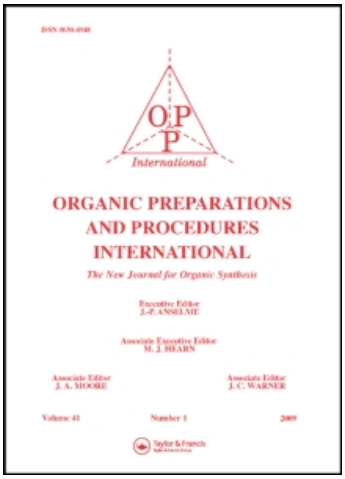


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

4-(2-ARYLALKENYL)-3-CYANO-2H-1-BENZOPYRAN-2-ONES

Y. Anghelova[a]; E. Dimitrova[a]
[a] Faculty of Chemistry, University of Sofia, Sofia, BULGARIA

To cite this Article Anghelova, Y. and Dimitrova, E.(1989) '4-(2-ARYLALKENYL)-3-CYANO-2H-1-BENZOPYRAN-2-ONES', Organic Preparations and Procedures International, 21: 3, 341 — 343
To link to this Article: DOI: 10.1080/00304948909356390
URL: http://dx.doi.org/10.1080/00304948909356390

washed with pre-cooled (0°) ethanol (200 ml), and then hexane (500 ml) to remove 2-methylaniline and water, and dried in a dessicator under reduced pressure. To the solid in a 1 L flask was added 500 ml of freshly distilled tetrahydrofuran (dried over calcuim hydride), and the whole stirred to give a heterogeneous suspension. Then solid sodium borohydride (10.0 g) was added during 15 minutes at 20° with vigorous stirring. Gas was slowly evolved, and the solid gradually dissolved. The mixture was kept well stirred at 20° for 10 hours. After rotary evaporation, the residue was poured into water (500 ml) and ice (ca 100 g). The whole was extracted twice with hexane (300 ml x 2) and the extract was washed with water (200 ml), and dried over anhydrous magnesium sulfate (20 g). The crude product was distilled under dry nitrogen to give 44.9 g (87%) of a colourless liquid bp. 203.5-205.0°, lit.[7] bp. 207-208°. Proton NMR showed less than 2% of o-toluidine on the basis of the area ratio of the 2-methyl and N-methyl proton peaks. TLC (silica-gel, benzene:hexane = 1:9) also indicated a pure product.

REFERENCES

1. A. Crochet, Jr. and B. C. DeWitt, Jr. Synthesis, 55 (1974).

2. R. M. Roberts and P. J. Vogt, J. Am. Chem. Soc., 78, 4778 (1956). Organic Synthesis, Col. IV, 420; T. Luh and S. Fung, Synth. Commun., 1979, 9, 757.

3. J. S. Buck and C. W. Ferry, Org. Syn., Col. II, 290.

4. M. Sekiya and K. Ito, Chem. Pharm. Bull. Japan, 15, 1339 (1967); S. B. Kadin, J. Org. Chem., 38, 1348 (1973).

5. A. R. Katritzky, W. Fan and K. Akutagawa, Tetrahedron, 42, 4027 (1986).

6. A. R. Katritzky, S. Rachwal and B. Rachwal, J. Chem. Soc. Perkin Trans. I,805 (1987).

7. J. Buckingham Ed., "Dictionary of Organic Compounds", Chapman and Hall, New York, 5th Ed., Vol. 2, 2068, D-95532 (1982).

****

4-(2-ARYLALKENYL)-3-CYANO-2H-1-BENZOPYRAN-2-ONES

Submitted by (12/26/87) Y. Anghelova* and E. Dimitrova

Faculty of Chemistry, University of Sofia
1126 Sofia, BULGARIA

As a continuation of our investigation of the condensation of CH-acids containing a methyl group in γ-position with respect to the electron-acceptor group,[1,2] we studied the condensation of 3-cyano-4-methylcoumarin (1) with aromatic aldehydes. Our initial experiments have shown that

TABLE 1. 4-(2-Arylalkenyl)-3-cyano-2H-1-benzopyran-2-ones (3)

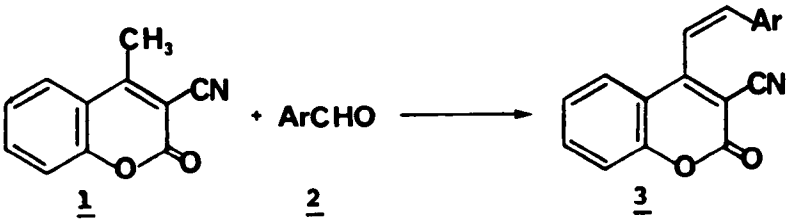
Product	mp (°C)	Yield (%)	m/e	UV spectra (CH_2Cl_2,nm)
3a	199-200	77	273	313, 350
3b	180-183	71	287	313, 358
3c	200-202	74	303	270, 358
3d	218-220	81	316	313, 510
3e	273-275	81	298	265, 340
3f	246-248	78	307	310, 350
3g	224-226	84	323	305, 358
3h	251-253	82	373	260
3i	203-205	79	317	295, 350
3j	270-272	73	274	310

TABLE 2. Elemental Analyses and ^1H nmr Data of 3

Cmpd.	Elemental Analyses Calcd. (Found) C	H	N	^1H nmr Data δ(DMSO-d_6, [a] TFA[b])
3a	79.12(78.99)	4.02(4.22)	5.12(4.98)	7.50-8.25 m
3b	79.38(79.20)	4.52(4.71)	4.87(4.74)	2.40 s, 3H(CH_3) 7.10-8.25 m,1OH(2C_6H_4,CH=CH)
3c	75.38(75.15)	4.28(4.37)	6.61(4.55)	3.89 s, 3H(OCH_3), 7.00-7.75 m, 1OH(C_6H_4, CH = CH)
3d	75.87(75.69)	5.05(5.23)	8.85(8.50)	3.50 s, 6H($2CH_3$), 7.60-8.25 m, 1OH(C_6H_4,CH= CH) (TFA)
3e	76.51(76.39)	3.35(3.47)	9.31(9.24)	7.50-8.50 m
3f	70.24(70.06)	3.25(3.38)	4.55(4.42)	7.00-8.25 m
3g	81.65(81.78)	4.02(3.97)	4.33(4.21)	7.00-8.25 m
3h	83.57(83.72)	4.01(4.21)	3.75(3.50)	7.50-8.75
3i	71.87(71.70)	3.46(3.67)	4.41(4.36)	Not soluble
3j	74.45(74.30)	3.65(3.83)	10.22(10.09)	Not soluble

[a] 3c, 3f, 3h; [b] 3a, 3b, 3d, 3e, 3g

the conditions used previously ($NaNH_2$ in HMPT)[1] do not lead to the desired result. By changing to the use piperidine in chloroform with azeotropic removal of water, we obtained the products 3a-j. The yields and physical constants of these compounds are summarized in Tables 1 and 2.



1 2 3

a) Ar = C_6H_5 b) Ar = p-MeC_6H_4 c) Ar = p-$MeOC_6H_4$ d) Ar = p-$Me_2NC_6H_4$
e) Ar = p-CNC_6H_4 f) Ar = p-ClC_6H_4 g) Ar = 1-$C_{10}H_7$ h) Ar = 9-$C_{14}H_9$
i) Ar = 3,4(OCH_2O)C_6H_3 j) Ar = 4-C_5H_4N

EXPERIMENTAL SECTION

Melting points were determined on a Boetius hot stage microscope and are uncorrected. IR spectra were recorded on a Specord 71-IR spectrophotometer, UV spectra on a Specord UV -VIS spectrophotometer, NMR spectra on Tesla BS 487C, 80 Hz, while mass spectra were performed on a JEOL D-300 at an ionization voltage of 70 eV.

4-(2-Arylakenyl)-3-cyano-2H-1-benzopyran-2-ones. General Procedure.- A mixture of 3-cyano-4- methyl-2H-1-benzopyran-2-one (3.72 g, 0.02 mole),[3] the aldehyde (0.02 mole), chloroform (20 ml) and piperidine (10 drops) was boiled for 7 hrs with azeotropic removal of water. After evaporation of chloroform, the solid residue was recrystallized from methylene chloride.

REFERENCES

1. C. Ivanov, Y. Anghelova and S. Spirova, Synthesis, 723 (1979).

2. E. Dimitrova and Y. Anghelova, Synth. Commun., 16, 1195 (1986).

3. C. H. Schroeder and K. P. Link, J. Am. Chem. Soc., 75, 1886 (1953).

4. I. I. Grandberg, L. K. Denissov and O. A. Popova, Khim. Geterocycl. Soed., 2, 147 (1987); C. A., 107, 217375p (1987).

5. N. C. Vulfson and L. C. Golovkina, Usp. Khim., 44, 1308 (1975).

****