SYNTHESIS OF 6- AND 7-NITRO-1-OXOISOCHROMAN-4-SPIRO-2'-OXIRANES

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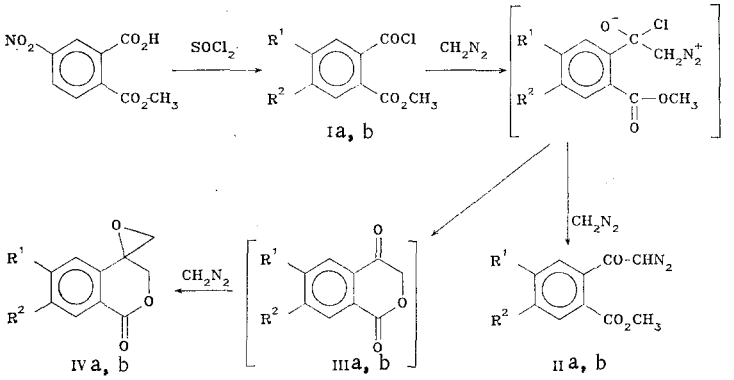
We have established that, in addition to the formation of diazo ketones IIa, b, cyclization to give 6- and 7-nitro-1-oxoisochroman-4-spiro-2'-oxiranes (IVa, b) in 12% yield, which evidently proceeds through intermediates IIIa, b, occurs in the Arndt–Eistert acylation of diazomethane by 5-nitro-2-carbomethoxybenzoyl (Ia) and 4-nitro-2-carbomethoxybenozyl (Ib) chlorides. A compound similar to intermediate III was isolated in the acylation of diazomethane with 2-carbomethoxy-3-methoxybenzoyl chloride [1]. However, the formation of oxiranes is one of the principal pathways in the reaction of diazomethane with ketones [2].



I, II, III, IV a $R^1=NO_2$, $R^2=H$; b $R^1=H$, $R^2=NO_2$

The formation of chlorides Ia, b from 5-nitro-2-carbomethoxybenzoic acid is evidently explained by the existence of an equilibrium between the isomeric chlorides [3].

The IVa, b structures are in agreement with the IR and PMR spectral data and the results of elementary analysis.

6-Nitro-1-oxoisochroman-4-spiro-2'-oxirane (IVa). This compound had mp 153-154°C (from benzene–hexane). IR spectrum (mineral oil): 1730 (C=O), 1605 and 1570 (C=C), and 1530 cm^{-1} (NO_2). PMR spectrum ($CDCl_3$): 3.24 (1H, d, J = 4.8 Hz, 3'-H), 3.38 (1H, q, J = 4.8 and 1.5 Hz, 3'-H), 4.32 (1H, d, J = 11.8 Hz, 3-H), 4.80 (1H, q, J = 11.8 and 1.5 Hz, 3-H), 8.10 (1H, d, 8-H), 8.32 (1H, q, 7-H), and 8.33 ppm (1H, d, 5-H).

7-Nitro-1-oxoisochroman-4-spiro-2'-oxirane (IVb). This compound had mp 164-165°C (from benzene–hexane). IR spectrum (mineral oil): 1730 (C=O), 1605 and 1570 (C=C), and 1530 cm^{-1} (NO_2). PMR spectrum ($CDCl_3$): 3.17 (1H, d, J = 5.0 Hz, 3'-H), 3.38 (1H, q, J = 5.0 and 1.8 Hz, 3'-H), 4.27 (1H, d, J = 11.8 Hz, 3-H), 4.80 (1H, q, J = 11.8 and 1.8 Hz, 3-H), 7.47 (1H, d, 5-H), 8.48 (1H, q, 6-H), and 8.98 ppm (1H, d, 8-H).

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