CONTROLLING EFFECT OF SUBSTITUENTS ON THE REDUCTION OF 4-SUBSTITUTED 3-NITROCOUMARINS BY SODIUM HYDROSULFITE

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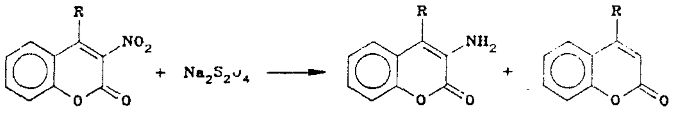
In all the cases which we have examined, the reaction of 3-nitro-4-aminocoumarins (I, R = NH_2, NHAlk, $NAlk_2$, and NHAr) with sodium hydrosulfite in the presence of added base results only in reduction of the nitro-group to amino, in 72-98% yields. The formation of 3-amino-4-hydroxycoumarin (IIa) from 3-nitro-4-hydroxycoumarin (Ia) under these conditions is just as well-defined (yield 75%).



I II III

I-III a R=OH; b R=OMe

Replacement of the hydroxyl group in (Ia) by methoxy markedly affects the reaction with coumarin (Ib). In this instance, a mixture of two products is obtained. When the reaction is carried out in aqueous methanol with the addition of sodium acetate, the mixture contains predominantly the expected 3-amino-4-methoxycoumarin (IIb), preparative yield 35%, mp 82-84°C (from aqueous methanol), ν (KBr): 3318-3348 (NH_2), 1692-1702 (C=O), 1637 (C=C), 1591 cm^{-1} (arom.). The mixture contained small amounts of 4-methoxycoumarin (IIIb). Replacement of the sodium acetate by sodium bicarbonate as base resulted in the formation of small amounts of the coumarin (IIb), but the coumarin (IIIb) predominated, preparative yield 28%, mp 120-122°C (from aqueous methanol) (according to [1], mp 124°C); ν (KBr): 1683-1700 (C=O), 1620 (C=C), 1602 cm^{-1} (arom.). PMR spectrum ($CDCl_3$), δ: 4.0 (s, 3H, OCH_3), 5.7 (s, 1H, C_3H), 7.1-7.8 ppm (m, 4H, arom.).

Finally, replacement of the nitro-group by hydrogen was the only reaction observed when 3-nitro-4-chlorocoumarin (I, R = Cl) was reduced with sodium hydrosulfite in aqueous solution with the addition of pyridine. In this case, the product was 4-hydroxycoumarin (IIIa), yield 27%, mp 209-210°C [2], which gave no depression of melting point on admixture with an authentic sample of (IIIa), and had an identical IR spectrum. Comparison of these findings with the reduction of 3-nitro-4-hydroxycoumarin (Ia) leads to the conclusion that replacement of the chlorine by hydroxyl in (I) (R = Cl) occurs following reduction.

LITERATURE CITED

1. I. M. Heilbron and D. N. Hill, J. Chem. Soc., 1707 (1927).
2. D. S. Tarbell and J. A. Price, J. Org. Chem., 22, 245 (1957).

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