

SYNTHESIS OF 1-BENZOTHIOPYRAN AND ITS RELATED COMPOUNDS

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It was found that in the reaction of S-phenyl 3-oxobutanethioates with polyphosphoric acid, most of these compounds afford 4H-1-benzothiopyran-4-ones (thiochromones) through rearrangement giving o-acetoacetylbenzenethiol derivative as an intermediate. The effect of the substituent of S-phenyl 3-oxobutanethioates on the formation of 2H-1-benzothiopyran-2-ones (thiocoumarins) was also discussed.

The physical properties of thiochromones and related compounds were characterized by means of mass, NMR, UV spectra and ESCA in order to distinguish thiochromones from thiocoumarins. In the mass spectra, the fragmentation due to the retro-Diels-Alder reaction directly from the molecular ion is the most useful for differentiation. In the NMR spectra, thiochromones show the characteristic deshielding effect of benzenoid proton in 5-position and in the UV spectra a very strong absorption band in the region 250-270 nm. In the ESCA, the $S_{(2p)}$ binding energies of thiopyrylium compounds were found to be 0.5 and 1.0 eV larger than that of bis(o-carboxyphenyl)-disulfide. These results gave direct evidence for a criterion of the aromatic character of sulfur-containing nonbenzenoid aromatics. The participation of the 3d-orbital on the sulfur atom in thiocoumarins was also discussed from the results of ESCA.

The chemical reactivities of the titled compounds on the methylation were studied. On the methylation of 2-methyl(thiochromones) with dimethyl sulfate, it was found that the blue benzothiopyrylium salts were formed by the self-condensation of alkylated derivative. A similar benzothiopyrylium perchlorate was also obtained by the treatment of 2-methyl(thiochromone) with AlH_3 and $HClO_4$. On the other hand, the methylation of thiocoumarin and carbostyryl derivatives afforded 2,7-dimethoxy-4-methyl-1-benzothiopyrylium salt and 2,7-dimethoxy-4-methylquinolinium salt, respectively. No alkylation reaction occurred, however, in the case of coumarin derivatives. The corresponding methylation of 4-methylquinolin-2-one afforded not only O-methylated derivative but also N-methylated derivative. The methylation of thiocarbonyl derivatives of carbostyryls and coumarins gave S-methylated quinolinium derivatives and also red products which could not be identified by the spectral data, respectively.