

Unusual Behaviour of 2,2-Dimethyl-2*H*-chromene Derivatives (Precocenes) in Phenylselenenylation¹

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Treatment of 2,2-dimethyl-2*H*-chromene derivatives (precocenes) (**1**) with benzeneselenenyl chloride in methylene dichloride solution affords a mixture of unusual phenylselenenylation products (**7**), (**8**), and (**9**) instead of the expected addition derivatives (**3**). In the case of 6-unsubstituted chromenes (**1a,d,e**), C-6 aromatic substitution (phenylselenenylation) takes place also.

Electrophilic addition of benzeneselenenyl compounds to unsaturated systems is a facile, well documented reaction.²⁻⁴ In most cases this reaction is fast and *anti* stereospecific with various olefins, although the regiochemistry control varies by the substitution pattern of the individual olefins.⁵

In continuation of our study on the synthesis⁶ and chemical transformations of benzopyran compounds⁷ (precocenes⁸) and that of the synthesis of selenium derivatives⁹ we attempted the addition of benzeneselenenyl chloride on precocene 1 (**1a**; X¹ = X² = X⁴ = H, X³ = OMe), precocene 2 (**1b**), and similar compounds (**1c–e**) (Scheme).

The resulting phenylselenenylated chlorochromans (**2**) were of promise as valuable intermediates in further chemical transformations and also as potential anti-juvenile hormone (AJH) compounds. The reactions of (**1a–e**) with benzeneselenenyl chloride, however, have led us to unexpected products. Thus, the reaction of 6,7-dimethoxy-2,2-dimethyl-2*H*-chromene (precocene 2) (**1b**) with 1 equiv. of benzeneselenenyl chloride in methylene dichloride gave rise to the formation of two compounds in a ratio of 7:4. Column chromatography on silica gel gave (**7b**) and (**8b**). An ¹H and ¹³C n.m.r. study revealed that both compounds were 3-substituted precocenes.

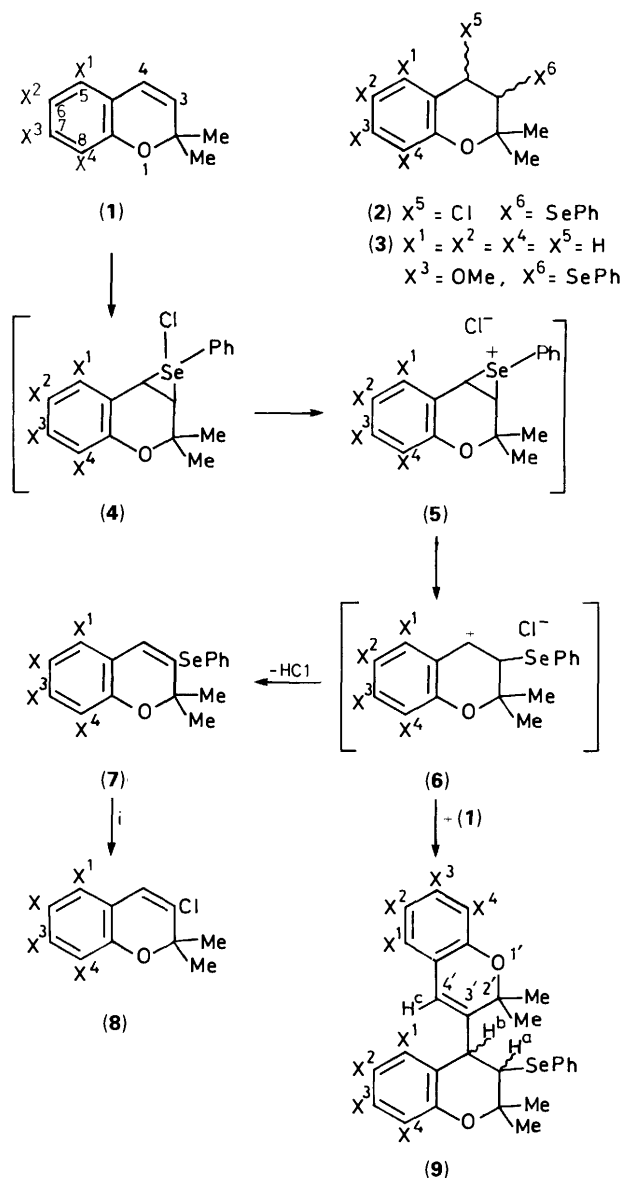
Further mass spectrometric study proved that instead of the expected (**2b**), the corresponding 3-phenylselenenyl compound (**7b**) and the 3-chloro derivative (**8b**) were obtained. Although neither the dehydrochlorination (**2**) → (**7**),[‡] nor the chlorination step (**7**) → (**8**)¹⁰ is unexpected, this reaction represents an unusual phenylselenenylation of unsaturated systems. Furthermore, in the case of the phenylselenenylation of other precocenes (**1a,d,e**) (X² = H), in addition to the formation of products of (**7**)- and (**8**)-type, aromatic electrophilic substitution (phenylselenenylation) and/or dimerization also took place. § The dimerization reaction required the attack of a carbonium ion of (**6**)-type on the 3,4-double bond of the starting precocenes (**1**) (see Scheme).

The latter were present during the reaction, since the transformation of (**1**) to (**8**) required 2 equiv. of benzeneselenenyl chloride per molecule of precocenes. The regiospecific addition of benzeneselenenyl chloride to precocenes was not unexpected.

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[‡] In most cases the dehydrochlorination of the primary addition products requires a base (refs. 3–5 and references cited therein). However, the spontaneous dehydrochlorination is also known [ref. 10(a)].

§ Both aromatic phenylselenenylation and chlorination can be expected.¹¹



Scheme. Reagent: i, PhSeCl in CH₂Cl₂. Substituents: (**1a**) X¹ = X² = X⁴ = H, X³ = OMe; (**1b**) X¹ = X⁴ = H, X² = X³ = OMe; (**1c**) X¹ = X⁴ = H, X² = OMe, X³ = OEt; (**1d**) X¹ = X³ = OMe, X² = X⁴ = H; (**1e**) X¹ = X² = H, X³ = X⁴ = OMe; in (**7**) and (**8**) X is either = X² or PhSe

Similar regiochemistry was observed earlier¹² in the case of the formation of the thermodynamic products from styrene derivatives. A similar, but saturated selenium-containing compound (3) has already been obtained by cyclofunctionalization.¹³

The structure of (7b) was corroborated by ¹H, ¹³C, and ⁷⁷Se n.m.r. and mass spectral experiments. Thus compound (7b) showed one signal in the 76.3 MHz ⁷⁷Se n.m.r. spectrum at δ 380.6 p.p.m. (downfield from dimethyl selenide). The shift for phenylselenenyl ethylene is 395 p.p.m.¹⁴

Thus molecule (7b) gave a selenium-containing molecular ion at m/z 376 (for C₁₉H₂₀O₃ ⁸⁰Se). High resolution mass spectrometry gave 374.0586 for the ⁷⁸Se containing molecular ion (Calc. 374.0585). There is a characteristic ($M - 15$)⁺ peak in the spectrum, typical of 2,2-dimethylchromenes. Treatment of (7b) with 1 equiv. of benzeneselenenyl chloride in methylene dichloride solution (room temp., 4 h) gave rise to the formation of (8a) and diphenyl diselenide, in an almost quantitative yield. The above finding corroborates the proposed scheme.

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