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New Synthesis of Stilbene and Heterocyclic Stilbene Analogs

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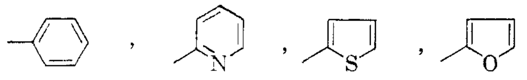
In searching for a more convenient procedure for Wittig's olefin synthesis, Pommer[1] found that the phosphonates obtained from trialkyl phosphites *via* the Michaelis-Arbuzov reaction[2] underwent reaction with aldehydes or ketones in the presence of a strong base to give good yields of olefins. Extensive application of the reaction was made in the carotenoid field. We had applied this reaction to the synthesis of a number of known compounds when Wadsworth and Emmons[3] reported its versatility. Because of the latter publication, we should like to report some of our results in this field.

Stilbene and the heterocyclic analogs, 2-stilbazole, 2-styrylfuran, and 2-styrylthiophene, are obtained in greater than 75% yield by the reaction of diethyl benzylphosphonate with the corresponding aldehyde, using sodium methoxide in dimethylformamide. The exothermic reaction gives the *trans*-olefin in a relatively pure state in 75-85% yields simply by treatment of the reaction mixture with water. The *trans* configuration is assigned to all these compounds on the basis of infrared analyses. A strong absorption at 10.2 to 10.4 μ in all these compounds is characteristic of *trans*-olefins.[4]

$$C_6H_5CH_2Br + (C_2H_5O)_3P \longrightarrow C_6H_5CH_2PO(OC_2H_5)_2 + C_2H_5Br$$

$$C_6H_5CH_2PO(OC_2H_5)_2 + ArCHO \xrightarrow[\text{DMF}]{\text{NaOCH}_3} C_6H_5CH{=}CHAr + (C_2H_5O)_2POONa + CH_3OH$$

Ar =

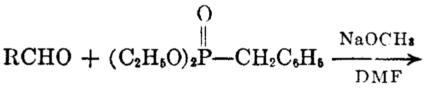


The best previous preparations of *trans*-stilbene are Emmons'[3] synthesis from diethyl benzylphosphonate and benzaldehyde with sodium hydride in dimethoxyethane and the Clemmensen reduction of benzoin.[5] *trans*-2-Stilbazole was obtained from 2-picoline and benzaldehyde[6] and from 2-picoline and toluene in acetic anhydride.[7] trans-2-Styrylthiophene[8] and *trans*-2-styrylfuran[9] were prepared by dehydration of the carbinol resulting from the action of benzylmagnesium chloride on the corresponding aldehydes.

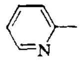
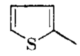
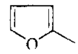
The superiority of the present method is shown in Table I.

TABLE I

PREPARATION OF STYRYL DERIVATIVES



$$RCHO + (C_2H_5O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}CH_2C_6H_5 \xrightarrow[\text{DMF}]{\text{NaOCH}_3} RCH{=}CHC_6H_5 + (C_2H_5O)_2POOH$$

R =	Yield, % Current	Yield, % Previous	M.P. Current[a]	M.P. Previous	Previous References
C_6H_5	85	53-57; 63	126-127[b]	123-124	5 3
	75	57; 51	92.5-93	91	7 6
	77	60	112-113[c]	111	8
	84	12	54-55[d]	49-50	9

[a] Melting points are corrected. [b] Recrystallized from ethanol-ethyl acetate. [c] Recrystallized from ethanol. [d] Recrystallized from methanol.

EXPERIMENTAL

Diethyl benzylphosphonate. Diethyl benzylphosphonate was prepared in 85% yield by the Michaelis-Arbuzov reaction,[2] involving benzyl bromide and triethyl phosphite.

Stilbene and heterocyclic stilbene analogs. Diethyl benzylphosphonate (0.05*M*) and sodium methoxide (10% excess) were combined in dimethylformamide in a three necked flask fitted with a thermometer, drying tube, dropping funnel, and magnetic stirrer. The aromatic or heterocyclic aldehyde (0.05*M*) in dimethylformamide (25-40 ml.) was added dropwise, with stirring and cooling in ice, at such a rate that the reaction temperature was maintained between 30° and 40°; a clear solution resulted. After standing for a short period of time, water was added to the solution, with cooling; the precipitated product was collected on a filter and washed with water. The compounds listed in the Table were prepared by this procedure.

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