STRUCTURE AND CONVERSIONS OF THE CONDENSATION PRODUCTS OF PHENOLS WITH UNSATURATED CARBONYL COMPOUNDS

I. Condensation of 3,4-Xylenol with Crotonaldehyde

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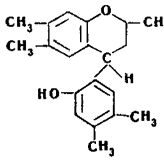
The reaction of 3,4-xylenol with crotonaldehyde leads to the formation of 2,6,7-trimethyl-4-(4',5'-dimethyl-2'-hydroxyphenyl)chroman, whose structure is verified by IR and UV spectra, by the synthesis of the methyl and the benzoyl esters, and by the investigation of the conditions and the products of pyrolisis.

In the literature there are contradictory data on the structure of the condensation products of xylenols with α,β-unsaturated aldehydes. It has been reported [1] that the condensation of 2,4-xylenol with acrolein in a cold and weakly acid medium leads to the formation of 3,5,7-trimethyl-2-(2',4'-dimethylphenoxy)chroman (I). Afterwards Clayton and coworkers established [2] that the condensation product of 2,4-xylenol with acrolein is 6,8-dimethyl-2-(2',4'-dimethylphenoxy)chroman (II), but 3,4-xylenol condenses with crotonaldehyde to form 4,6,7-trimethyl-2-(3',4'-dimethylphenoxy)chroman (III). It is true that Clayton proposed structures II and III merely on the basis of the determination of the methyl group content. No other evidence was presented in the investigation.

This paper presents a detailed investigation of the structure of the product of the condensation of 3,4-xylenol with crotonaldehyde (IV).

By acylation with acetic anhydride in pyridine [3] it was established that product IV contains 5.96% of free hydroxyl groups; but when calculated to the aforementioned formula IV it amounts to 5.73%. Compound IV forms esters with methyl chloride and benzoyl chloride. The bromine number, determined according to McIllene's method [4], was 54.05; when calculated according to formula IV, it amounted to 53.92, and according to formula III, 80.97. The course of the analysis indicated that all the bromine entered into a substitution reaction.

Pyrolisis of IV yielded 3,4-xylenol and chromene (V), whose UV spectrum is analogous to that of 2,2,4-trimethylchrom-3-ene, obtained by Baker and coworkers by the pyrolisis of the condensation product of phenol with mesityl oxide [5]. Therefore, in V the double bond is also linked to the benzene nucleus, and V may be characterized as 2,6,7-trimethylchrom-3-ene. The UV spectrum confirms that the residue of the second 3,4-xylenol molecule is linked to the fourth carbon atom of the pyran ring, and not to the second, as is indicated by structure III. The IR spectrum of IV* exhibits absorption bands in the 855–870 and in the 885 cm^{-1} regions, which are characteristic of 2,4,5-trisubstituted phenols, and a valence vibrations band of the phenolic hydroxyl* with a characteristic frequency of 3620 cm^{-1} [7].



The previously presented evidence permits us to attribute to the condensation product of 3,4-xylenol with crotonaldehyde the structure 2,6,7-trimethyl-4-(4',5'-dimethyl-2'-hydroxyphenyl)chroman (IV).

3-4-Xylenol does not react with V under the conditions for synthesizing IV. By increasing the reaction time to 8 days, IV is formed with a 0.1% yield. Thus, in our experiments the condensation of 3,4-xylenol with crotonaldehyde does not go through the stage of chromene formation, as supposed by Baker [5] for the condensation reaction of phenol with mesityl oxide.

EXPERIMENTAL

2,6,7-Trimethyl-4-(4',5'-dimethyl-2'-hydroxyphenyl)chroman (IV). To 24.4 g (0.2 mole) of 3,4-xylenol were added at room temperature 7.0 g (0.1 mole) of crotonaldehyde and 40.0 of a 10% solution of dry hydrogen chloride in glacial acetic acid. The mixture was stirred until a homogeneous mass was obtained, and was allowed to stand for three days. The mass was then treated with water and a 10% potassium hydroxide solution. The residue insoluble in alkali was treated with steam. The residue was a light-gray powder, completely soluble in Claisen alkali, which on acidifying with dilute hydrochloric acid at 0°–2° C separates out as a white precipitate. This was filtered off, washed with water, and dried in a vacuum dessicator over phosphoric anhydride. Yield 26.4 g (89.2%); mp 65°–67° C. Found: C 80.89%; H 8.30%; OH 5.96; bromine number 54.05; MW 316.0 (by the cryoscopic method in benzene). Calculated for $C_{20}H_{24}O_2$: C 80.97%; H 8.97%; OH 5.73%; bromine number 53.92; MW 296.4.

Methyl Ester of IV. 14.8 g (0.05 mole) of IV, 18.5 g (0.13 mole) of methyl iodide, and 2.4 g of potassium hydroxide in 20 ml of methanol were boiled for 10 hours. The methanol and the methyl iodide were distilled off, and the residue was distilled in vacuo. Yield 7.6 g (55.8%); mp 45°–47° C, bp 203°–205° C (2 mm). Found: C 81.78%; H 8.52%; MW 303.0. Calculated for $C_{21}H_{26}O_2$: C 81.24%; H 8.44%; MW 310.40.

Benzoyl Ester of IV. 13.0 g (0.043 mole) of IV, 50 ml pyridine, and 30.5 g (0.21 mole) of benzoyl chloride were boiled for 10 hours.

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*The IR spectrum of a paste of IV in vaseline oil was recorded on a IKS-14 apparatus

*The IR spectrum of a solution of IV in CCl_4 was recorded on a UR-10 apparatus provided with a LiF prism.

The reaction mass was treated with hot water, and the residue extracted with carbon tetrachloride. Yield 8.5 g (56.0%; mp 62°–63° C, bp 242°–244°C (3 mm). Found, %: C 80.75; H 7.03; saponification number 140.8. Calculated for $C_{27}H_{28}O_3$, %: C 80.96; H 7.04; saponification number 139.8.

2, 6, 7-Trimethylchrom-3-ene (V). 7.5 g (0.025 mole) of IV was heated for 6 hr at 270° C in a flask provided with a reflux condenser. The product of the pyrolisis was distilled at atmospheric pressure. The distillate was treated with a 10% solution of potassium hydroxide. The oil insoluble in alkali is separated and distilled under vacuum. Yield 1.05 g (24%) of V, colorless, oily liquid, bp 124°–125° C (5 mm), d_4^{20} 1.0013, n_D^{20} 1.5310. Found: C 82.80; H 8.58%; MR_D 53.80; bromine number 92.16. Calculated for $C_{12}H_{14}O$: C 82.71%; H 8.27%; MR_D 52.99; bromine number 91.74. UV absorption spectrum in ethanol: λ_{max}, nm 230, 250, 290; λ_{min}, nm 240, 265, 285. The UV spectrum was recorded on a SF-4 apparatus.

On acidifying the alkaline solution, 3, 4-xylenol separated out, and was identified by the mixed melting point with a sample of pure 3, 4-xylenol.

The IR spectra were recorded and interpreted by M. N. Volkotrub, senior scientific coworker at the Scientific Institute for the Investigation of Polymer Chemistry (NIIkhimpolimer).

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