Reactions of 4,6-Bis(acetyl)resorcinol with Alkoxycarbonylalkylidene(triphenyl)phosphoranes. Preparation of Coumarin Derivatives

D. N. Nicolaides*, K. C. Fylaktakidou, C. Bezergiannidou-Balouktsi and K. E. Litinas

Laboratory of Organic Chemistry, University of Thessaloniki,
540 06 Thessaloniki, Greece
Received August 9, 1993

Reaction of compound **1** with ylide **2a** affords compounds **3a, 3b** and coumarins **4a, 5a, 5b, 6a** in 77% total yield. Reaction of **1** with ylide **2b** affords coumarin **4b**. The acetylderivatives obtained, react further with ylides **2a-c** to give pyrano[3,2-*g*]chromene-2,8-diones **6b-d**.

J. Heterocyclic Chem., **31**, 173 (1994).

Wittig olefination of *o*-hydroxycarbonyl-aromatic compounds with the title ylides, followed by further lactonization of the (*o*-hydroxyaryl)esters formed, is a well known method for the preparation of coumarin derivatives [1-8]. Usually, a direct lactonization, especially of the initial *Z* esters occurs, while in the case of the *E* isomers, obtained in several cases, this transformation can proceed by their heating at high temperature [2,6], better in diethylaniline solutions [8] and/or photochemically [4]. 4-Carbethoxycoumarins are also obtained [9,10] by treatment of *o*-quinones with ylide **2a**, while treatment of 10-(4-methoxy-benzylidene)-9-(10*H*)-phenanthrone with the same ylide leads into the formation of the corresponding 4-aryldibenzocoumarin [11]. Furthermore, we recently found that the simple coumarin as well as the above mentioned carbethoxycoumarin react further by heating with ylide **2a** to give the corresponding Wittig-olefination product of their lactone carbonyl [12]. Our continuous interest in the preparation and study of coumarins [10-16] prompted us to examine the title reactions. The reactions studied and products obtained are depicted in Scheme 1.

A toluene solution of 4,6-bis(acetyl)resorcinol (**1**) and two equivalents of ethoxycarbonylmethylene(triphenyl)-phosphorane (**2a**) was heated under reflux for 6 hours and the reaction mixture separated by column chromatography to give ethyl *E*-3-(5-acetyl-2,4-dihydroxyphenyl)-2-butenoate (**3a**) (11%), ethyl *E*-3-(5-acetyl-2-ethoxy-4-hydroxyphenyl)-2-butenoate (**3b**) (16%), the known [17] 6-acetyl-7-hydroxy-4-methyl-2*H*-1-benzopyrane-2-one (**4a**) (7%), ethyl *E*-3-(7-hydroxy-4-methyl-2-oxo-2*H*-1-benzopyrane-6-yl)-2-butenoate (**5a**) (21%), ethyl *E*-3-(7-ethoxy-4-methyl-2-oxo-2*H*-1-benzopyrane-6-yl)-2-butenoate (**5b**) (3%) and the known [18] 4,6-dimethyl-2*H*-8*H*-benzo[1,2-*b*:5,4-*b*]dipyran-2,8-dione (**6a**) (19%). Compound **3a** was heated in an oil bath at 170° for 8 hours to give compound **4a** (79%). A thermal transformation of the ester **5a** to dicoumarin **6a** (78%) was also observed, when the former was heated at 210° for 16 hours.

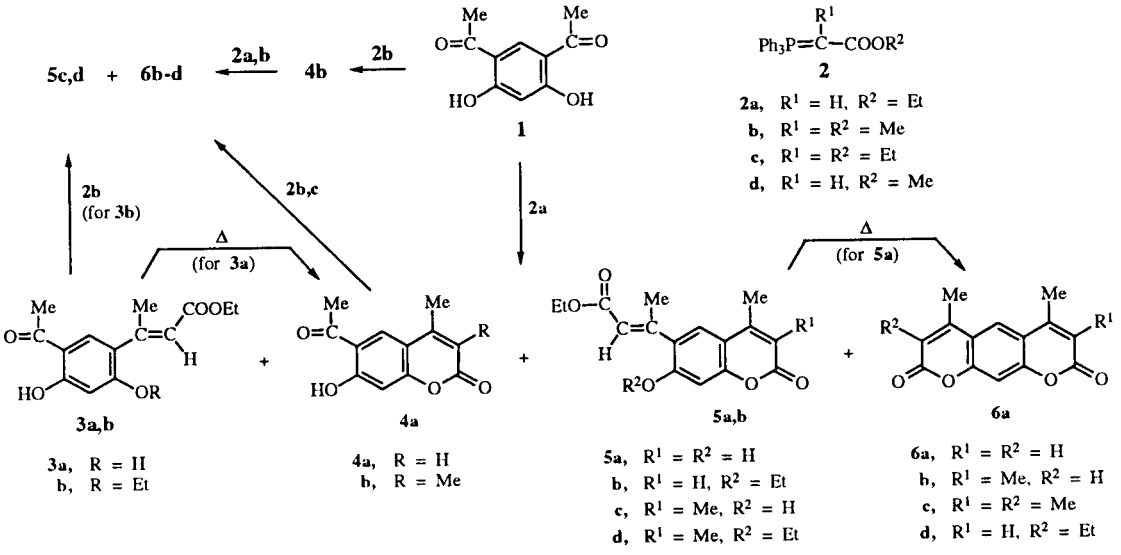
Treatment of compound **1** with an equimolar amount of α-ethoxycarbonylethylidene(triphenyl)phosphorane **2b** in refluxing toluene for 9 hours gave 6-acetyl-3,4-dimethyl-7-hydroxy-2*H*-1-benzopyran-2-one (**4b**) in 7% yield. The starting compound **1** was recovered in 63% yield. A mixture of compounds **3b** and **2b** (excess) was heated at 210° for 15 hours to give ethyl *E*-3-(3,4-dimethyl-7-ethoxy-2-oxo-2*H*-1-benzopyran-6-yl)-2-butenoate (**5d**) (12%). Treatment of compound **4a** with an excess of ylides **2b** and **2c** in refluxing toluene for 20 hours and 5 days respectively gave the corresponding dicoumarins **6b** (80%) and **6d** (15%). Finally, a similar treatment of compound **4b** with ylide **2a**, for 2 hours, gave compounds **6b** (46%) and **5c** (44%) while reaction with ylide **2b**, for 40 hours, afforded the tetramethyldicoumarin **6c** (84%).

Compound **6a** was prepared previously [19] also by heating of compound **4a** with ylide **2a**. The structures for new compounds agree well with their analytical and spectral data, as well as with the further transformations of some of them.

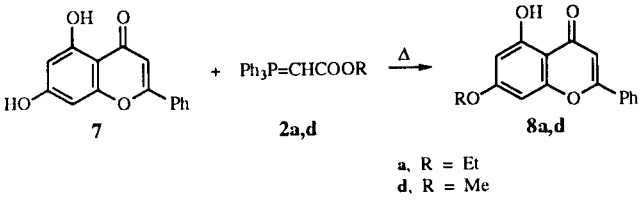
Although the recorded mp (208-210°) of compound **4b** differs from that given for it in the old literature [20], its recorded ^{1}H nmr spectrum is almost identical to that reported for it recently [21]. The recorded mp of prepared compound **6c** (345-348°) also differs from that given in the literature [22] for 3,4,6,7-tetramethylpyrano[3,2-*g*]-chromene-2,8-dione (mp 253-255°). Most probably the previously reported [22] dicoumarin with the lower mp is the angular isomer 3,4,9,10-tetramethylpyrano[2,3-*f*]-chromene-2,8-dione, in agreement with a relative study on melting points of linear and angular isomers [18], and also because in contrast to the reported old method of preparation, which can lead to both isomeric dicoumarins, in our case there does not exist any structural possibility other than structure **6c**. In agreement with the suggested structure **6c** for the compound in question its recorded ^{1}H nmr spectrum showed two singlets for the protons of the two symmetric pairs of four methyl groups.

The *E* configuration for compounds **3a, 5a, 5c** was assigned on the basis of their resistance to lactonization.

Scheme 1



Scheme 2



The same configuration was also assigned for the *o*-ethoxy esters **3b, 5b, 5d** from the comparison of their ^{1}H nmr spectra, and especially of the absorptions of the vinyl (δ 5.89-5.98) and methyl protons (δ 2.48-2.56) of their ester-groups to those of the corresponding protons of the similar compounds **3a, 5a, 5c** (δ 5.98-6.01, and δ 2.54-2.56 respectively). Compound **3b** remained unchanged after heating in refluxing toluene for 5 hours, or after keeping at 220° for 12 hours, in agreement with the suggested ethoxy substitution in its 2-position, as well as with its further transformation to compound **5d**. More evidence is necessary to explain the formation of these unexpected but interesting ethoxy derivatives.

It is of interest to notice that similar alkoxy derivatives were also obtained as the sole products from the reaction of chrysin (**7**) with ylides **2a** and **2d** at high temperatures. A mixture of equimolar amounts of compounds **7** and **2d** was heated at 200-210° for 5 days to give the 7-methoxy derivative **8d** (*tectochrysin* [23]) in 10% yield. Similarly by heating a mixture of **7** and **2a** at 235-245° for 4 days the 7-ethoxy derivative **8a** was obtained in 13%. When a solution of compound **7**, of an excess (2.5 equivalents) of compound **2a** and of traces of benzoic acid in toluene was refluxed for 40 hours compound **8a** was obtained in 25% yield. Probably a nucleophilic attack of the hydroxyl group (the more active in the cases of compounds **3a, 7**) of the corresponding hydroxy-precursors to the alkyl of the alkoxy group of the ylides used, can account for the formation of the alkoxy derivatives **3b, 5b, 5d, 8a** and **8d.**

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The ir spectra were obtained using a Perkin-Elmer 297 spectrophotometer as Nujol mulls. The ^{1}H nmr spectra were recorded with deuteriochloroform or trifluoroacetic acid as solvent on a Bruker Model AW 80 (80 MHz) spectrometer, with tetramethylsilane as the internal standard. Mass spectra were determined on a VG-250 spectrometer with ionization energy maintained at 70 eV. Microanalyses were performed on a Perkin-Elmer 240B CHN analyser. Light petroleum refers to the fraction of 40-60°.

Reaction of 4,6-Bis(acetyl)resorcinol (**1**) with Ethoxycarbonylmethylene(triphenyl)phosphorane (**2a**). Preparation of Compounds **3a, 3b, 4a, 5a, 5b** and **6a**.

A solution of compounds **1** (4.66 g, 24 mmoles) and **2a** (16.70 g, 48 mmoles) in toluene (60 ml) was heated at reflux for 6 hours and the solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate, preadsorbed on silica gel and then was chromatographed on silica gel column (7:3 light petroleum/ethyl acetate as eluent) to give in order of elution the following compounds:

Ethyl *E*-3-(5-Acetyl-2-ethoxy-4-hydroxyphenyl)-2-butenoate (**3b**).

This compound was obtained as white crystals (0.91 g, 16%), mp 77-79° (dichloromethane-light petroleum); ir: 3520, 3390, 3070, 1710, 1635, 1620, 1520 cm^{-1}; ^{1}H nmr (deuteriochloroform):δ 1.29 (t, J = 7 Hz, 3H), 1.41 (t, J = 7 Hz, 3H), 2.45 (s,

3H), 2.56 (s, 3H), 4.07 (q, J = 7 Hz, 2H), 4.21 (q, J = 7 Hz, 2H), 5.89 (s, 1H), 6.38 (s, 1H), 7.45 (s, 1H), 12.74 (s, 1H, -OH, deuterium oxide-exchangeable); ms: m/z 292 (M^+, 100), 277 (28), 263 (7), 247 (52), 231 (20), 219 (80), 203 (98), 190 (27), 175 (58).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.94; H, 6.81.

Ethyl *E*-3-(7-Ethoxy-4-methyl-2-oxo-2*H*-1-benzopyran-6-yl)-2-butenoate (**5b**).

This compound was obtained as white crystals (0.26 g, 3%), mp 173-175° (dichloromethane-light petroleum); ir: 1720, 1705, 1620, 1608 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.31 (t, J = 7 Hz, 3H), 1.44 (t, J = 7 Hz, 3H), 2.39 (s, 3H), 2.51 (s, 3H), 4.13 (q, J = 7 Hz, 2H), 4.21 (q, J = 7 Hz, 2H), 5.92 (s, 1H), 6.11 (s, 1H), 6.73 (s, 1H), 7.33 (s, 1H); ms: m/z 316 (M^+, 100), 271 (59), 255 (10), 243 (82), 229 (77), 214 (63.5), 201 (24), 186 (64), 185 (53).

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.41; H, 6.38.

Ethyl *E*-3-(5-Acetyl-2,4-dihydroxyphenyl)-2-benzoate (**3a**).

This compound was obtained as white crystals (0.70 g, 11%), mp 109-111° (dichloromethane-light petroleum); ir: 3490, 3390, 3060, 1680, 1620, 1595 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (t, J = 7 Hz, 3H), 2.52 (s, 3H), 2.57 (s, 3H), 4.22 (q, J = 7 Hz, 2H), 5.97 (s, 1H), 6.17 (br s, 1H, OH, deuterium oxide-exchangeable), 6.39 (s, 1H), 7.52 (s, 1H), 12.59 (s, 1H, OH, deuterium oxide-exchangeable); ms: m/z 264 (M^+, 25), 218 (82), 203 (100), 190 (11), 175 (31), 147 (6).

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.64; H, 6.06. Found: C, 63.72; H, 6.09.

Ethyl *E*-3-(7-Hydroxy-4-methyl-2-oxo-2*H*-1-benzopyran-6-yl)-2-butenoate (**5a**).

This compound was obtained as white crystals (1.44 g, 21%), mp 308-310° (dichloromethane-light petroleum); ir: 3345, 3070, 1735, 1712, 1630, 1608 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.32 (t, J = 7 Hz, 3H), 2.40 (s, 3H), 2.55 (s, 3H), 4.23 (q, J = 7 Hz, 2H), 5.99 (s, 1H), 6.17 (s, 1H), 6.88 (s, 1H, OH, deuterium oxide-exchangeable), 7.01 (s, 1H), 7.33 (s, 1H); ms: m/z 288 (M^+, 23), 242 (100), 214 (73), 186 (53), 185 (30), 158 (7), 149 (23).

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.86; H, 5.35.

6-Acetyl-7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one (**4a**).

a) This compound was obtained from the reaction between compounds **1** and **2a** as pale yellow crystals (0.375 g, 7%), mp 208-210° (dichloromethane-light petroleum); (lit [17] 212°); ir: 3055, 1725, 1718, 1655, 1610 cm^{-1}; ^1H nmr (deuteriochloroform): 2.45 (s, 3H), 2.68 (s, 3H), 6.16 (s, 1H), 6.81 (s, 1H), 7.96 (s, 1H), 12.61 (s, 1H); ms: m/z 218 (M^+, 76), 203 (100), 190 (8), 175 (44.5), 131 (10).

b) Compound **3a** (40 mg, 0.15 mmole) was heated at 170° for 8 hours to give compound **4a** (26 mg, 79%).

4,6-Dimethylpyrano[3,2-*g*]chromene-2,8-dione (**6a**).

a) This compound was obtained from the reaction between compounds **1** and **2a** as white crystals (1.1 g, 19%), mp 332-335° (dichloromethane-light petroleum) (lit [18] 333-334°).

b) Compound **5a** (80 mg, 0.28 mmole) was heated at 210° for 16 hours to give compound **6a** (53 mg, 78%).

6-Acetyl-3,4-dimethyl-7-hydroxy-2*H*-1-benzopyran-2-one (**4b**).

A solution of compound **1** (4.85 g, 25 mmoles) and ylide **2b** (8.70 g, 25 mmoles) in toluene (50 ml) was heated at reflux for 9 hours. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel column (7:3 light petroleum/ethyl acetate as eluent) to give pale yellow crystals of compound **4b** (0.40 g, 7%), mp 208-210° (dichloromethane-light petroleum) (lit [20] 168°); ir: 3060, 1710, 1650, 1640, 1610, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.17 (s, 3H), 2.39 (s, 3H), 2.66 (s, 3H), 6.79 (s, 1H), 7.92 (s, 1H), 12.50 (s, 1H); ms: m/z 232 (M^+, 100), 217 (90), 189 (54), 161 (15.5).

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.33; H, 5.34.

Ethyl *E*-3-(3,4-Dimethyl-7-ethoxy-2-oxo-2*H*-1-benzopyran-6-yl)-2-butenoate (**5d**).

A mixture of compounds **3b** (0.292 g, 1 mmole) and **2b** (0.8 g, 1.79 mmoles) was heated in an oil bath at 210° for 15 hours. The reaction mixture was then dissolved in dichloromethane, preadsorbed on silica gel and chromatographed on silica gel column (7:1 light petroleum/ethyl acetate as eluent) to give white crystals of compound **5d** (40 mg, 12%), mp 114-116° (dichloromethane-light petroleum); ir: 1720, 1700, 1625, 1608 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (t, J = 7 Hz, 3H), 1.42 (t, J = 7 Hz, 3H), 2.17 (s, 3H), 2.33 (s, 3H), 2.48 (s, 3H), 4.06 (q, J = 7 Hz, 2H), 4.21 (q, J = 7 Hz, 2H), 5.89 (s, 1H), 6.77 (s, 1H), 7.31 (s, 1H); ms: m/z 330 (M^+, 100), 285 (32), 257 (43), 243 (24), 228 (49), 199 (44).

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 68.80; H, 6.87.

3,4,6-Trimethylpyrano[3,2-*g*]chromene-2,8-dione (**6b**).

a) A solution of compounds **4a** (0.1 g, 0.46 mmole) and **2b** (0.28 g, 0.8 mmole) in toluene (4 ml) was heated at reflux for 20 hours. The solvent was evaporated under reduced pressure and the residue was triturated with ethyl acetate to give pale yellow crystals of compound **6b** (94 mg, 80%), mp 329-332° (dichloromethane-light petroleum); ir: 1720, 1615 cm^{-1}; ^1H nmr (deuteriochloroform-trifluoroacetic acid): δ 2.27 (s, 3H), 2.57 (s, 3H), 2.61 (s, 3H), 6.49 (s, 1H), 7.35 (s, 1H), 7.94 (s, 1H); ms: m/z 256 (M^+, 100), 228 (47), 213 (12), 200 (44), 185 (31).

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.48; H, 4.81.

b) A solution of compounds **4b** (0.1 g, 0.43 mmole) and **2a** (0.27 g, 0.77 mmole) in toluene (2 ml) was heated at reflux for 2 hours. Upon cooling pale yellow crystals of compound **6b** precipitated (51 mg, 46%).

Ethyl *E*-(7-Hydroxy-3,4-dimethyl-2-oxo-2*H*-1-benzopyran-6-yl)-2-butenoate (**5c**).

This compound was obtained from the above reaction between compounds **4b** and **2a**, after the precipitation of compound **6b** (method b) and column chromatography of the residue on silica gel column (4:1 light petroleum/ethyl acetate as eluent) as white crystals (57 mg, 44%), mp 305-307° (dichloromethane-light petroleum); ir: 1718, 1698, 1680, 1622, 1612 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.32 (t, J = 7 Hz, 3H), 2.20 (s, 3H), 2.36 (s, 3H), 2.56 (s, 3H), 4.22 (q, J = 7 Hz, 2H), 6.01 (s, 1H), 6.86

(s, 1H, -OH, deuterium oxide-exchangeable), 7.01 (s, 1H), 7.33 (s, 1H); ms: m/z 302 (M^+, 27), 256 (100), 228 (67), 213 (9), 200 (39), 185 (20).

Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.68; H, 6.11.

3,4,6,7-Tetramethylpyrano[3,2-*g*]chromene-2,8-dione (**6c**).

A solution of compound **4b** (0.1 g, 0.43 mmole) and **2b** (0.46 g, 1.32 mmoles) in toluene (2 ml) was heated at reflux for 40 hours. The solvent was evaporated under reduced pressure and the residue was triturated with ethyl acetate to give beige crystals of compound **6c** (98 mg, 84%), mp 334-336° (dichloromethane/light petroleum); ir: 1732, 1702, 1616 cm^{-1}; ^1H nmr (deuteriochloroform/trifluoroacetic acid): δ 2.27 (s, 6H), 2.58 (s, 6H), 7.34 (s, 1H), 7.96 (s, 1H); ms: m/z 270 (M+, 100), 242 (25), 227 (10), 214 (31), 199 (34).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.88; H, 5.31.

3-Ethyl-4,6-dimethylpyrano[3,2-*g*]chromene-2,8-dione (**6d**).

A solution of compound **4a** (0.218 g, 1 mmole) and ylide **2c** (0.67 g, 1.77 mmoles) in toluene (4 ml) was heated at reflux for 5 days. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel column (5:1 light petroleum/ethyl acetate as eluent) to give yellow crystals of compound **6d** (39 mg, 15%), mp 215-218° (dichloromethane/light petroleum); ir: 1730, 1715, 1635, 1620 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.14 (t, J = 7 Hz, 3H), 2.48 (s, 6H), 2.70 (q, J = 7 Hz, 2H), 6.26 (s, 1H), 7.17 (s, 1H), 7.74 (s, 1H); ms: m/z 270 (M^+, 100), 255 (89), 242 (20.5), 227 (53), 213 (8), 199 (32.5), 185 (8).

Anal. Calcd. for $C_{16}H_{14}O_4$; C, 71,10; H, 5.22. Found: C, 70.88; H, 5.17.

7-Ethoxy-5-hydroxyflavone (**8a**).

a) A mixture of chrysin (**7**) (0.254 g, 1 mmole) and ylide **2a** (0.348 g, 1 mmole) was heated at 235-245° for 4 days. The reaction mixture was separated by column chromatography [silica gel, dichloromethane/ethyl acetate] to give compound **8a** (36 mg, 13%), mp 145-147° (dichloromethane/light petroleum); ^1H nmr (deuteriochloroform): δ 1.44 (t, J = 7 Hz, 3H), 4.09 (q, J = 7 Hz, 2H), 6.33 (s, 1H), 6.46 (s, 1H), 6.63 (s, 1H), 7.04-7.28 (m, 1H), 7.36-7.62 (m, 3H), 7.75-8.04 (m, 2H); ms: m/z 282 (M^+, 82), 267 (12), 254 (100), 239 (7), 238 (9), 226 (53), 198 (19.5).

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.62; H, 5.21.

b) A solution of compounds **7** (0.254 g, 1 mmole), **2a** (0.871 g, 2.5 mmoles) and benzoic acid (20 mg), in toluene (8 ml) was heated at reflux for 40 hours. The solvent was removed in a rotary evaporator and the residue was dissolved in dichloromethane preadsorbed on silica gel and separated by chromatography on a silica gel column (7:3 light petroleum/ethyl acetate as eluent) to give compound **8a** (70 mg, 25%).

5-Hydroxy-7-methoxyflavone (Tectochrysin) (**8d**).

A mixture of compounds **7** (0.254 g, 1 mmole) and **2d** (0.334 g, 1 mmole) was heated at 200-210° for 5 days to give compound **8d** (sublimed on the upper parts of the apparatus) (26 mg, 10%), mp 164-166° (methanol) (lit [23] 165-166°).

REFERENCES AND NOTES

[1] M. von Strandtmann, D. Connor and J. Shavel, Jr., J. *Heterocyclic Chem.*, **9**, 175 (1972).

[2] R. S. Mali and V. J. Yadav, *Synthesis*, 464 (1977).

[3] R. S. Mali, S. G. Tilve, K. S. Patil and G. Nagarajan, *Indian J. Chem.*, **24B**, 1271 (1985).

[4] R. S. Mali, S. G. Tilve, S. N. Yeola and A. R. Manekar, *Heterocycles*, **26**, 121 (1987).

[5] R. S. K. Deshmukli and M.V. Paradkar, *Synth. Commun.*, **18**, 589 (1988).

[6] N. Britto, V. G. Gore, R. S. Mali and A. C. Ranade, *Synth. Commun.*, **19**, 1899 (1989).

[7] G. Guillaumet, M. Hretani and G. Coudert, *Tetrahedron Letters*, **29**, 2665 (1988).

[8] H. Ishii, Y. Kaneko, H. Miyazaki and T. Harayama, *Chem. Pharm. Bull.*, **39**, 3100 (1991).

[9] H. J. Bestmann and H. J. Lay, *Tetrahedron Letters*, 2101 (1969).

[10] D. N. Nicolaides, S. G. Adamopoulos, D. A. Lefkaditis and K. E. Litinas, *J. Chem. Soc., Perkin Trans. I*, 2127 (1990).

[11] D. N. Nicolaides, S. G. Adamopoulos, D. A. Lefkaditis and K. E. Littinas, *J. Chem. Soc., Perkin Trans. I*, 3159 (1991).

[12] D. N. Nicolaides, S. G. Adamopoulos, D. A. Lefkaditis, K. E. Litinas and P. V. Tarantili, *J. Chem. Soc., Perkin Trans. I*, 283 (1992).

[13] K. E. Litinas, D. N. Nicolaides and E. Varella, *J. Heterocyclic Chem.*, **27**, 769 (1990).

[14] D. N. Nicolaides, C. Bezergiannidou-Balouktsi, K. E. Litinas, E. Malamidou-Xenikaki, D. Mentzafos and A. Terzis, *J. Chem. Res., (S)*, 108 (1993); *(M)* 826 (1993).

[15] D. N. Nicolaides, C. Bezergiannidou-Balouktsi, K. E. Litinas, E. Malamidou-Xenikaki, D. Mentzafos and A. Terzis, *Tetrahedron*, **49**, 9127 (1993).

[16] C. Bezergiannidou-Balouktsi, K. E. Litinas, E. Malamidou-Xenikaki and D. N. Nicolaides, *Liebigs. Ann. Chem.*, 1175 (1993).

[17] R. D. Desai and M. Ekhlas, *Proc. Indian Acad. Sci.*, **8A**, 567 (1938); *Chem. Abstr.*, **33**, 3356 (1939).

[18] A. G. Osborne, *Tetrahedron*, **39**, 1523 (1983).

[19] C. P. Rapat, M. V. Paradkar and S. V. Sohoni, *Indian J. Chem. Sect. B*, **21B**, 1123 (1982); *Chem. Abstr.*, **99**, 22210q, (1983).

[20] R. R. Agarwal and S. Dutt, *J. Indian Chem. Soc.*, **14**, 109 (1937).

[21] D. Vedaldi, F. Dall'Acqua and F. Baccichetti, *Farmaco*, **46**, 1381 (1991).

[22] L. L. Woods and M. M. Fooladi, *Trans. Kans. Acad. Sci.*, **70**, 530 (1967); *Chem. Abstr.*, **70**, 37678g (1969).

[23] E. M. Gaydou and J. P. Bianchini, *Bull. Soc. Chim. France*, **43** (1978).