ABSTRACT

Darzens Reaction of 2-Bromo-4,6-dimethoxy-3(2*H*)-benzofuranone with Aromatic Aldehydes to form Flavonoids

The aim of this study was to determine the products of the reaction of 2-bromo-4,6-dimethoxy-3(2*H*)-benzofuranone with various aromatic aldehydes under the condition of Darzens condensation and to explain the mechanism of this reaction.

Darzens condensation of aldehydes with α-halo carbonyl compounds furnishes epoxides. The first step involves the aldol reaction of a halocarbon and an aldehydic carbonyl group. The second step is intramolecular S_N2 substitution, when the negatively charged oxygen attacks the carbon with a halogen (as a leaving group), forming the epoxide.

Due to this, 3'-phenylspiro[benzofuran-2(3*H*),2'-oxiran]-3-one is an expected product of the reaction of benzaldehyde with 2-bromobenzofuranone, and its hydrogenolysis would produce auronol. However, the reaction of 2-bromo-4,6-dimethoxy-3(2*H*)-benzofuranone with benzaldehyde, 3,4-dimethoxybenzaldehyde, 2-chlorobenzaldehyde, and 2-bromobenzaldehyde afforded corresponding flavonols and, in certain cases, also *O*-benzofuranyl-substituted flavonols as isolated products.

Initially formed epoxides are probably unstable. The epoxy ring opens due to methoxide attack followed by furanone ring opening, and subsequent recyclization gives rise to the six-membered pyranone ring of flavonol. Reaction of flavonol with another bromobenzofuranone can produce unexpected 1:2 adducts as minor products. Their structure was confirmed by mass spectrometry and NMR spectroscopy. The structure of the hexamethoxy adduct was confirmed by X-ray crystallographic analysis.