SYNTHESIS OF NEW (*Z*)-3-ARYLIDENECHROMANONES BY THE PHOTOISOMERIZATION OF (*E*)-3-ARYLIDENECHROMANONES

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Abstract: An efficient procedure has been developed for the synthesis of (*Z*)-3-arylidenechromanones **2a-g** by the photoisomerization of (*E*)-3-arylidenechromanones **1a-g** in acid-free anhydrous benzene.

Introduction

Synthetic (*E*)-3-arylidenechromanones are known for a long time. Their synthesis was performed mainly by the acid-catalyzed condensation of chromanones and aromatic aldehydes (1-4) or in a few cases in the presence of base catalyst (5,6). Contrary to the (*E*) isomers, the synthesis of the (*Z*)-3-arylidenechromanones has hitherto been hardly mentioned in the literature (7,8). Donnelly and O'Boyle reported (7) the preparation of (*Z*)-3-benzylidenechromanone but without experimental details of the reaction conditions and physical data of the product. We also described the synthesis of (*Z*)-3-benzylidenechromanone by the photoisomerization of the corresponding (*E*) isomer (8).

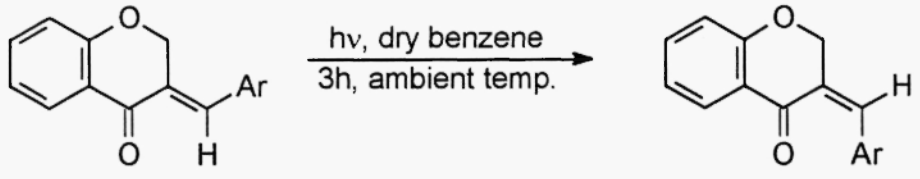
Formerly we have worked out a simple and convenient method for the synthesis of (*E*)-3-arylidenechromanones by the piperidine-catalyzed reaction of chromanone with aromatic aldehydes (9,10). Since the comparative investigations of the reactivities of the (*E*) and (*Z*) isomers of the 3-arylidenechromanones seems to be an interesting challenge, it requires the development of versatile procedures for the preparation of the (*Z*) isomers as well. Synthesis of the closely related (*Z*)-3-arylideneflavanones has been thoroughly investigated (11-14) and we have utilized these results for our study on the preparation of a series of new (*Z*)-3-arylidenechromanones reported herein.

Results and Discussion

(*E*)-3-Arylidenechromanones (**1a-g**) were dissolved in anhydrous benzene dried on sodium and irradiated with a 400-W mercury arc lamp at ambient temperature until an equilibrium was reached

(3 h) with approx. $Z:E$ = 4:1 isomeric ratio detected by thin-layer chromatography (TLC) and ^{1}H NMR spectroscopy. The previous drying of the solvent with sodium is essential to eliminate the acid traces, which may help the reconversion of the (*Z*) isomers formed into the starting (*E*)-3-arylidenechromanones. In the lack of the pretreatment of the benyene lower $Z:E$ ratio and more significant decomposition was observed. The mixtures were then separated by column chromatography to obtain (*Z*)-3-arylidenechromanones (**2a-g**) (Scheme, Tables 1 and 2).

Scheme



1 **2**

a, Ar = 4-Methylphenyl; **b**, Ar = 4-Methoxyphenyl; **c**, Ar = 4-Ethoxyphenyl; **d**, Ar = 4-Chlorophenyl; e, Ar = 4-Bromophenyl; **f**, Ar = 2-Naphthyl; **g**, Ar = 2-Thienyl

Although the yields are relatively low (40-50%, *cf.* Table 2), over the isomerized and starting materials no other substances could be detected in the solution. On the chromatographic column, however, some colored material remained certainly containing decomposition products decreasing the yield of the photoisomerization.

The structures of the compounds prepared (**2a-g**) were elucidated by microanalysis and by IR and ^{1}H NMR spectroscopy. The relevant data are summarized in Tables 1 and 2. A characteristic C=O band is found between 1660 and 1676 cm^{-1} and the C=C band at ca. 1602-1604 cm^{-1}. There is almost no difference between the IR spectra of the (*E*) (9) and (*Z*) isomers but they corroborate the α,β-unsaturated ketone character of the compound in each case. However, the ^{1}H NMR spectra of these two isomers are characteristically different. In the ^{1}H NMR spectra of compounds **2a-g** a singlet CH_2 signal was measured at about 5 ppm, and the singlet CH signal appears between 6.85 and 7.09 ppm, respectively; while in the ^{1}H NMR spectra of the starting (*E*)-3-arylidenechromanones (**1a-g**) the CH_2 signal appears between 5.36 and 5.50 ppm and the CH signal between 7.82 and 8.00 ppm. This considerable upfield shift of both the CH_2 and CH signals measured for the (*Z*) isomers makes possible an unambiguous differentiation of the two isomers. It has also turned out that the $E \rightarrow Z$ isomerization is almost independent of the electronic character of the substituent if the arylidene moiety is a substituted benzylidene group.

Table 1. Selected IR and ^{1}H NMR spectral data for compounds **2**

Compound	ν_{max} (cm^{-1})		δ (ppm)	
	C=O	C=C	CH_2	CH
2a	1668	1606	5.02	6.91
2b	1664	1602	4.99	6.86
2c	1660	1606	4.98	6.85
2d	1672	1606	4.99	6.89
2e	1676	1604	5.02	6.88
2f	1670	1604	5.07	7.09
2g	1664	1604	5.03	7.08

In summary, it can be concluded that we managed to develop a simple and general procedure providing (*Z*)-3-arylidenechromanones by the photoisomerization of the appropriate (*E*) isomers under strictly acid-free reaction conditions. These conditions are the prerequisite of a successful procedure since the (*Z*) isomers are extremely sensitive to acids and reconvert into the starting materials. Our present results made easily available a large variety of the previously inaccessible (*Z*)-3-arylidenechromanones.

Experimental

IR spectra were measured for KBr discs with a Perkin-Elmer 16 PC instrument. ^{1}H NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200 MHz in $CDCl_3$ (internal standard Me_4Si, δ = 0.0 ppm) at room temperature. Starting materials **1a-g** were synthesized according to known procedures (9,10).

General procedure for the preparation of (Z)-3-Arylidenechromanones **2**

(*E*)-3-Arylidenechromanones (**1a-g**, 10.0 mmol) were dissolved in anhydrous benzene (280 ml) and irradiated with a 400-W mercury arc lamp at ambient temperature for 3 h. The solvent was evaporated *in vacuo* (ca. 20 Torr) and the residue was purified on silica gel (Merck) column using benzene:hexane (4:1 or 3:2 v/v) as eluent to afford compounds **2a-g** (Tables 1 and 2).

Table 2. Physical constants and analytical data for compounds **2**

Com-pound	mp. (°C)	Yield (%)	Mol. Formula	Elemental Analysis (%)			
				Found		Calcd.	
				C	H	C	H
2a	59-60	50	$C_{17}H_{14}O_2$	81.75	5.68	81.58	5.73
2b	74-75	52	$C_{17}H_{14}O_3$	76.51	5.41	76.68	5.30
2c	80-81	40	$C_{18}H_{16}O_3$	77.24	5.72	77.13	5.66
2d	98-99	53	$C_{16}H_{11}ClO_2$	71.08	4.13	70.99	4.10
2e	152-153	41	$C_{16}H_{11}BrO_2$	61.12	3.60	60.98	3.52
2f	114-115	47	$C_{20}H_{14}O_2$	83.71	4.98	83.89	4.93
2g	80-81	43	$C_{14}H_{10}O_2S$	69.30	4.27	69.41	4.16

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References

(1) F. Arndt and G. Källner, *Ber. Dtsch. Chem. Ges.*, 57, 202 (1924)
(2) P. Pfeifer and E. Döhring, *Ber. Dtsch. Chem. Ges.*, 71, 279 (1938)
(3) O. Dann and H. Hofmann, *Chem. Ber.*, 95, 1446 (1962)
(4) O. Dann and H. Hofmann, *Chem. Ber.*, 98, 1498 (1965)
(5) P. Pfeiffer and H.J. Elmer, *Chem. Ber.*, 53, 945 (1920)
(6) J. Andrieux, D.H.R. Barton and H. Patin, *J. Chem. Soc., Perkin Trans. 1*, 359 (1977)
(7) J.A. Donnelly and P. O'Boyle, *Chem. Commun.*, 1060 (1969)
(8) G. Tóth, A. Lévai, Á. Szöllösy and H. Duddeck, *Tetrahedron*, 49, 863 (1993)
(9) A. Lévai and J. B. Schág, *Pharmazie*, 34, 749 (1979)
(10) A. Lévai and Z. Szabó, *Pharmazie*, 47, 56 (1992)
(11) D.D. Keane, K.G. Marathe, W.I. O'Sullivan, E.M. Philbin, R.M. Simons and P.C. Teague, *J. Org. Chem.*, 35, 2286 (1970)
(12) D.D. Dhavale, P. Joshi, and K.G. Marathe, *J. Chem. Soc., Perkin Trans 2*, 449 (1987)
(13) G. Tóth, Á. Szöllösy, A. Lévai,. Gy. Oszbach, W. Dietrich, H. Kühne, *Magn. Reson. Chem.*, 29, 801 (1991)
(14) Cs. Nemes, A. Lévai, T. Patonay, G. Tóth, S. Boros, J. Halász, W. Adam, D. Golsch, *J. Org. Chem.*, 59, 900 (1994)

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