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ACETYLENIC COMPOUNDS AS INTERMEDIATES IN HETEROCYCLIC SYNTHESIS: REACTION OF 1-ACETYLENYLANTHRAQUINONES WITH HYDRAZINE

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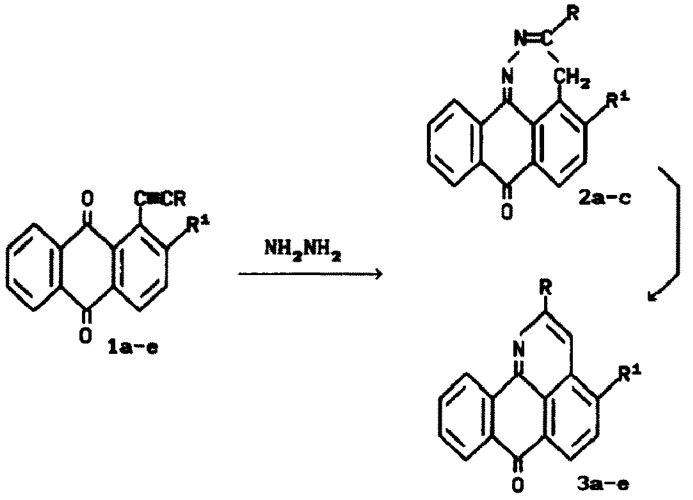
Key words: 4*H*-anthra*[9,1-cd]*-1,2-diazepin-8-ones, 7H-dibenzo*[de,h]*quinolin-7-ones, 1-acetylenylanthraquinones, hydrazine, cyclocondensation.

Abstract: Reaction of 1-acetylenic derivatives of anthraquinone with hydrazine affording substituted 4*H*-anthra*[9,1-cd]*-1,2-diazepin-8-ones and 7H-dibenzo*[de,h]*quinolin-7-ones is reported.

Acetylenic derivatives of quinones due to increased electrophilicity of the triple bond readily add secondary amines[1]. We have supposed that hydrazine as an *N*-dinucleophile can react with 1-acetylenylanthraquinones being added consecutively to the triple bond and the carbonyl group in the *peri*-position to yield anthra*[9,1-cd]*-1,2-diazepin-8-ones. This possibility appears to be interesting the more so, as only very few anthradiazepines have been described and their properties studied insufficiently[2].

Reaction of anthraquinonylacetylenes **1a-c** with NH_2NH_2 was found to occur on heating in pyridine (or also in ethanol) and to be complete within 0.5 - 1.5 *h* at 90-115°C. Two main types of products are separated easily by column chromatography. The first of them are the expected 3-substituted 4*H*-anthra*[9,1-cd]*-1,2-diazepin-8-ones **2a-c** having the apparently strained heterocycle with the methylene group out of the molecule plane[3]. The other unexpected products are 2-substituted 7H-dibenzo*[de,h]*quinolin-7-ones **3a-c** that contain only one nitrogen atom in a molecule[4].

Diazepines **2**, under the conditions of their formation in the presence of NH_2NH_2 excess, recyclize to the pyridoanthrones **3**. **2b** is transformed into **3b** completely after boiling with NH_2NH_2 in pyridine for 9.5 *h* (yield 77%). This reaction does not take place in the presence of other bases (KOH, Et_3N).



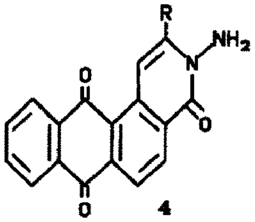
Scheme 1

Table 1. Cyclocondensation of **1** with NH_2NH_2

Substrate	R	R^1	Products		Isolated yields (%) of 2	and 3
1a	Bu	H	**2a**	**3a**	50	20
1b	Ph	H	**2b**	**3b**	70	17
1c	CH_2OPh	H	**2c**	**3c**	63	28
1d	Bu	COOMe	-	**3d**	-	37^a
1e	Bu	$CH(OEt)_2$	-	**3e**	-	75^b

[a] Simultaneously 4*H*-3-amino-2-butylnaphtho[*2,3-f*]isoquinoline-4,7,12-trione **4** is obtained (35 %)[5]. [b] In ethanol, 78°C, 13 *h*.

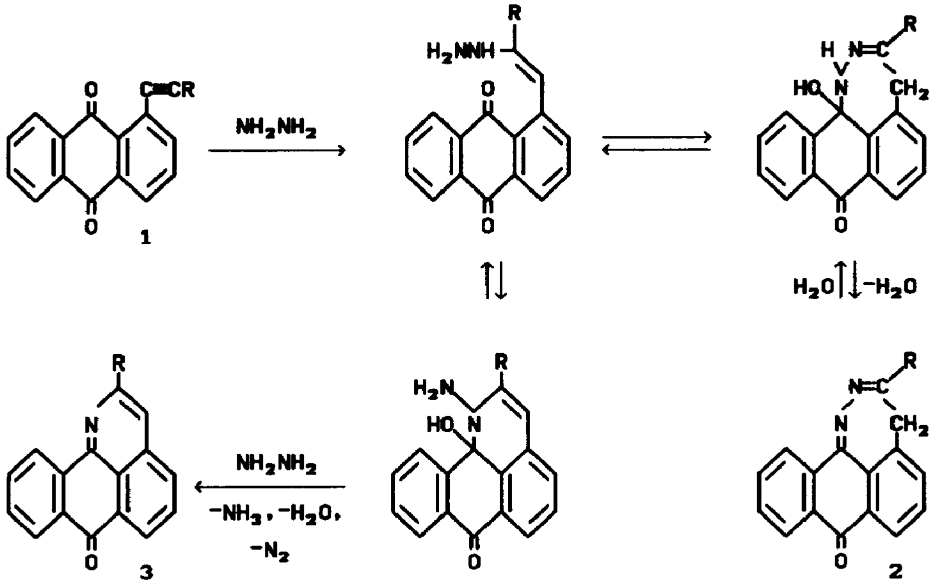
Bulky substituents in position 2 of the initial anthraquinone **1** probably create an additional steric hindrance for the **1**→**2** cyclization and/or destabilize **2** and thus accelerate the **2**→**3** reaction. Indeed, ester **1d** with NH_2NH_2 in ethanol at 78°C (1.5 *h*) does not form anthradiazepine **2d** but yields pyridoanthrone **3d** besides *N*-aminolactam **4**, *i.e.* the product of the interaction of the reagent with the methoxycarbonyl group and the triple bond of the substrate[6]. The cyclocondensation of **1e** with NH_2NH_2 in ethanol leads to pyridine **3e** in 75% yield (Table 1). For comparison, under the same conditions, **1b** gives **2b** and **3b** in 55 and 19% yields,



4

respectively. To recyclize **2b** entirely and to obtain only **3b**, it is necessary to continue heating the reaction mixture for additional 16 *h* (30 *h* totally).

These facts are a background for some speculations concerning possible routes of the reaction.



Scheme 2

To summarize, cyclocondensation of 1-acetylenylanthraquinones **1** with NH_2NH_2 is shown to offer a novel and relatively simple route to pyridoanthrones **3** and poorly known anthradiazepines **2**.

References and Notes

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2. Hromatka, O.; Knollmüller, M.; Maier, K.A. *Monatsh. Chem.* **1967**, *98* (4), 1537.
3. All novel compounds were characterized and gave ^{1}H NMR, IR spectroscopic and microanalytical data in accordance with assigned structures. **2a**: m.p. 116 - 117°C (decomp., C_6H_6 - hexane); δ_H ($CDCl_3$) 0.88 (3H, m, *J*=7.2 *Hz*, CH_3), 1.32 (2H, m, *J*=7.2 *Hz*, γ-CH_2), 1.67 (2H, m, *J*=7.2 *Hz*, β-CH_2), 2.55 (2H, t, *J*=7.2 *Hz*, α-CH_2), 2.94 (1H, d, *J*=12.2 *Hz*, C^4H), 3.64 (1H, d, *J*=12.2 *Hz*, C^4H), 7.40 - 7.75 (4H, m, $H^{5,6,10,11}$), 8.15 - 8.40 (3H, m, $H^{7,9,12}$). **2b**: m.p. 238 - 239°C (C_6H_6); 3.13 (1H,

d, *J*=13.5 *Hz*, C^4H), 4.43 (1H, d, *J*=13.5 *Hz*, C^4H), 7.30 - 8.55 (12H, m, H^{arom}). **2c**: m.p. 183 - 184°C (C_6H_6); 2.92 (1H, d, *J*=12.4 *Hz*, C^4H), 4.03 (1H, d, *J*=12.4 *Hz*, C^4H), 4.83 (2H, s, CH_2O), 6.75 - 7.10 (3H, m, Ph), 7.25 - 7.85 (6H, m, Ph, $H^{5,6,10,11}$), 8.10 - 8.45 (3H, m, $H^{7,9,12}$).

4. **3a**: m.p. 97 - 98°C (C_6H_6 - hexane); 1.00 (3H, m, *J*=7.0 *Hz*, CH_3), 1.20 - 2.10 (4H, m, γ- and β-CH_2), 3.06 (2H, t, *J*=7.0 *Hz*, α-CH_2), 7.35 (1H, s, H^3), 7.60 - 8.65 (6H, m, $H^{4-6,8-10}$), 8.97 (1H, d, *J*=7.2 *Hz*, H^{11}). **3b**: m.p. 207 - 208°C (C_6H_6). **3c**: m.p. 173 - 174°C (C_6H_6). **3d**: m.p. 143.5 - 144.5°C (C_6H_6 - hexane); 1.00 (3H, t, *J*=7.0 *Hz*, CH_3), 1.20 - 2.10 (4H, m, γ- and β-CH_2), 3.07 (2H, t, *J*=7.0 *Hz*, α-CH_2), 4.05 (3H, s, $COOCH_3$), 7.50 - 7.95 (2H, m, $H^{9,10}$), 8.36 (1H, d, *J*=7.8 *Hz*, H^8), 8.45 - 8.55 (2H, m, $H^{5,6}$), 8.57 (1H, s, H^3), 8.97 (1H, d, *J*=7.8 *Hz*, H^{11}). **3e**: m.p. 75 - 76°C (hexane); 1.00 (3H, t, *J*=7.0 *Hz*, $CH_3(CH_2)_3$), 1.25 (6H, t, *J*=7.0 *Hz*, CH_3CH_2O), 1.30 - 2.10 (4H, m, $CH_3(CH_2)_2CH_2$), 3.08 (2H, t, *J*=7.0 *Hz*, $CH_2C_3H_7$), 3.64 (4H, q, *J*=7.0 *Hz*, OCH_2), 6.08 (1H, s, CH), 7.50 - 8.65 (5H, m, $H^{5,6,8-10}$), 8.00 (1H, s, H^3), 8.98 (1H, d, H^{11}); **3e** undergoes acidic hydrolysis to 2-butyl-4-formylanthra*[9,1-bc]*pyridin-7-one, yield 83.5%, m.p. 128 - 129°C (C_6H_6 - hexane), δ_H 10.45 (1H, s, CHO).
5. **4**: m.p. 189 - 190°C (C_6H_6 - hexane); 1.00 (3H, t, CH_3), 1.20 - 1.90 (4H, m, β- and γ-CH_2), 2.95 (2H, t, α-CH_2), 5.05 (2H, s, NH_2), 7.35 (1H, s, H^1), 7.65 - 7.90 (2H, m, $H^{9,10}$), 8.15 - 8.40 (3H, m, $H^{6(5),8,11}$), 8.78 (1H, d, $H^{5(6)}$); ν 1625, 1655, 1675 (O=C-C=C-C=O, CO), 3230, 3330 (NH_2).
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