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OXYTHALLATION OF FLAVENES.I;DIRECT CONVERSION OF FLAVENES TO FLAVONES WITH THALLIUM(III) NITRATE.

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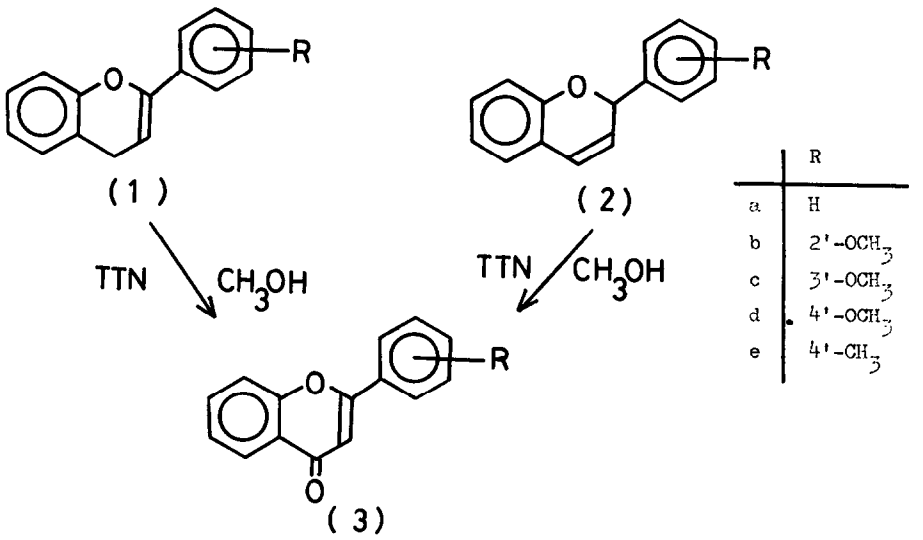
Summary : Oxythallation of flav-2-enes and flav-3-enes with 2 moles equivalent of TTN in methanol gives flavones.

Oxidation of olefins with thallium(III) nitrate (TTN) in hydroxylic solvents gives in principle two major products, glycol and carbonyl derivatives,via S_N2 and Wagner-Meerwein rearrangement type reactions of the alkylthallium(III) adduct respectively.[1]
The composition of the product depends on the migrating power of the substituent and on stereoelectronic factors.
We now report the direct conversion of flav-2-enes(1)(prepared by acid cyclization of 2-hydroxydihydrochalcones[2]) and flav-3-enes (2)(prepared by reductive cyclization of 2 -hydroxychalcones[3]) to flavones (3)(yield ≃ 20%) by oxythallation with 2 moles equivalent of TTN in methanol.



Thus, a solution of TTN (0.04 mole) in methanol (25 ml) is added to a stirred solution of the flavene (0.02 mole) in methanol (25 ml) at room temperature. After stirring overnight the inorganic salt is removed by filtration,the filtrate diluted with water and extracted with chloroform,separation by p.l.c. and recrystallization gives the pure flavone (3).

The flavones were identified by analysis,m.p., u.v., i.r. and n.m.r. spectroscopy and mass spectrometery,[4,5] all flavones except(3e) have been reported previously.[6,7]

The reaction involve two successive oxidation steps whose mechanisms as yet undetermined , however,an intermediate of flavenic structure may be involved further study is in progress.

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