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Chemistry of Coumarins. Some Novel Heterocycles from Deoxygenation of 4-Arylamino-3-nitrocoumarins

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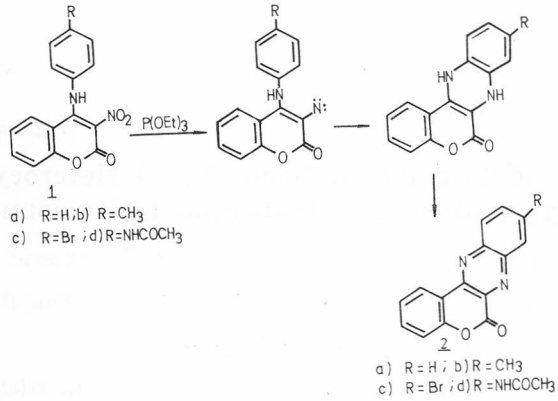
Reaction of 4-arylamino-3-nitrocoumarins with triethyl phosphite was investigated. The yet unreported 6-H-1-benzopyrano-[4,3-b]quinoxalin-6-one (*2a*) system was synthesized and characterized on the basis of spectral and analytical data. Four derivatives (*2a*—*2d*) were obtained in good yields ranging from 68 to 76%.

It has been known for some years that deoxygenation of aromatic nitro-compounds affords products formally derivable from nitrene intermediates[1]. In the phenyl o-nitrophenyl sulfide series a new rearrangement was discovered[2,3], in which a spirocyclic intermediate is implicated in the formation of phenothiazines[4,5]. The amine analogs also react by rearrangement[6], whereas the sulfone gives a mixture of rearranged and unrearranged products[7]. The possibility of synthesizing new ring system prompted an investigation of phosphite deoxygenation of 4-arylamino-3-nitrocoumarins derivatives. This paper presents the continuation of our studies towards the synthesis of new heterocyclic systems annelated on coumarin ring in position 3, 4[8–13].

RESULTS AND DISCUSSION

The 4-arylamino-3-nitrocoumarins (*1a*—*1d*), prepared from 4-chloro-3-nitrocoumarin and the appropriate arylamine prepared according to the published procedure[12], were heated under reflux for 3 to 20 hours with $P(OEt)_3$. The reaction was monitored by TLC on silica gel using benzene-acetic acid-ethylmethylketone (8 : 1 : 1) as eluant. The 4-anilino-3-nitrocoumarin (*1a*) gave the novel heterocyclic ring system 6H-1-benzopyrano[4,3-b]quinoxalin-6-one (*2a*) in 71% yield. The IR spectrum of *2a* shows an absorption due to the carbonyl group of the pyrone ring at 1760 cm^{-1}, while the absorption due to the C=N group was observed at 1620 and (C=C) aromatic absorption at 1605 cm^{-1}. Additional confirmation of the structural assignment was obtained by the identification of a mass peak corresponding to *m/e* 248 ($M^{+\cdot}$). The NMR data are consistent with structure *2a*. Similarly, the products *2b*, *2c* and *2d* were obtained in 72, 76 and 68% yields, respectively.

The formation of the products (*2a—2d*) can be explained according to the Scheme



The nitrene formed on deoxygenation of aromatic nitro group by triethyl phosphite attacks the ring junction forming intermediate dihydroquinoxaline derivative. However, we were not able to isolate this intermediate. Namely, carrying out the reaction of *1a* with $P(OEt)_3$ for 24 hours under nitrogen we isolated the starting material (*1a*) in over 90% yield and among other compounds the product (*2a*) was detected by TLC. It seems that the oxidation of dihydroquinoxaline derivative, possibly by means of dissolved oxygen, is the driving force of the reaction.

EXPERIMENTAL

Melting points are uncorrected. The IR spectra were taken on a Perkin-Elmer M-377 spectrophotometer in KBr pellets, the NMR spectra were recorded on a Perkin-Elmer R 12 B instrument and the mass spectra were obtained from a Hitachi Perkin-Elmer RMV-G1.

General Producere for the Synthesis of Compounds 2a—2d

4-Arylamino-3-nitrocoumarin, *1a-1d,* (3.5 mmol) was dissolved in dimethylformamide (20 ml) .Triethyl phosphite (1.79 g, 10.8 mmol) was added to the solution and the mixture was refluxed for 4—20 hours. The reaction mixture was allowed to coll and upon reaching ambient temperature was poured into ice-cold water (300 ml). The resulting precipitate was filtered off and recrystallized from acetonitrile.

6H-1-Benzopyrano[4,3-b]quinoxalin-6-one (2a)

Reflux 4 hours; yield 71%, m. p. 244—246 °C.
IR (KBr-pellet): 3050 (CH_{arom}), 1760 (pyrone C=O), 1620 (C=N), 1605 ($C=C_{arom}$), 760 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.30—8.65 (m, 8H, arom.) ppm. MS *m/e* (relative intensity): 248 (100), 221 (13), 220 (85), 192 (29), 191 (12), 164 (11), 102 (26), 89 (12), 76 (19), 75 (23), 63 (22).

Anal. for $C_{15}H_8N_2O_2$ (248.23) calc'd.: C 72.60; H 3.22; N 11.28%
found: C 72.35; H 2.95; N 11.21%

6H-1-Benzopyrano[4,3-b]-9-methylquinoxalin-6-one (2b)

Reflux 20 hors; yield 72%; m. p. 260—262 °C.
IR (KBr-pellet): 3050 (CH_{arom}), 2910 (CH_3), 1750 pyrone C=O), 1615 (C=N), 1605 (C=C_{arom}), 760 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.35—8.70 (m, 7H, arom.) 2.52 (s, 3H, CH_3) ppm; MS *m/e* (relative intensity): 262 (100), 235 (11), 234 (69), 233 (62), 205 (18).

Anal. for $C_{16}H_{10}N_2O_2$ (262.26) calc'd.: C 73.30; H 3.81; N 10.68%
found: C 73.58; H 3.61; N 10.37%

6H-1-Benzopyrano[4,3-b]-9-bromoquinoxalin-6-one (2c)

Reflux 8 hours; yield 76%; m. p. 278—280 °C.
IR (KBr-pellet): 3070 (CH_{arom}), 1750 (pyrone C=O), 1620 (C=N), 1605 (C=C_{arom}) 760 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.27—8.65 (m, 7H, arom.); MS *m/e* (relative intensity): 329 (15), 328 (100); 327 (17); 326 (96), 300 (54), 298 (53), 219 (15), 191 (39), 164 (19).

Anal. for $C_{15}H_7N_2O_2Br$ (327.12) calc'd.: C 55.08; H 2.14; N 8.56%
found: C 54.86; H 2.04; N 8.21%

6H-1-Benzopyrano[4,3-b]-9-acetamidoquinoxalin-6-one (2d)

Reflux 3 hours; yield 68%; m. p. > 320 °C.
IR (KBr-pellet): 3320 (NH), 1740 (pyrone C=O), 1670 (amide C=O), 1620 (C=N), 1600 (C=C_{arom}), 770 cm^{-1}; MS *m/e* (relative intensity): 305 (55), 264 (19), 263 (100), 236 (13), 235 (35), 208 (6), 107 (11). Compound *2d* is unsoluble for NMR measurements in usual solvents.

Anal. for $C_{17}H_{11}N_3O_3$ (305.28) calc'd.: C 66.69; H 3.91; N 13.71%
found: C 66.42; H 3.80; N 13.69%

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SAŽETAK

Kemija kumarina. — Novi heterocikli dobiveni deoksigenacijom 4-arilamino-3-nitrokumarina

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Proučavana je reakcija 4-arilamino-3-nitrokumarina s trietilfosfitom. Sintetiziran je novi heterociklički sistem, 6H-1-benzopirano[4,3-b] kinoksalin-6-on (*2a*), koji je karakteriziran spektroskopskim i analitičkim podacima. Dobivena su četiri derivata (*2a-2d*) u dobrom iskorištenju (68 do 76%).