LETTERS TO THE EDITOR

SYNTHESIS OF 4H-1,3-OXAZINIUM SALTS FROM AN N-ETHYLNITRILIUM SALT AND CARBONYL COMPOUNDS

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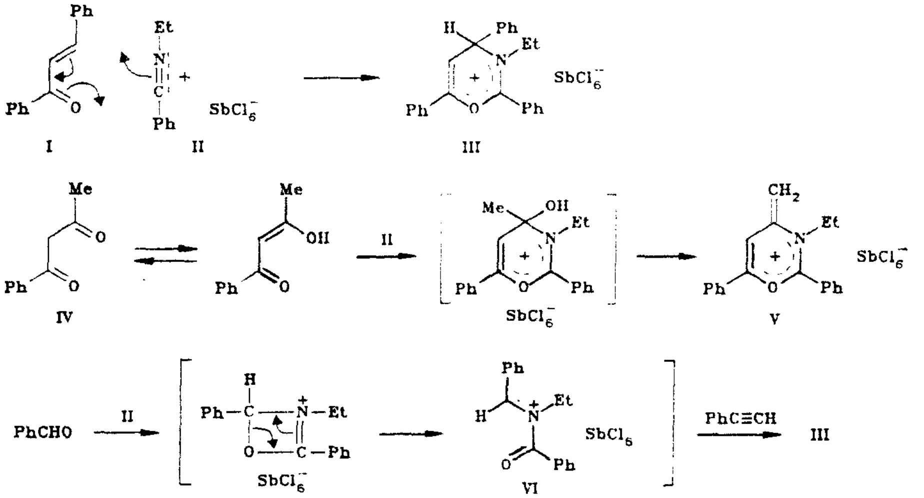
The known syntheses of 4H-1,3-oxazinium salts are based on the cycloaddition of nitriles to β-chloro ketones or of acetylenes to N-(chloroalkyl)amides [1]. In the first of these reactions the nitrile nucleophilically attacks the carbonium ion generated from the β-chloro ketone by the action of a Lewis acid. We have found that the possibilities of the synthesis of 4H-1,3-oxazinium salts are expanded substantially if the nitrile is converted to an electrophilic reagent — a nitrilium salt, which readily undergoes cycloaddition reactions with accessible carbonyl compounds with various structures.

Brief (1-2 min) refluxing of a mixture of equimolar amounts of chalcone I and N-ethylnitrilium salt II in dichloroethane gave 2,4,6-triphenyl-3-ethyl-4H-1,3-oxazinium hexachloroantimonate (III). Similar [4+2]-cycloaddition occurs under the same conditions in the reaction of benzoylacetone (IV) with salt II to give 4-methylene-4H-1,3-oxazinium hexachloroantimonate V.



In addition, we observed that the reaction of the same nitrilium salt II with benzaldehyde can be used to obtain N-acyliminium cations VI, which, in the second of the known reactions [1], are formed from N-(chloroalkyl)amides. Stirring salt II with PhCHO in dichloroethane (20 min, 20°C) and the subsequent addition of phenylacetylene give the same 4H-1,3-oxazinium salt III (maintenance at 0°C for 2 h).

Compound III ($C_{24}H_{21}Cl_6NOSb$). This compound had mp 190°C (dec.). IR spectrum: 1702, 1623 cm^{-1}. PMR spectrum (in $C_6D_5NO_2$): 1.53 (3H, t, J = 7.0 Hz, CH_3), 3.7-4.5 (2H, m, J = 7.0 Hz, CH_2), 6.12 and 6.35 (1H each, d, J = 4.0 Hz, 4- and 5-H), 7.25-8.25 ppm (15H, m, Ph). The yield was 55% (41% from PhCHO).

Compound V ($C_{19}H_{18}Cl_6NOSb$). This compound had mp 172°C (dec.). IR spectrum: 1665, 1609, 1591, 1567 cm^{-1}. PMR spectrum: 1.78 (3H, t, J = 7.0 Hz, CH_3), 4.55 (2H, q, J = 7.0 Hz, 3-CH_2), 5.43 (2H, s, CH_2=), 7.0 (1H, s, 5-H), 7.4-8.5 ppm (10H, m, Ph). The yield was 35%.

The results of elementary analysis for C and H were in agreement with the calculated values.

LITERATURE CITED

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