</td>
<td>5.01</td>
<td></td>
</tr>
</tbody>
</table>

(279.4) found 82.03 7.67 5.03

Received: October 29, 1984
(Revised form: December 12, 1984)

* Address for correspondence.
** AT & T Bell Laboratories Corporate Research Fellow, 1983. Present address: Chemistry Department. California Institute of Technology, Pasadena, California 91125, U.S.A.

1 Haddon, R. C., Chichester, S. V., Mayo, S. L., Marshall, J. H., to be published.
6 Neidlein, R., Behzadi, Z. Chem. Unserer Zeit. 1978, 102, 150.
9 Bradley, W., Jadhav, G. V. J. Chem. Soc. 1948, 1622.