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# STUDIES IN PHENOLIC MANNICH BASES - REACTION WITH ACETYLENES

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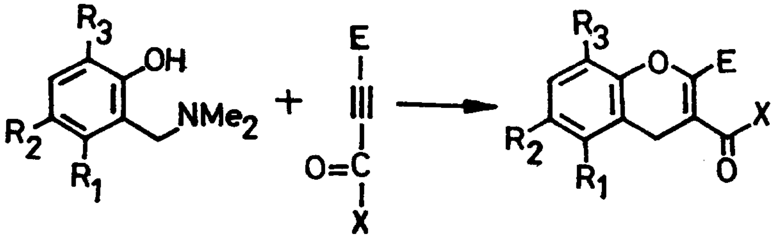
Abstract: 3-Formyl, 3-benzoyl and 2,3-dibenzoyl-4H-Chromenes have been synthesised by the reaction of phenolic Mannich bases with electron-deficient acetylenic systems.

In connection with our work in the area of heterocyclic synthons, we were interested in studying the reaction of o-phenolic Mannich bases with electron-rich and electron-deficient acetylenic systems. We have observed that in contrast to the behaviour of olefinic dienophiles which invariably require relatively drastic conditions[1], propargyl aldehyde and aryl ethynyl ketones react readily, furnishing respectively the hitherto unknown $\Delta^2$-chromenes, functionalised at the $C_3$-position.

When a mixture of the β-naphthol Mannich base and p-chlorophenyl ethynyl ketone in dioxan was refluxed and cooled, crystals of the unknown 3-(p-chlorobenzoyl)-4H-chromene, IIIe, separated out (yield 75%, m.p. 198-99°C). The other regioisomer was not formed as shown by NMR and TLC analysis of the crude product. The reaction was extended to a few other aryl ethynyl ketones, 2-propynal, and dibenzoyl acetylene, as outlined in Table I.

The spectral and analytical data of all these products were consistent with the assigned structures. In the case of the aldehyde IIIb, the structure was further confirmed by reducing it to the dihydro derivative which was identical to the product obtained from the hydrogenation of the known isomeric 3-formyl-2H-chromene[2]. Generally o-quinonemethides are postulated as intermediates in the formation of benzopyrans from the reaction of phenolic Mannich bases and olefins. The final product is visualised to arise via a subsequent (4 + 2) cycloaddition. However such a mechanism is unlikely in the case of the reactions described above, in view of the relatively mild conditions under which the reactions occur, compared to the drastic conditions demanded by the electron-deficient olefinic dienophiles. Hence the following mechanism may be suggested, based on the observation that aryl ethynyl ketones have been found to undergo the Michael addition with great ease with phenols and other nucleophiles[3].

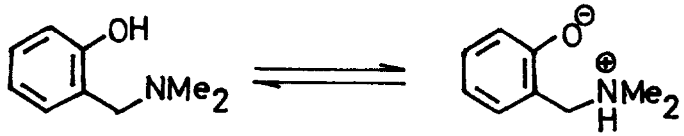


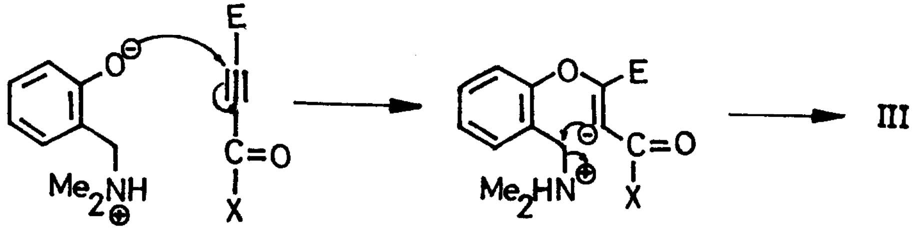
I II III

Table I

Preparation of $\Delta^2$-Chromenes

| S. No. | I | | | II | | III | Melting point |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | E | X | Yield (%) | (°C) |
| 1 a | H | H | $CH_3$ | H | H | 30 | 57-8 |
| b | -HC=CH-CH=CH- | | $CH_3$ | H | H | 60 | 114-116 |
| c | H | Cl | H | H | H | 40 | 130-131 |
| d | H | $CH_3$ | H | H | H | 40 | 82-84 |
| 2 a | H | $CH_3$ | - | H | p-methoxyphenyl | 50 | 163-5 |
| b | -CH=CH-CH=CH- | | - | H | p-methoxyphenyl | 50 | 186-188 |
| c | -CH=CH-CH=CH- | | - | H | α-naphthyl | 60 | 191-192 |
| d | -HC=CH-CH=CH- | | - | H | 3,4-methylene-dioxyphenyl | 55 | 180-182 |
| e | -HC=CH-CH=CH- | | - | H | p-chlorophenyl | 75 | 198-199 |
| f | H | Cl | - | H | 3,4-methylene-dioxyphenyl | 40 | 170-72 |
| 3 a | -HC=CH-CH=CH- | | - | $-\overset{}{\underset{\displaystyle O}{\overset{\Vert}{C}}}-Ph$ | phenyl | 35 | 137-139 |





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