FORMATION OF [1,3]BENZOXAZINO[3,4-c]BENZOXAZINES[1,3]

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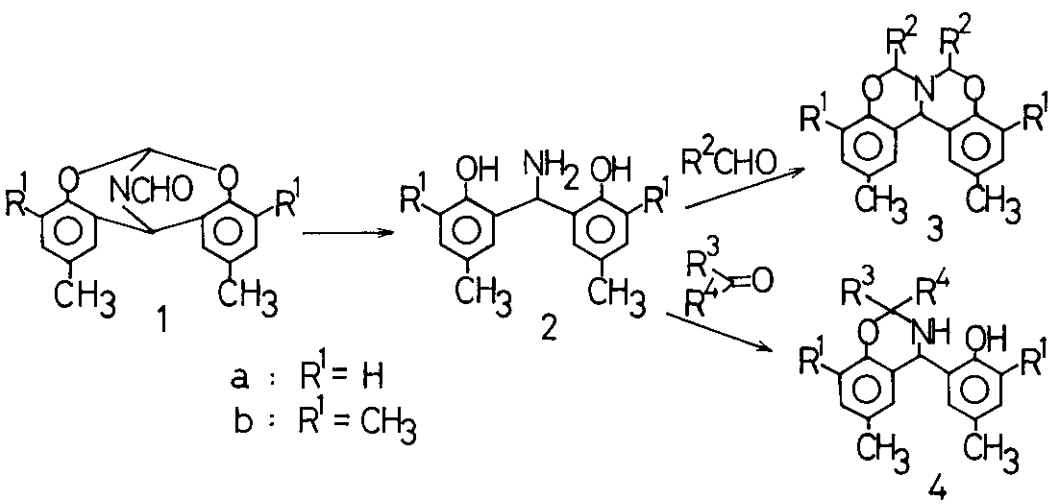
Abstract --- The reaction of 1,1-bis(2-hydroxy-3-alkyl substituted-5-methylphenyl)methylamines with aldehyde gave [1,3]benzoxazino[3,4-c]benzoxazines[1,3], and with ketones gave oxazines.

In a previous paper[1], the author showed that the reaction of 2-alkyl substituted p-cresols with Vilsmeir reagent ($POCl_3$-DMF adduct) gave N-formyl-6,12-epimino-2,10-dimethyl-4,8-dialkyl substituted-6H,12H-dibenzo[d,g][1,3]dioxocins (1) and the acid hydrolysis of these compounds gave 1,1-bis(2-hydroxy-3-alkyl substituted-5-methylphenyl)methylamines (2).
In the present paper, the author wish to report that in the reaction of 2, aldehydes gave [1,3]benzoxazino[3,4-c]benzoxazine[1,3] derivatives (3) and ketones gave oxazine derivatives (4).



As a typical example, the mixture of one mole equivalent of 2a and 20 mole equivalent of formal (30% solution) was stirred at 60-70°C for 4 hr to give 2,12-dimethyl[1,3]benzoxazino[3,4-c]benzoxazine[1,3] (3a) as colorless needles.

The structure of 3a was confirmed by spectral data. The ir spectra of 3a have no characteristic absorptions of NH,OH and C=N.
In a similar manner, 3_{b-d} were obtained by the reaction of 2_b with the corresponding aldehydes. The mp and yield of these compounds are shown in Table 1.
The reaction of 2a with acetone gave 2,2,6-trimethyl-4-(2-hydroxy-5-methylphenyl)-2H,3,4-dihydrobenzo[e][1,3]oxazine (4a). The structure of 4a was comfirmed by spectral data. The ir spectrum of 4a have characteristic absorptions of OH and NH, and no characteristic absorption of C=N. Similarly, 4_{b-d} was obtained by the reaction of 2_b with ketones shown in Table 2.

Table 1. MP and Yield of 3

No	R_1	R_2	MP °C	Yield (%)
3a	H	H	172 - 173	86
3b	$-CH_3$	H	173 - 174	89
3c	$-CH_3$	$-C_3H_7$	136 - 137	75
3d	$-CH_3$	$-C_6H_5$	183 - 184	85

Table 2. MP and Yield of 4

No	R_1	R_3	R_4	MP °C	Yield (%)
4a	H	$-CH_3$	$-CH_3$	149 - 150	82
4b	$-CH_3$	$-CH_3$	$-CH_3$	157 - 158	84
4c	$-CH_3$	$-(CH_2)_5-$		138 - 139	54
4d	$-CH_3$	$-CH_3$	$-C_6H_5$	170 - 171	68

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Reference

1) S. Morimura, T. Hata, and C. Tamura, Nippon Kagaku Kaishi, 1980, 233.
2) All new compounds reported herein gave satisfactory elementary analyses and showed molecular ion peaks in their mass spectra consistent with the proposed structure. In addition, all spectral data were consistent with the assigned structure.

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