INSTANCE OF DIRECT REPLACEMENT OF A NITRO GROUP ATTACHED TO AN UNSATURATED CENTER OF A COUMARIN BY A MERCAPTO GROUP

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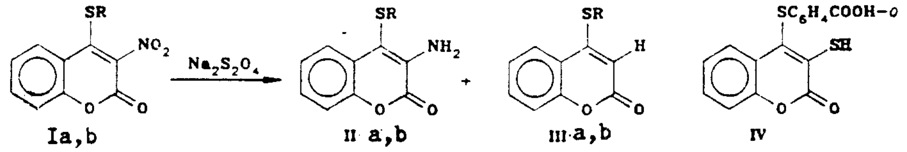
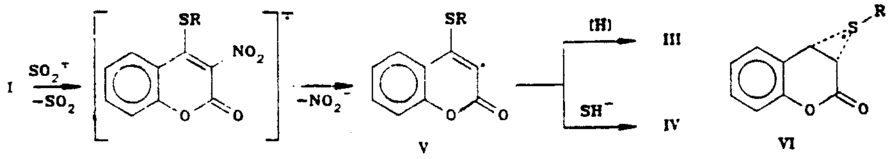
We have observed that 4-S-benzyl-3-nitrocoumarin (Ia), like the 4-methoxy analog [1], on reduction with sodium hydrosulfite is converted to a mixture of two compounds: 3-amino-4-S-benzylcoumarin (IIa) [26% yield, mp 101-102°C [from alcohol–chloroform (5:1)], ν (in KBr): 3472 and 3364 (NH_2), 1711 and 1693 (C=O), 1606 and 1580 cm^{-1} (C=C)] and a product that does not contain nitrogen, viz., 4-S-benzylcoumarin (IIIa) [42% yield, mp 176-177.5°C [from alcohol–dioxane (2:1), ν (in KBr): 1718 (C=O), 1603 and 1592 cm^{-1} (C=C). PMR spectrum ($CDCl_3$), δ: 4.21 (2H, s, CH_2), 6.19 (1H, s, 3-H), 7.06-7.78 ppm (8H, m, Br)].



I-III aR=CH_2Ph; bR=o-$HOOCC_6H_4$

Replacement of the benzyl residue in starting coumarin I by a 2-carboxyphenyl group leads to a qualitatively new result since, in addition to amine IIb [isolated in the form of the sesquihydrate, 21% yield, mp 225.5-226.5°C (from water), ν (in KBr): 3454 and 3352 (NH_2), 1704 (C=O), 1609 and 1585 cm^{-1} (C=C)] and reduction product IIIb [25% yield, mp 223.5-224.5°C (from water), ν (in KBr): 2500-3500 (OH), 1684 (C=O), 1611 and 1587 (C=C), δ_{OH} 1562 cm^{-1}. PMR spectrum (CF_3CO_2H), δ: 5.90 (1H, s, C_3H), 6.90-7.81 ppm (8H, m, Ar)], we detected a product of a new transformation pathway, viz., 4-S-(2-carboxyphenyl)-3-mercaptocoumarin (IV) [isolated in the form of the monohydrate, 19% yield, mp 337-338°C (327-328°C in some determinations) (from water), ν (in KBr): 2500-3500 (OH), 1701 and 1680 (C=O), 1617 and 1602 (C=C), δ_{OH} 1560 cm^{-1}]. The presence of a mercapto group in coumarin IV was confirmed by, in addition to the results of elementary analysis, precipitation in the form of the Cu(I) salt, reaction with $PdCl_2$, and catalytic acceleration of the iodine–azide reaction.

The results presented here and in [1] regarding the reduction of 3-nitro-4-hetero-substituted coumarins with sodium hydrosulfite, which is capable in solution of generating the powerful one-electron reducing agent, the sulfur dioxide anion radical $S_2O_4^{2-} \rightleftharpoons 2SO_2^{\cdot-}$ [2], and hydrogen sulfide [3], make it possible to propose an $S_{RN}1$ mechanism for substitution of the nitro group:



The results are in agreement with the concept of the maximum contribution of S(II) (as compared with N and O) to stabilization of radical intermediate V in view of the ability to form bridged intermediate VI with expansion of the valence shell of the bridge sulfur atom.

LITERATURE CITED

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