ON THE FORMATION OF 3,4-DICHLORO-2,2-DIMETHYL-2*H*-CHROMENES FROM 2,2-DIMETHYL-4-CHROMANONES

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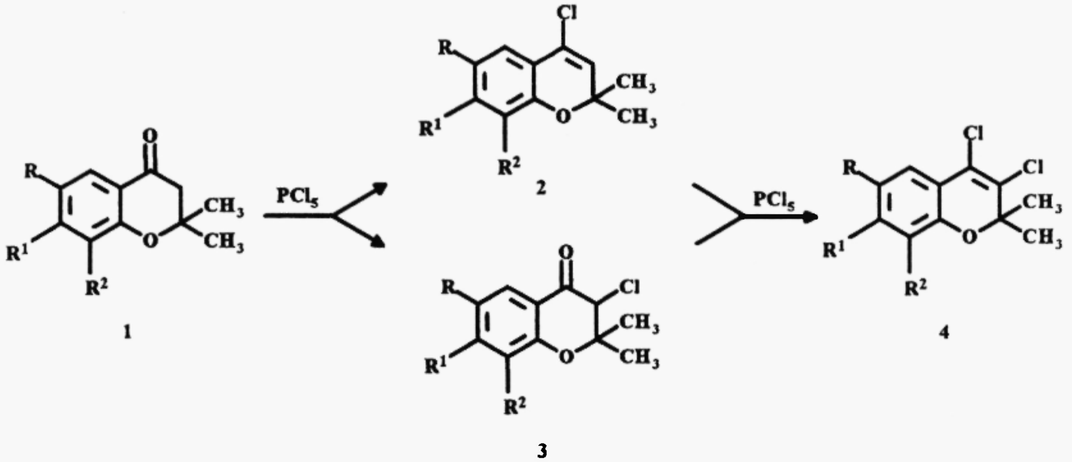
Abstract: The reaction of 7-methoxy-2,2-dimethyl-4-chromanone and PCl_5 is reinvestigated. The product distributions for the reactions of several acetoxy derivatives of 2,2-dimethyl-4-chromanones and PCl_5 have been studied to confirm an extended pathway.

In the course of our research project different 3,4-dichloro-2,2-dimethyl-2*H*-chromenes (**4**) were needed for the syntheses of target compounds with insecticidal activity (1). We attempted the preparation of **4a** (R, R^2 = H, R^1 = MeO) according to the literature procedure (2) (4h reflux in CCl_4 using a *1:1* **1a** and PCl_5 molar ratio). We obtained 14% **2a** and 54% **4a** (3) after TLC mesh chromatography (4). This result was unexpected because it was reported (2) that under these conditions 98% **4a** had been prepared and no conditions had been found which led to the formation of the corresponding 4-chloro-2*H*-chromene (**2a**) without further chlorination. We repeated the experiment using *1:1.5* **1a** and PCl_5 molar ratio: 7% **2a** and 60% **4a** were obtained after chromatography. Applying *1:3* **1a** and PCl_5 molar ratio the reaction mixture did not contain **2a**.

According to Camps and co-workers (5) we repeated the preparation of **4a** using *1:2* **1a** and PCl_5 molar ratio (4h in CCl_4 at room temperature). We got practically the expected result but a small amount of **2a** was detected by TLC from the reaction mixture (compared to an authentic sample (6)). These results suggest that, as well the formation of 4-chloro-2*H*-chromenes (**2**) and their further chlorination at C-3 as the formation of 3-chloro-2,2-dimethyl-4-chromanones (**3**) are involved in the pathway of this reaction (5).

Scheme



To prove this assumption we made a control experiment in which **2a** was quantitatively converted into **4a** using *1:1* **2a** and PCl_5 molar ratio (4h reflux in CCl_4). We have confirmed the original pathway (*via* **3**) suggested by Camps et. al. (5) and the extended one (*via* **2**) outlined in the Scheme investigating the product-distribution for the reactions between different acetoxy derivatives of 2,2-dimethyl-4-chromanones (**1b-f**) and PCl_5. The results are referred in the Table.

Table[a]

Starting chromanone (**1**)				Products, Yield (%)		
	R	R^1	R^2	**2**	**3**	**4**
a	H	MeO	H	4	3	83
b	H	AcO	H	7	35	50
c	H	AcO	AcO	57	11	19
d	tBu	AcO	H	23	39	29
e	AcO	iPrO	H	4	6	80
f	AcO	MeO	H	5	4	75

[a] Typical procedure: 2 mmol of chromanone (**1a-f**) was refluxed in 10 mL of CCl_4 with 4 mmol of PCl_5 until the starting material consumed (1- 5h based on TLC monitoring). The mixture was poured into 50 mL cold, $KHCO_3$ solution, extracted with $CHCl_3$ and the organic layer was washed with water, dried and evaporated. The residue was subjected to TLC mesh column chromatography (7). All new compounds gave satisfactory elemental microanalyses and their sructures had been proved by ^{1}H-NMR and MS .

Table shows that the acetoxy-substituent at different positions on the aromatic ring has remarkable influence on the product-distribution. From this observation one can prepare such acetoxy derivatives of 4-chloro-2*H*-chromenes (2) which cannot be prepared by the method (using PCl_3) described eariier (6). It is important to note, that these chloro-benzopyran derivatives (**2**,**3** and **4**) are versatile intermediates for a wide variety of further transformations in the field of benzopyranoid chemistry (8-11).

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