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UNUSUAL RECYCLIZATION OF 2-METHYL-1-PHENYLISO-QUINOLINIUM IODIDE TO 1-PHENYL-1,4-DIHYDRO-3H-ISOCHROMAN-3-ONE

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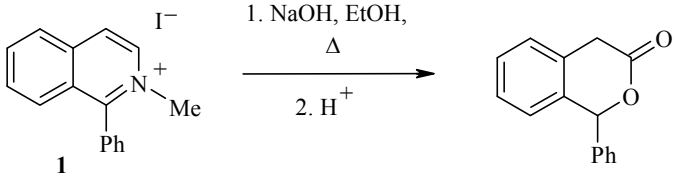
The formation of an isochroman-3-one was unexpectedly observed during the course of studying the rearrangement of 1-substituted isoquinolinium salts in the presence of O-nucleophiles.

Hence refluxing 2-methyl-1-phenylisoquinolinium iodide (**1**) with a solution of sodium hydroxide in alcohol and subsequent treatment with acid gave a high yield of the 1-phenyl-1,4-dihydro-3H-isochroman-3-one (**2**). It was found that compound **2** is only formed after the acidification of the reaction mixture at the separation stage.



1 **2** (77%)

The following mechanism of formation of the isochroman-3-one **2** can be proposed. In the presence of a nucleophile, opening of the pyridine ring of the molecule **1** occurs to form an acyclic imine (route A or B), subsequent hydrolysis of which gives the intermediate **I** containing an aldehyde and a keto group. A subsequent hydride shift from the formyl fragment to the keto group (Cannizzaro reaction) to the intermediate **C** occurs to give carboxyl and alcohol groups, intramolecular esterification of which (in acidic medium) forms the isochroman-3-one **2**.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz respectively) using $CDCl_3$ at a temperature of 23 and 25ºC with TMS as internal standard. Mass spectra for the reported compounds were obtained on a Kratos MS-90 instrument with an ionization energy of 70 eV. Monitoring of the reaction course and the purity of the products was carried out by TLC on Silufol-254 (254 nm) and Alufol plates in the systems benzene or benzene–ethyl acetate (from 5:1 to 1:1).

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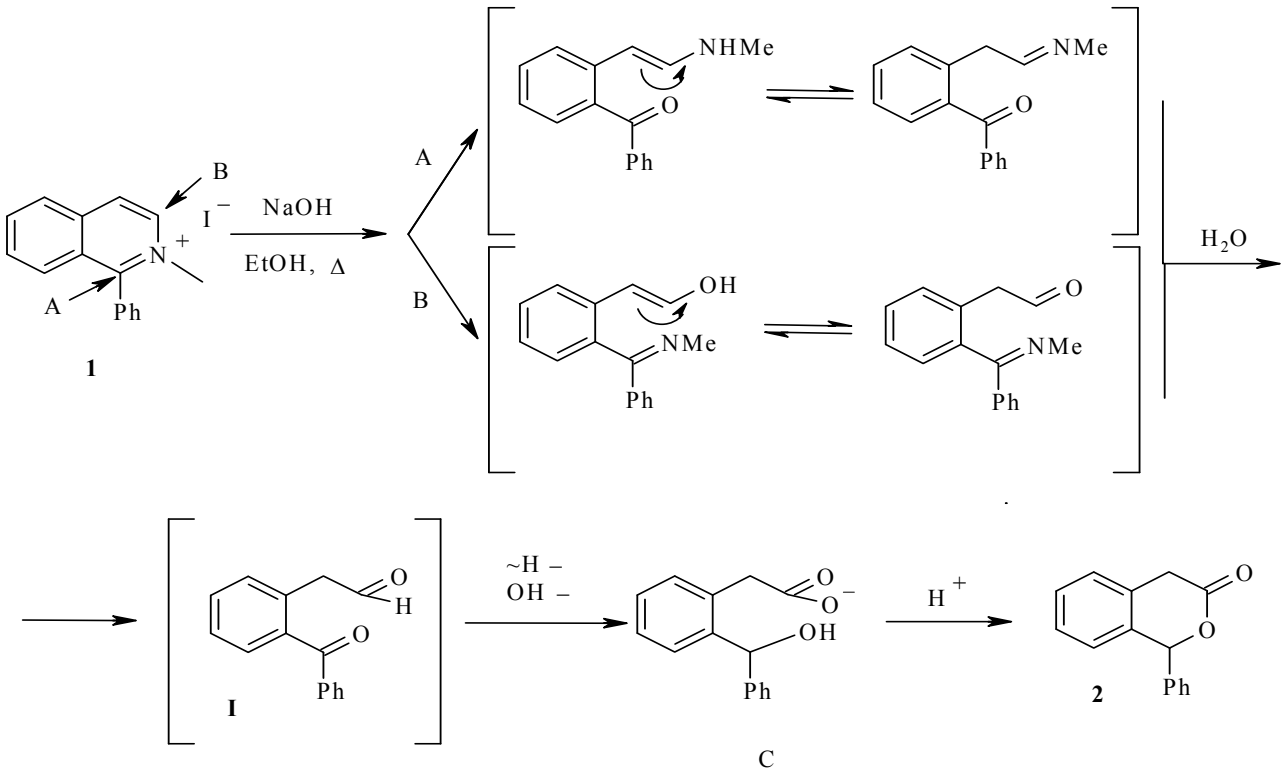

1-Phenyl-1,4-dihydro-3H-isochroman-3-one (2). A mixture of 2-methyl-1-phenylisoquinolinium iodide (0.347 g, 1 mmol) and a solution of sodium hydroxide (10%, 4-5 ml) was refluxed in alcohol for 23 h, cooled to room temperature, and the solvent was evaporated *in vacuo*. The residue was dissolved in water and the contaminant was extracted with benzene. The aqueous phase was acidified, extracted with benzene, and the benzene extracts were dried over $CaCl_2$. Solvent was removed *in vacuo* to give the isochroman-3-one **2** (0.172 g, 77%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.63 (1H, d, *J* = 18.2, CH_2); 3.75 (1H, d, *J* = 18.2, CH_2); 6.39 (1H, s, CH); 6.95 (1H, d, *J* = 7.5, H Ar); 7.41-7.21 (8H, m, C_6H_5, C_6H_3). ^{13}C NMR spectrum, δ, ppm: 36.54, 82.10, 126.05, 127.33, 127.52, 128.80, 128.91, 128.99, 130.99, 134.63, 136.90, 170.74. Mass spectrum, *m/z* (I_{rel}, %): 224 $[M]^+$ (17), 180 (96), 179 (100), 178 (50), 165 (43), 152 (16), 119 (13), 105 (52), 89 (38), 77 (54).

REFERENCES

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