SYNTHESIS OF COUMARANS FROM ALKENYLPHENOLS

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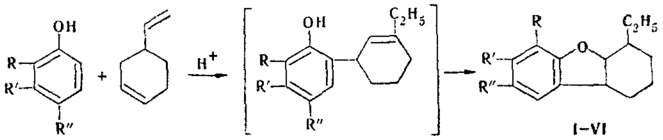
A number of substituted coumarans, the structures of which were confirmed by UV and PMR spectroscopy, were synthesized by the reaction of phenols with 4-vinyl-1-cyclohexene in the presence of KU-2 cation-exchange resin.

The cyclization of o-alkenylphenols to chromans and coumarans is one of the simple methods for the synthesis of compounds of this class [1]. We have synthesized a number of substituted coumarans that have not been described in the literature by reaction of phenols with 4-vinyl-1-cyclohexene in the presence of KU-2 cation-exchange resin.



I–VI

The structure of the compounds was confirmed by means of UV and PMR spectroscopy. The UV spectrum contains maxima at 285-289 nm (log ε 3.45-3.47), which is characteristic for the spectra of coumarans [2]. The PMR spectral data are presented in Table 1.

TABLE 1. Chemical Shifts in the PMR Spectra of Coumarans

Compound	Substituents			Chemical shifts, δ, ppm					
	R	R'	R''	—CH— —O—	CH_2, CH	CH_3	$C(CH_3)_3$	CH_2- CH_2-	C_6H_5
I	H	H	H	2,88m*	1,02—2,20	—	—	0,85 t J = 7,5 Hz	6,35—7,00 m
II	CH_3	H	H	2,89 m	1,10—1,94	2,07 s	—	0,90 t	6,20—6,90 m
III	H	CH_3	H	2,89 m	1,18—2,00	2,18 s	—	0,92 t	6,65 d J = 8,0 Hz 6,44 s 6,38 d
IV	H	H	CH_3	2,83 m	1,00—1,90	2,10 s	—	0,84 t	6,69 q 6,59 d J = 2,0 Hz 6,58 d J = 8,0 Hz
V	H	H	$C(CH_3)_3$	2,83 m	1,10—1,90	—	1,20 s	0,86 t	6,92 q 6,79 d J = 2,5 Hz 6,54 d J = 8,5 Hz
VI	$C(CH_3)_3$	H	CH_3	2,89 m	1,18—2,00	2,14 s	1,29 s	0,93 t	6,74 d 6,48 d J = 2,0 Hz

*The abbreviations used here and subsequently are as follows: s is singlet, d is doublet, t is triplet, q is quartet, and m is multiplet.

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*Deceased.

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TABLE 2. Properties of Coumarans

Compound	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Emperical formula	Found, %		Calc., %		Yield, %
				found	calc.		C	H	C	H	
II	120 (2)	1,0296	1,5381	65,61	65,11	$C_{15}H_{20}O$	83,1	9,3	83,3	9,3	33
III	123 (2)	1,0306	1,5401	65,77	65,11	$C_{15}H_{20}O$	82,9	9,3	83,3	9,3	68
IV	124 (2)	1,0324	1.5412	65,75	65,11	$C_{15}H_{20}O$	83,1	9,2	83,3	9,3	89
V	146 (2)	1,0130	1,5288	78,00	77,82	$C_{18}H_{26}O$	83,9	9,9	83,8	10,1	66
VI	135 (2)	1,0007	1,5313	84,09	83,58	$C_{19}H_{28}O$	83,5	10,9	83,8	10,3	30

EXPERIMENTAL

The PMR spectra of CCl_4 solutions were recorded with a JNM-C60-HL spectrometer at 60 MHz with hexamethyldisiloxane (HMDS) as the internal standard. The UV spectra of CCl_4 solutions were recorded with a Hitachi recording spectrophotometer.

2-Ethyl-2,3,4,5,11,12-hexahydrodibenzofuran (I). A 5.4-g (0.05 mole) sample of 4-vinyl-1-cyclohexene was added dropwise with stirring at 127-128° to a mixture of 9.4 g (0.1 mole) of phenol and 3 g of KU-2 cation-exchange resin, after which the mixture was held at the same temperature for 2 h. The catalyst was separated, and the reaction products were dissolved in sulfuric acid. The sulfuric acid solution was treated with a Claisen solution to remove neutral compounds from the acidic compounds. The ether layer was neutralized, dried, and distilled to give 3 g (30%) of I with bp 120° (2 mm), d_4^{20} 1.0452, and n_D^{20} 1.5443. Found %: C 83.1; H 8.8; M 201; MR_D 60.99. $C_{14}H_{18}O$. Calculated %: C 83.2; H 8.9; M 202; MR_D 60.50.

Compounds II-VI were similarly obtained (Table 2).

LITERATURE CITED

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2. D. Gagniant and P. Gagniant, Bull. Soc. Chim. France, 838 (1957).