

A Convenient One-Pot Synthesis of Chromones via Basefree Intramolecular Wittig Reactions

Kee-Jung Lee*, Seongkon Kim, and Hokoon Park

Division of Chemistry, Korea Institute of Science and Technology, Seoul 130-650

Received December 10, 1990

The Wittig reaction¹ is widely applied in modern synthetic organic chemistry. The starting phosphonium salt for the Wittig reaction is usually prepared by treatment of triphenylphosphine with halide.² Sometimes it can be used for the Wittig reaction without an auxiliary base.^{3,4}

Recently, we have reported⁵ a simple preparation of 1,3-benzoxazepines base upon the Staudinger reaction followed by an intramolecular aza-Wittig reaction of *o*-acyloxyphenacyl azides. In this communication, we wish to reveal an extension of the usefulness of *o*-hydroxyphenacyl halide as synthon for the one-pot preparation of chromones, although a convenient synthesis of chromones was already reported⁶ from the reaction of *o*-hydroxyphenacylidetriphenylphosphorane.

The phosphonium salt **2** was readily obtained from the reaction of triphenylphosphine with 5-methyl-2-hydroxyphenacyl chloride (**1**) in refluxing toluene for 2 h (yield 88%, ³¹P-NMR 22.08 ppm). However, unexpectedly, we have found a conversion of the phosphonium salt **2** into the phosphorane **3** thermally without an auxiliary base for the prolonged reaction time (20 h, yield 80%, ³¹P-NMR 17.64 ppm, *m/z* = 410). Also, the reaction of *o*-acetoxyphenacyl bromide (**5**) with triphenylphosphine in refluxing toluene⁷ for 5 h without a base gave the 2-methylchromone (**6**, yield 75%) presumably via *o*-hydroxyphenacylidetriphenylphosphorane. Therefore, we believe that these conversions may not involve an intramolecular nucleophilic reaction of *o*-hydroxy group to the

Table 1. Chromones **4** Prepared

R	Yield(%)	mp.(°C) ^a	¹ H-NMR δ (CDCl ₃ /TMS) ^b	
			3-H	6-CH ₃
4a Me	75 ^c	102-103	6.15	2.43
4b <i>c</i> -Pr ^d	73	79-80	6.18	2.42
4c COOEt	71	97-98	7.10	2.46
4d C ₆ H ₅	83	118-119 (122) ¹⁰	6.80	2.45
4e C ₆ H ₄ <i>p</i> -OCH ₃	83	170-171	6.72	2.45

^a Reported mp. is given in parenthesis. ^b Reported on a Bruker AM-200 spectrometer. ^c Obtained with acetic anhydride. ^d Cyclopropyl.

phosphorus⁸ to afford the unisolable intermediate, 4-oxo-1,2-benzoxaphosphorine, but a simple thermal dehydrohalogenation of the phosphonium salts.

Attempt to achieve an one-pot synthesis of **4** from **1** in toluene without base was also successful. Although, complete conversion of the phosphonium salt **2** into the phosphorane **3** was sluggish, however, one-pot procedure was fast enough to synthetic utility. The isolated yields of the corresponding pure chromones **4** are shown in Table 1.

The general experimental procedure is as follows: To a stirred solution of 5-methyl-2-hydroxyphenacyl chloride⁹ (**1**, 1.84 g, 10 mmol) in toluene (30 ml) is added triphenylphosphine (2.88 g, 11 mmol) and the appropriate acid chloride (12 mmol) at room temperature. The mixture is heated under reflux for 16 h. The mixture is concentrated under reduced pressure, and the residual material is chromatographed on a silica gel column (hexane/EtOAc) to give **4** as crystals.

In conclusion, this procedure provides a facile and one-pot synthesis of chromones using available reagents in a simple manner.

Acknowledgement. The authors are indebted to the Ministry of Science and Technology for financial support.

References

- G. Wittig and F. Geissler, *Ann.*, **580**, 44 (1953).
- A. Maeycker, *Organic Reactions*; Wiley, New York, **14**, 270 (1965).
- G. P. Schiemenz, J. Becker, and J. Stockigt, *Chem. Ber.*, **103**, 2077 (1970).
- G. Koßmehl and R. Nuck, *Chem. Ber.*, **112**, 2342 (1979).
- K. J. Lee, D. O. Choi, S. Kim, J. U. Jeong, and H. Park, *Synthesis*, 455 (1990).
- A. Hercouet and M. Le Corre, *Synthesis*, 597 (1982).
- According to the reference 6, *o*-acetoxyphenacyltriphenylphosphonium bromide was obtained quantitatively within 1 h.
- A. Hercouet and M. Le Corre, *Tetrahedron Lett.*, 2145 (1979).
- K. Fries and G. Finck, *Chem. Ber.*, **41**, 4271 (1908).
- O. Dann and G. Mylius, *Ann.*, **587**, 1 (1954).

