

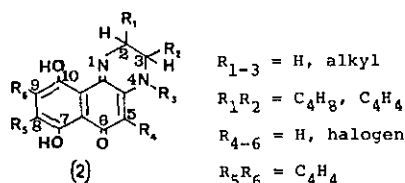
NOVEL RING-CLOSURE REACTION BETWEEN QUINONES AND DIAMINES

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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-closed 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-closed 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-acetyletylenediamine 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-dihydroxy-anthraquinone 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-closed 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-closed product (6), which was oxidized to (2) by atmospheric oxygen.



RUN	Diamine	Products (Yield, %)
1	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	2a (45.7)
2	$\text{H}_2\text{NCH}(\text{CH}_2)_4\text{CHNH}_2$	2b (46.1), (59.9)
3	$\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{NH}_2$	2c (39.3)
4	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NHC}_2\text{H}_5$	2d (28.9) 3d (-)
5	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NHC}_6\text{H}_5$	2e (8.0) 3e (-)
6	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NHC}_6\text{H}_5$	2f (0) 3f (49.0)
7	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NHCOC}_2\text{H}_5$	2a (trace) 3g (44.8)

