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An Unusual Direction of the Richter Synthesis. 1*H*-Naphtho[2,3-*g*]indazole-6,11-diones

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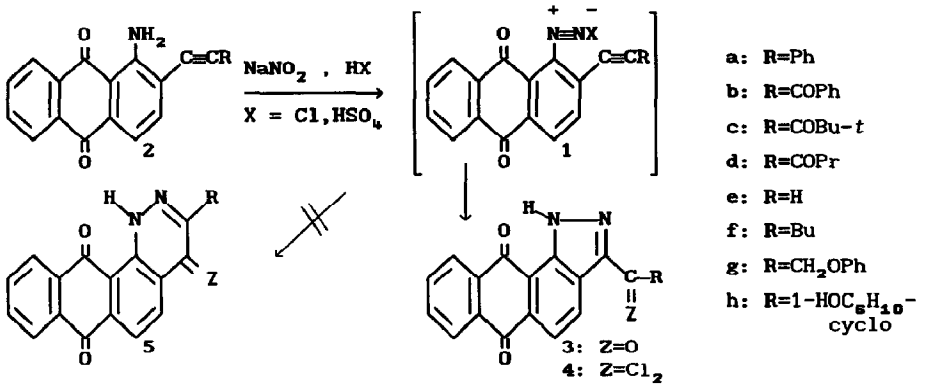
Abstract: Diazotization of 2-acetylenic derivatives of 1-aminoanthraquinone followed by intramolecular cyclization leads to the formation in good yields of 1*H*-3-acyl- or 1*H*-3-(1,1-dichloroalkyl)naphtho[2,3-*g*]indazole-6,11-diones, rather than 3-substituted 4-hydroxynahtho[2,3-*h*]cinnoline-7,12-diones, the normal Richter synthesis products.

In our study of *vic*-functionalized aryl- and hetarylacetylenes as key intermediates in the synthesis of condensed heterocyclic compounds,[1] we have cyclized 2-acetylenic anthraquinone-1-diazonium salts **1**. This reaction in the benzene and related series is usually considered to be a method of preparation of 4-hydroxycinnolines or their analogs (the Richter synthesis).[2] However, we have found that the cyclization of **1** does not lead to formation of the pyridazine ring but, in contrast to all known instances, results in closure to a 5-membered pyrazole ring.

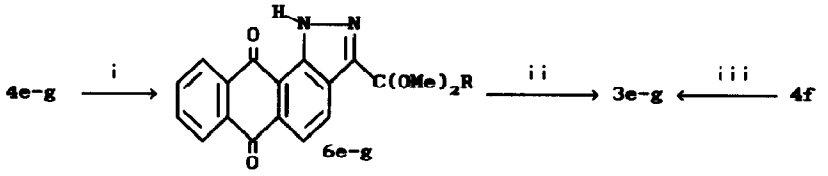


Scheme 1

Amines **2** are diazotized in a mixture of dilute HCl and dioxan at 20°C. Under these conditions the resulting diazonium salts readily cyclize to naphtho[2,3-*g*]indazoles **3**,**4** (yields 60-80%).[3] The reaction of **1a-d** with the triple bond conjugated with a carbonyl

group or a benzene ring affords ketones **3a-d** whereas other salts **1e-h** give dichlorides **4e-h**. When H_2SO_4 is used instead of HCl, the diazotization of **2** and subsequent cyclization of **1** always yields ketones **3**, as was shown for **2f,h**.

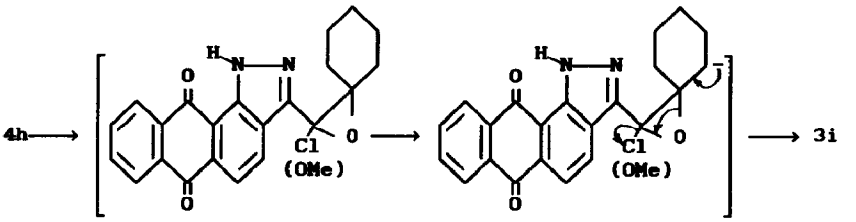
By the action of MeONa in MeOH, dichlorides **4** are transformed readily into dimethylacetals **6**[3] that can be hydrolyzed to **3** in the usual manner. In acidic medium hydrolysis of **4** proceeds very slowly.



i, MeONa in MeOH, 20°C; ii, 20% aq. HCl, dioxan, 20°C, 0.5-1h; iii, 50% aq. H_2SO_4, dioxan, reflux, >50h.

Scheme 2

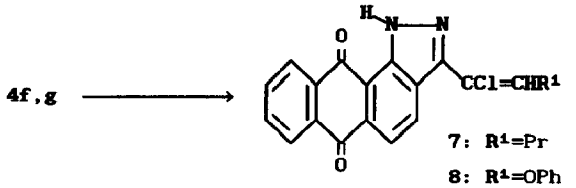
The dichloride **4h** reacts with MeONa in an alternative manner, giving the ketone **3i**, presumably in accordance with Scheme 3.



i: R=1-C_6H_9-cyclo

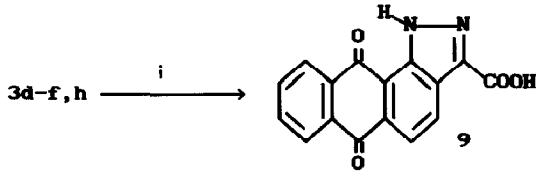
Scheme 3

The naphthoindazole structures of compounds **3,4** have been proved as follows:
(1) Dichlorides **4f,g** are dehydrohalogenated to monochlorides **7** and **8** respectively by BuLi or even by a weak base such as $NaHCO_3$. The structure of **7,8** was reliably determined by means of ^1H NMR spectra and elemental analysis.[4] These compounds could not be formed from **5f,g** (Z=Cl_2) without a skeletal rearrangement.



Scheme 4

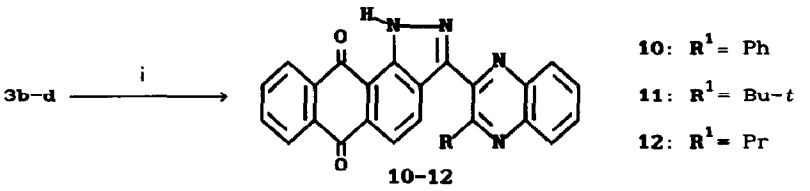
(2) The presence of the formyl group in **3e** is revealed by the ^{13}C NMR spectrum (δ_{CHO}=186.7 ppm,d). There is no formyl group in the isomeric naphthocinnoline **5e** (Z=O).
(3) Chromic acid oxidizes **3d-f,h** to the carboxylic acid **9**.[5]



i, $K_2Cr_2O_7$, 25% aq. H_2SO_4, AcOH, reflux, 1.5-3h

Scheme 5

Oxidation products of the corresponding compounds **5** would have different compositions and structures.
(4) **3b-d**, like other α-diketones, react easily with *ortho*-diaminobenzene, yielding quinoxalines **10-12**.



i, *o*-$NH_2C_6H_4NH_2$, PhMe, HCOOH, reflux, 10-30 min

Scheme 6

(5) The cyclohexenylketone **3i** is dehydrogenated to the phenylketone **3a** (active MnO_2, toluene, reflux, 45h). Hence, **3a** like the other compounds **3** is a derivative of 1*H*-naphtho[2,3-*g*]indazole.

In conclusion, the intramolecular cyclization of 2-acetylenic anthraquinone-1-diazonium salts provides an effective method for the synthesis of 3-substituted 1*H*-naphtho[2,3-*g*]indazole-6,11-diones **3,4**. The initial acetylenic compounds **2** are readily available.[6] It is apparent also that today's knowledge of the Richter synthesis is still insufficient and needs to be enlarged.

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3. All new compounds gave satisfactory microanalytical and spectroscopic data. Examples of typical ^{1}H NMR spectra for **3**, **4** and **6** are given below. **3d**: δ (d_6- DMSO) 0.95 (t, J=6.7Hz, 3H, CH_3), 1.70 (sxt, J=6.7Hz, 2H, β-CH_2), 2.93 (t, J=6.7Hz, 2H, α-CH_2), 7.80-8.05 (m, 2H, $H^{8,9}$), 8.05-8.35 (m, 2H, $H^{7,10}$), 8.15 (d, J=9.0Hz, 1H, $H^{4(5)}$), 8.60 (d, J=9,0Hz, 1H, $H^{5(4)}$), 14,90 (br.s, 1H, NH). **4f**: ($CDCl_3$) 1.00 (t, J=7.0Hz, 3H, CH_3), 1.20-2.00 (m, 4H, β-, γ-CH_2), 2.93 (t, J=7.0Hz, 2H, α-CH_2), 7.70-7.90 (m, 2H, $H^{8,9}$), 8.20-8.45 (m, 2H, $H^{7,10}$), 8.12 (d, J= 8.3Hz, 1H, $H^{4(5)}$), 8.62 (d, J=8.3Hz, 1H, $H^{5(4)}$), 11.85 (br.s, 1H, NH). **6e**: ($CDCl_3$) 3.48 (s, 6H, OMe), 5.82 (s, 1H, OCHO), 7.70-7.90 (m, 2H, $H^{8,9}$), 8.20-8.35 (m, 2H, $H^{7,10}$), 8.08 (d, J=9.0Hz, 1H, $H^{4(5)}$), 8.40 (d, J=9.0Hz, 1H, $H^{5(4)}$), 11.88 (br.s, 1H, NH).

4. **7**: ($CDCl_3$) 1.05 (t, J=7.7Hz, 3H, CH_3), 1.65 (sxt, J=7.7Hz, 2H, CH_2CH_3), 2.50 (q, J=7.7Hz, 2H, CH_2CH=), 6.63 (t, J=7.7Hz, 1H, CH=), 7.70-7.90 (m, 2H, $H^{8,9}$), 8.12 (d, J=8.4Hz, 1H, $H^{4(5)}$), 8.20-8.40 (m, 2H, $H^{7,10}$), 11.87 (br.s, 1H, NH). **8**: (d_6-DMSO) 7.10-7.55 (m, 6H, Ph, CH=), 7.80-8.10 (m, 2H, $H^{8,9}$), 8.15-8.40 (m, 2H, $H^{7,10}$), 8.20 (d, J=8.5Hz, 1H, $H^{4(5)}$), 8.55 (d, J=8.5Hz, 1H, $H^{5(4)}$), 14.15 (s, 1H, NH).

5. **9** was characterized as its methyl ester, MS m/z 306; (d_6-DMSO) 4.00 (s, 3H, Me), 7.85-8.05 (m, 2H, $H^{8,9}$), 8.05-8.30 (m, 3H, $H^{4(5),7,10}$), 8.50 (d, J=8.5Hz, 1H, $H^{5(4)}$), 14,43 (br.s, 1H, NH).

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