NOVEL RING-CLOSURE REACTION BETWEEN QUINONES AND DIAMINES

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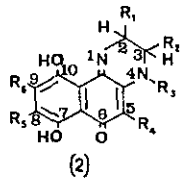
A convenient one step synthesis of hydroquinoxaline derivatives was established by the reaction of quinones with 1,2-diamines under mild conditions. This novel ring-closure reaction will be a useful method to prepare a variety of hydroquinoxaline derivatives.

The reaction of naphthazarin (1) with ethylenediamine at 0 °C for 2 h gave the ring-closured product (2a), 7,10-dihydroxy-2,3,4-trihydrobenzo[f]quinoxaline-6-one, in 46% yield. The similar reactions of (1) with 1,2-diamines gave the corresponded ring-closured products (2). Some results are shown in the Table. The reaction of (1) with N-alkylethylenediamines gave (2) in lower yield together with (3), but not (4). The reaction of (1) with N-phenyl- or N-acetylethylenediamine gave only (3) but not (2), respectively. Both 2-amination and the ring-closure reaction were greatly inhibited by the steric requirement of N-substituents. The reaction of 1,4-dihydroxyanthraquinone with 1,2-diamines in the presence of copper salts gave the corresponded annelation derivatives of (2). The reaction of 2,3-dichloronaphthazarin with 1,2-phenylenediamine under higher temperature also gave the corresponded ring-closured product. The mechanism for the preparation of (2) was proposed as follows; the initial Michael addition of amine to (1) gave the adduct (5) which was followed by the intramolecular nucleophilic substitution of the 2'-amino group to the carbonyl group at 1-position to give the leuco ring-closured product (6), which was oxidized to (2) by atmospheric oxygen.



(2)

R_{1-3} = H, alkyl

R_1R_2 = C_4H_8, C_4H_4

R_{4-6} = H, halogen

R_5R_6 = C_4H_4

RUN	Diamine	Products (Yield,%)	
1	$H_2N(CH_2)_2NH_2$	2a (45.7)	
2	$H_2NCH(CH_2)_4CHNH_2$	2b (46.1),(59.9)	
3	$H_2NCH(CH_3)CH_2NH_2$	2c (39.3)	
4	$H_2N(CH_2)_2NHCH_3$	2d (28.9)	3d (-)
5	$H_2N(CH_2)_2NHC_2H_5$	2e (8.0)	3e (-)
6	$H_2N(CH_2)_2NHC_6H_5$	2f (0)	3f (49 0)
7	$H_2N(CH_2)_2NHCOCH_3$	2a (trace)	3g (44.8)