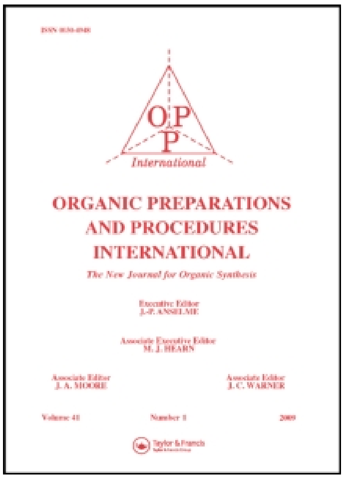

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A SIMPLE PROCEDURE FOR THE CYCLIZATION OF 2'-HYDROXYCHALCONES INTO FLAVANONES

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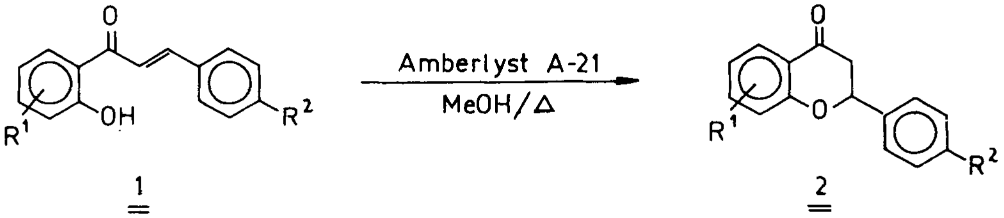
Cyclization of 2'-hydroxychalcones (**1**) into the respective flavanones (**2**) is one of the basic reactions in flavonoid chemistry. Isomerization **1** ⟶ **2** can be accomplished in the presence of either acidic[1,2] or basic[1,3] reagents or by photocyclization[4]. However, the yields are often low and are dependent upon the substituents of **1** (each substrate requires separate optimization) and the isolation of compounds **2** is difficult. In this paper we report a mild and simple procedure for the cyclization of **1** into **2**.

The kinetic investigation[5] of the reaction **1a** ⟶ **2a** has established that the cyclization in the presence of various tetraalkylammonium hydroxides proceeds similarly to that performed with sodium hydroxide. This observation directed our attention to the application of the basic anion exchange resins. It has been found that flavanones **2a**-**k** can be obtained with good yield from the respective substituted 2'-hydroxychalcones (**1a**-**k**) in refluxing methanol in the presence of the weakly basic Amberlyst A-21 resin.



When the more basic Varion AD resin was used the yields were lower, and a significant part of the substrate (40-50%) was found to be steadily absorbed on the resin (Table). The application of Amberlyst A-21 resulted in the conversion of the variously substituted 1 in equally good yield; somewhat lower yields were observed only in the case of chalcones with low solubility (cf. 1k ⟶ 2k) and poorly crystallizable flavanones (cf. 1c ⟶ 2c). Further utilization of this reaction for the preparation of flavanones is being investigated.

EXPERIMENTAL SECTION

IR spectra were determined on a Perkin-Elmer 283 spectrometer, in KBr disc. ^{1}H-NMR spectra were measured on a Bruker WP 200 SY instrument, in $CDCl_3$ with TMS as internal standard; mps. are uncorrected. Amberlyst A-21 was obtained from Serva Feinbiochemica (Heidelberg) or Fluka, Varion AD was obtained from Nitrokemia (Balatonfüzfő, Hungary).

General Procedure. - 2'-Hydroxychalcone (10 mmol) and Amberlyst A-21 (or Varion AD) (3.5 g) in methanol (60 ml) was stirred at reflux temperature for 4-7 hrs. The resin was filtered and washed with hot methanol (2x20 ml). The combined filtrates were evaporated and the residue (containing small amount of 1 besides the major product 2) was subjected to fractional crystallization from methanol; the only exception was 2i, which was isolated by column chroma-

TABLE Physical Data of Flavanones 2

	R^1	R^2	Yield(%) A-21	Yield(%) V-AD	Reported Yield(%)	mp. (°C)	Lit.mp. (°C)	Ref.
2a	H	H	71.7	42.5	80	76	76	6
2b	H	MeO	53.3	34.1	20	85-87	90	2b
2c	H	Me	41.1	27.1	-	65-66	-	-
2d	H	Cl	55.2	28.0	25	94-95	87	2b
2e	H	CN	54.7	-	31	116-118	120	2b
					a)		187	7
2f	5-MeO	H	66.7	28.9	60	143-144	148-150	8
					a)		145	9
2g	7-MeO	H	63.7	40.6	a)	87-89	89	10
2h	7-$PhCH_2O$	H	60.1	-	50	123-125	126	11
2i	7-Me	H	52.7	-	20	75-77	76	12
2j	7-Cl	H	64.4	25.2	a)	54-56	54-55.5	13
2k	7,8-$(PhCH_2O)_2$	H	31.7	-	-	113-115	-	-

a) not reported

2c: Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.05; H, 5.92. Found: C, 80.66; H, 6.01. IR: 1691 (νC = O). ^{1}H-NMR: δ 5.40 (H-2), 3.05 (H-3a), 2.84 (H-3e), 2.38 (Me). $J_{3a,3e}$ = 17.35 Hz, $J_{2,3a}$ = 13.6 Hz, $J_{2,3e}$ = 3.5 Hz.

2e: Anal. Calcd. for $C_{16}H_{11}NO_2$: N, 5.62. Found: N, 5.38. IR: 2225 (νC≡N), 1668 (νC = O). ^{1}H-NMR: δ 5.57 (H-2), 3.01 (H-3a), 2.93 (H-3e); $J_{3a,3e}$ = 16.9 Hz, $J_{2,3a}$ = 13.3 Hz, $J_{2,3e}$ = 2.9 Hz.

2k: Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.45; H, 5.64. IR: 1682 (νC = O). ^{1}H-NMR: δ 5.43 (H-2), 5.21, 5.08 (2xPh$\underline{CH_2}$O), 3.02 (H-3a), 2.88 (H-3e). $J_{3a,3e}$ = 16.9 Hz, $J_{2,3a}$ = 13.2 Hz, $J_{2,3e}$ = 2.75 Hz.

tography (Kieselgel 60, eluent: dichloromethane-petroleum ether (3:1)). The results are summarized in the Table; yields refer to pure, crystalline 2. The known products were identified by mp., mixed mp., IR and ^{1}H-NMR spectra.

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