

## A New and Convenient Wittig-type Reaction for the Preparation of Pyrromethenone Derivative

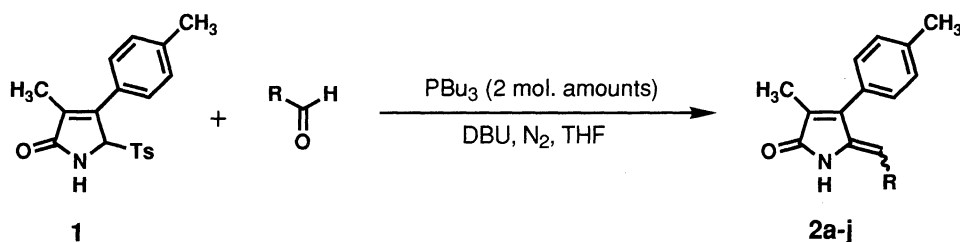
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The reaction of 5-(*p*-toluenesulfonyl)-3,4-disubstituted  $\Delta^3$ -pyrrolin-2-one with aldehydes in the presence of tributylphosphine and 1,8-diazabicyclo[5.3.0]undec-7-ene gave the corresponding 5-exomethylene compounds in good yields. A pyrromethenone derivative as a potential equivalent to C/D ring component of phytochromobilin dimethyl ester was effectively prepared by means of the present method.

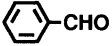


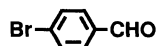
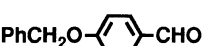
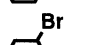
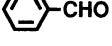
In the previous papers,<sup>1)</sup> we have reported that *N*-(*p*-toluenesulfonylmethyl)-*p*-toluenesulfonamide and *N*-(2-methylthio-1-*p*-toluenesulfonylethyl)methanesulfonamide react with a variety of nucleophiles in the presence of a base to afford the corresponding substitution products through elimination and addition process in good yields. In the preceding paper, we also described in this connection that 3-methyl-5-(*p*-toluenesulfonyl)-4-*p*-tolyl- $\Delta^3$ -pyrrolin-2-one (**1**), which is prepared regioselectively by hydrolysis of 2-bromo-3-methyl-5-(*p*-toluenesulfonyl)-4-tolylpyrrole in aqueous trifluoroacetic acid, reacts with various nucleophiles such as alcoholate, thiolate, amine, and organocopper reagent to give the corresponding substitution products in high yields.<sup>2)</sup> Herein we wish to report the Wittig-type reaction of compound **1** with various aldehydes for the preparation of the corresponding 5-exomethylene derivatives (**2**) including a pyrromethenone derivative (**5**).

To a mixed solution of **1**, an equimolar amount of benzaldehyde, and two molar amounts of tributylphosphine (PBU<sub>3</sub>)<sup>3)</sup> in dry THF was added slowly a solution of an equimolar amount of 1,8-diazabicyclo[5.3.0]undec-7-ene (DBU) in dry THF at room temperature. After stirring for 5.5 h and separation by a preparative TLC (SiO<sub>2</sub>, hexane:AcOEt = 3:1 V/V), (*E*)- and (*Z*)-5-exomethylene compounds **2a** were obtained in 43% and 21% yields (total yield: 64%), respectively (Run 1 in Table 1). The *E*-isomer thus obtained was readily converted to the thermodynamically favored *Z*-isomer by treatment with iodine in CH<sub>2</sub>Cl<sub>2</sub> at room temperature in quantitative yield. In a similar way, the products **2b-j** were prepared in good yields as shown in Table 1.<sup>4)</sup>



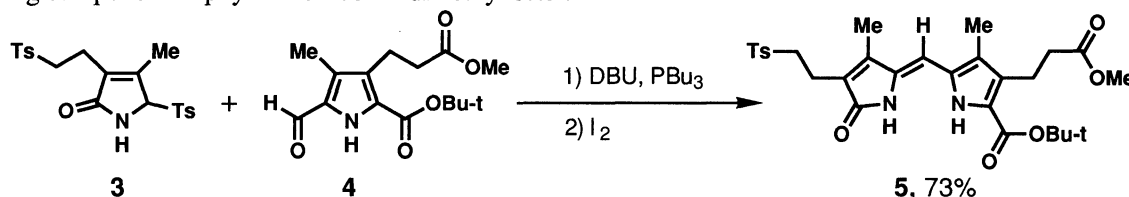
Next, the present method was employed for the condensation of the pyrrolinone **3** with the aldehyde **4**<sup>5)</sup> as shown below to afford the desired product **5** with *Z*-configuration, which is regarded as a potential equivalent to

Table 1. The Reaction of **1** with Various Aldehydes

Run	Aldehyde (mol. amount)	DBU (mol. amount)	Conditions	Total Yield / %	Product <sup>a)</sup>	Ratio of Z / E isomers <sup>b)</sup>
1	 -CHO (1)	1	r.t., 5.5 h	64	<b>2 a</b>	33 / 67
2	 -CHO (1)	1	r.t., 10 min	82	<b>2 b</b>	32 / 68 <sup>c)</sup>
3	 -CHO (1)	1	r.t., 10 min	50	<b>2 c</b>	63 / 37 <sup>d)</sup>
4	 -CHO (1)	1	r.t., on <sup>e)</sup>	56	<b>2 d</b>	Z only
5	 -CHO (2)	1	r.t., on <sup>e)</sup>	54	<b>2 e</b>	48 / 52 <sup>c)</sup>
6	 -CHO (3)	2	r.t., 2 d	52	<b>2 f</b>	67 / 33
7	 -CHO (2)	2	r.t., 2.5 h	85	<b>2 g</b>	42 / 58 <sup>c)</sup>
8	(E)-PhCH=CH-CHO (2)	2	r.t., on <sup>e)</sup>	87	<b>2 h</b>	f)
9	EtO <sub>2</sub> C-CHO (2)	2	r.t., 2 d	98	<b>2 i</b>	55 / 45
10	CH <sub>3</sub> -CHO (10)	2	r.t., on <sup>e)</sup>	56	<b>2 j</b>	63 / 37

a) All the products gave the satisfactory spectral data. b) NOE was observed for the protons of ortho-position of tolyl group of Z-isomer by irradiation on the exoolefinic proton, but not for those of E-isomer. c) E-isomer was partially isomerized to Z-isomer during silica gel TLC separation. d) Obtained as a mixture of Z- and E-isomers. The ratio was determined by 400 MHz <sup>1</sup>H-NMR spectrum. e) Means overnight. f) Not determined.

C/D ring component of phytochromobilin dimethyl ester.<sup>6)</sup>



As mentioned above, it was found that the tosyl group at position 5 of **1** plays an important role to produce the Wittig-type intermediate in the presence of tributylphosphine. Related works directed toward the synthesis of bilins are undertaking in our laboratory.

#### References

- 1) H. Kinoshita, K. Inomata, M. Hayashi, T. Kondoh, and H. Kotake, *Chem. Lett.*, **1986**, 1033; H. Kinoshita, S. Tanaka, and K. Inomata, *ibid.*, **1989**, 1107.
- 2) H. Kinoshita, Y. Hayashi, Y. Murata, and K. Inomata, see the preceding report of this issue.
- 3) When a small excess molar amounts of triphenylphosphine was used instead of PBU<sub>3</sub>, no reaction took place.
- 4) The reason for variation of E/Z ratios of **2a-j** is unclear, but it may reflect kinetically favored formation of E-isomer as well known for phosphonium ylides and an involvement of a thermodynamic equilibrium between E- and Z-isomers of **2** under the reaction conditions and/or during the work-up procedure; J. Fuhrhop and G. Penzin, "Organic Chemistry," Verlag Chemie, Weinheim (1983), p.28.
- 5) A. Gossauer and P. Mieke, *Ann.*, **1974**, 352.
- 6) J. P. Weller and A. Gossauer, *Chem. Ber.*, **113**, 1603 (1980).

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