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FORMATION AND CLEAVAGE OF THE QUINAZOLINIUM RING IN VILSMEIER–HAACK FORMYLATION OF 4-DIALKYLAMINO-SUBSTITUTED NAPHTHALIC ACID DERIVATIVES

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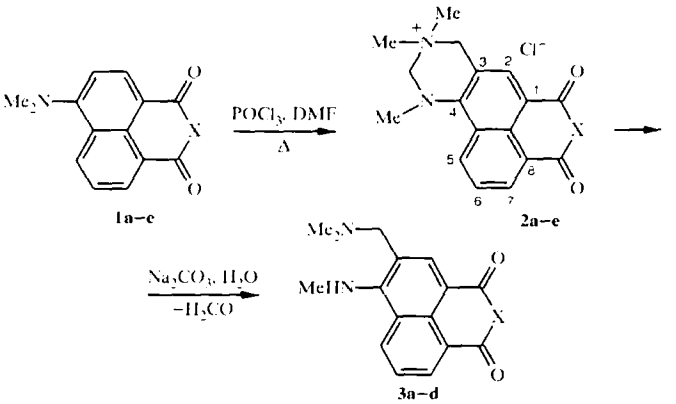
When 4-dimethylamino-substituted N-arylimides of naphthalic acid **1a-c** are heated with $POCl_3$ and DMF (Vilsmeier–Haack reaction conditions), instead of the expected 3-formyl-substituted derivatives, the diazinium salts **2a-c** are formed [1]. In alkaline medium, the quaternized heterocycle is cleaved, but the exact structure of the compounds formed has remained undetermined.

We have observed that methylimide **1d** and anhydride **1e** also undergo heterocyclization, and the base hydrolysis products are 4-methylamino-substituted **3a-d**. The 4-diethylamino-substituted derivative **4** reacts similarly. But the quaternary salt **5** is not isolated in pure form, and its hypothetical structure is established in analogy with molecules **2a-e** and based on the structure of compound **6**.



1–3a X = NPh, **b** X = *p*-Me–C_6H_4N, **c** X = *p*-MeO–C_6H_4N, **d** X = NMe, **e** X = O

5,9,9,11-Tetramethyl-4,6-dioxo-5,6,8,9,10,11-hexahydro-4H-isoquino[4,5-*gh*]quinazolin-9-ium Chloride (2d). Yield 51%; mp 235°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 3.33 (6H, s, $^+N(CH_3)_2$); 3.42 (3H, s, CH_3); 3.70 (3H, s, 4-NCH_3); 5.01 (2H, s, CH_2); 5.22 (2H, s, CH_2); 7.84-8.55 ppm (4H, m, arom.). Found, %: N 12.23; Cl 10.15. $C_{18}H_{20}N_3O_2Cl$. Calculated, %: N 12.15; Cl 10.25.

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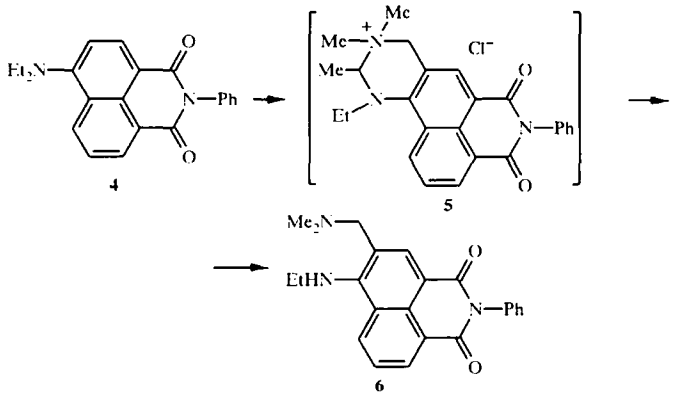

9,9,11-Trimethyl-4,6-dioxo-8,9,10,11-tetrahydro-4H,6H-isochromeno[4,5-*gh*]quinazolin-9-ium Chloride (2e). Yield 20%; mp 253°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 3.27 (6H, s, $^+N(CH_3)_2$); 3.69 (3H, s, 4-NCH_3); 4.98 (2H, s, CH_2); 5.18 (2H, s, CH_2); 7.89-8.67 ppm (4H, m, arom.). Found, %: N 8.10; Cl 10.85. $C_{17}H_{17}N_2O_3Cl$. Calculated, %: N 8.42; Cl 10.65.

5-Dimethylaminomethyl-6-methylamino-2-phenyl-2,3-dihydro-1H-benzo[*de*]isoquinoline-1,3-dione (3a). Yield 40%; mp 222-223°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 2.20 (6H, s, $N(CH_3)_2$); 3.43 (3H, s, 4-NCH_3); 3.64 (2H, s, 3-CH_2); 7.70 (1H, s, NH); 7.30-8.78 ppm (9H, m, arom.). Found, %: N 11.17. $C_{22}H_{21}N_3O_2$. Calculated, %: N 11.69.

5-Dimethylaminomethyl-6-methylamino-2-(4-methylphenyl)-2,3-dihydro-1H-benzo[*de*]isoquinoline-1,3-dione (3b). Yield 50%; mp 214-216°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 2.20 (6H, s, $N(CH_3)_2$); 2.39 (3H, s, CH_3); 3.43 (3H, s, 4-NCH_3); 3.64 (2H, s, 3-CH_2); 7.70 (1H, s, NH); 7.16-8.79 ppm (8H, m, arom.). Found, %: N 10.53. $C_{23}H_{23}N_3O_2$. Calculated, %: N 11.25.

5-Dimethylaminomethyl-2-(4-methoxyphenyl)-6-methylamino-2,3-dihydro-1H-benzo[*de*]isoquinoline-1,3-dione (3c). Yield 62%; mp 214-215°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 2.20 (6H, s, $N(CH_3)_2$; 3.42 (3H, s, 4-NCH_3); 3.64 (2H, s, 3-CH_2); 3.82 (3H, s, OCH_3); 7.70 (1H, s, NH); 7.05-8.77 ppm (8H, m, arom.). Found, %: N 10.60. $C_{23}H_{23}N_3O_3$. Calculated, %: N 10.79.

5-Dimethylaminomethyl-2-methyl-6-methylamino-2,3-dihydro-1H-benzo[*de*]isoquinoline-1,3-dione (3d). Yield 48%; mp 139-142°C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 2.20 (6H, s, $N(CH_3)_2$); 3.34 (3H, s, CH_3); 3.41 (3H, s, 4-NCH_3); 3.64 (2H, s, 3-CH_2); 7.68 (1H, s, NH); 7.63-8.74 ppm (4H, m, arom.). Found, %: N 13.78. $C_{17}H_{19}N_3O_2$. Calculated, %: N 14.13.

5-Dimethylaminomethyl-6-ethylamino-2-phenyl-2,3-dihydro-1H-benzo[*de*]isoquinoline-1,3-dione (6). Yield 20%; mp 215-218°C (benzene). ^{1}H NMR spectrum (300 MHz, DMSO-d_6): 1.30 (3H, t, CH_3); 2.22 (6H, s, $N(CH_3)_2$); 3.66 (2H, s, 3-CH_2); 3.77 (2H, d, 4-NCH_2); 7.66 (1H, s, NH); 7.31-8.69 (9H, m, arom.). Found, %: N 10.87. $C_{23}H_{23}N_3O_2$. Calculated, %: N 11.25.

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