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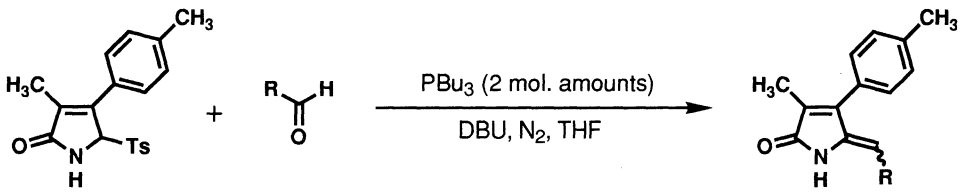
A New and Convenient Wittig-type Reaction for the Preparation of Pyrromethenone Derivative

Hideki KINOSHITA,* Hla NGWE, Kazuhiro KOBORI, and Katsuhiko INOMATA*
Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Ishikawa, 920-11

The reaction of 5-(*p*-toluenesulfonyl)-3,4-disubstituted Δ^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,[1] 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=Ts)-4-*p*-tolyl-Δ^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.[2] 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**).

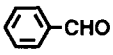
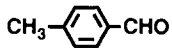
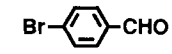
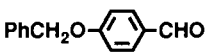
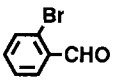
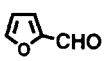
To a mixed solution of **1**, an equimolar amount of benzaldehyde, and two molar amounts of tributylphosphine (PBu_3)[3] in dry THF was added slowly a solution of an equimolar amount of 1,8-diazabicyclo[5.3.0]undec-7-ene (DBU) in dry THF at room temperature. After stirring for 5.5 h and separation by a preparative TLC (SiO_2, 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_2Cl_2 at room temperature in quantitative yield. In a similar way, the products **2b-j** were prepared in good yields as shown in Table 1.[4]



1 **2a-j**

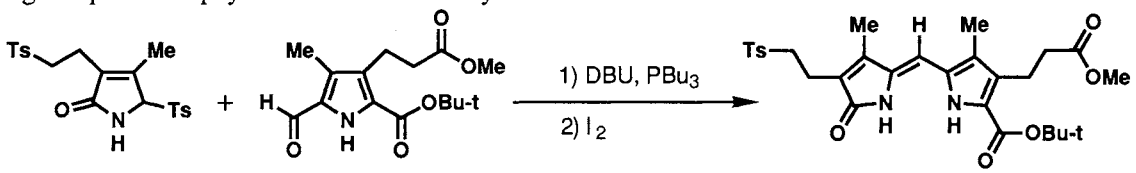
Next, the present method was employed for the condensation of the pyrrolinone **3** with the aldehyde **4**[5] as shown below to afford the desired product **5** with Z-configuration, which is regarded as a potential equivalent to

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

Run	Aldehyde (mol. amount)		DBU (mol. amount)	Conditions	Total Yield / %	Product[a]	Ratio of Z / E isomers[b]
1		(1)	1	r.t., 5.5 h	64	**2a**	33 / 67
2		(1)	1	r.t., 10 min	82	**2b**	32 / 68[c]
3		(1)	1	r.t., 10 min	50	**2c**	63 / 37[d]
4		(1)	1	r.t., one[e]	56	**2d**	Z only
5		(2)	1	r.t., one[e]	54	**2e**	48 / 52[c]
6		(3)	2	r.t., 2 d	52	**2f**	67 / 33
7		(2)	2	r.t., 2.5 h	85	**2g**	42 / 58[c]
8	(E)-PhCH=CH-CHO	(2)	2	r.t., one[e]	87	**2h**	f)
9	EtO_2C-CHO	(2)	2	r.t., 2 d	98	**2i**	55 / 45
10	CH_3-CHO	(10)	2	r.t., one[e]	56	**2j**	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 mixturte of Z- and E-isomers. The ratio was determined by 400 MHz ^{1}H-NMR spectrum. e) Means overnight. f) Not determined.

C/D ring component of phytochromobilin dimethyl ester.[6]



3 **4** **5**, 73%

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_3, 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. Miehe, *Ann.*, **1974**, 352.

6) J. P. Weller and A. Gossauer, *Chem. Ber.*, **113**, 1603 (1980).

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