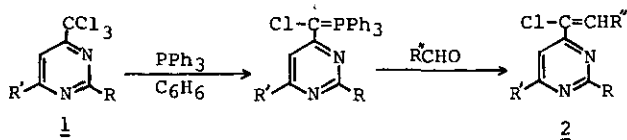


STUDIES ON as-TRIAZINE DERIVATIVES. III.<sup>1</sup> PREPARATION OF  
3-ALKENYL-1,2,4-TRIAZINE DERIVATIVES BY MEANS OF WITTIG REACTION

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**Abstract**—The reaction of 3-trichloromethyl-5,6-diphenyl-1,2,4-triazine with triphenylphosphine proceeded reductively, and  $\alpha$ -[3-(5,6-diphenyl-1,2,4-triazinyl)] methylenetriphenylphosphorane was obtained as stable, yellow prisms. The phosphorane smoothly reacted with various aldehydes in boiling benzene to give the corresponding 3-alkenyl compounds, whereas the reaction with ketones failed to give any significant products under the same conditions.

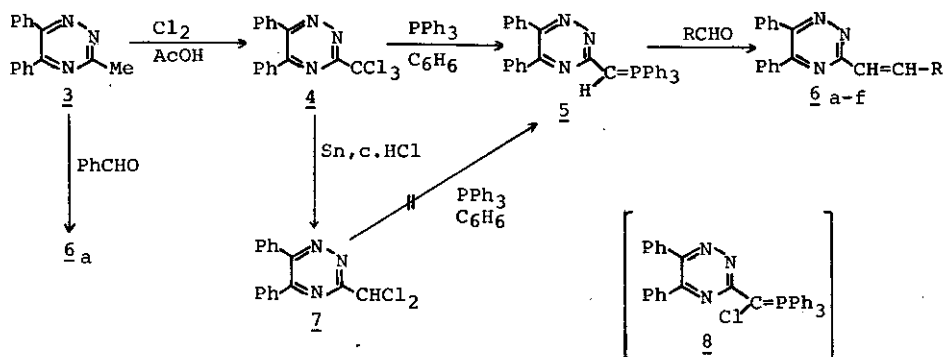
As reported in the preceding paper<sup>1</sup>, 3-methyl-5,6-diphenyl-as-triazine (3) was found to be smoothly chlorinated to 3-trichloromethyl-5,6-diphenyl-as-triazine (4) by treatment with chlorine gas in acetic acid in the presence of sodium acetate. Recently, Kato et al. reported<sup>2</sup> that 4-trichloromethylpyrimidines (1) reacted with two equivalent amounts of triphenylphosphine to give chloropyrimidinylmethylenetriphenylphosphorane, which underwent the Wittig reaction with aldehydes to afford the corresponding 4-chloroethenylpyrimidines (2).



Scheme 1

These findings stimulated us to apply such kind of reactions to the field of as-triazine chemistry, because the synthesis of as-triazine derivatives having an unsaturated side chain is considered to be difficult by ring-closure reactions.<sup>3</sup> In the present paper we describe the reaction of 4 with triphenylphosphine and the condensation of the resultant phosphorane with carbonyl compounds.

On treatment with two molecular amounts of triphenylphosphine in dry benzene under nitrogen, 4 was transformed into  $\alpha$ -(5,6-diphenyl-3-as-triazinyl)methylenetriphenylphosphorane (5), mp 214-215°C(decomp.), orange yellow needles, in 46 % yield. The elemental analysis ( $C_{34}H_{26}N_3P$ ) and MS (m/e 507) clearly demonstrated the product (5) to contain no chlorine atom. Reaction conditions for the preparation of 5 were investigated and the improved yield of the product was obtained by treatment with excess triphenylphosphine at room temperature under nitrogen as shown in Table 1. 3-Dichloromethyl-5,6-diphenyl-as-triazine (7), obtained by the reduction of 4 with tin in conc. hydrochloric acid<sup>1</sup>, was unchanged by treatment with triphenylphosphine under the same conditions. Accordingly, the formation of 5 is reasonably speculated to result from the reduction of  $\alpha$ -chloro- $\alpha$ -(5,6-diphenyl-3-as-triazinyl)methylenetriphenylphosphorane (8) with triphenylphosphine, although the isolation of the intermediate (8) was unsuccessful.



Scheme 2

Table 1. Reaction Conditions for the Preparation of as-Triazinyl-methylenetriphenylphosphorane (5)

Run	Molar Ratio		Reaction Conditions <sup>a)</sup>		Yield of <u>5</u> (%)
	<u>as</u> -Triazine	PPh <sub>3</sub>	Temp.	Time (h)	
1	1	2	room temp.	12	46
2	1	2	reflux	2	30
3	1	3	room temp.	12	59
4	1	3	reflux	2	66
5	1	4.5	room temp.	12	82
6	1	4.5	room temp.	72	86
7	1	4.5	reflux	2	79

a) The reactions were carried out in dry benzene under nitrogen.

Next, the condensation of 5 with carbonyl compounds was investigated. As shown in Table 2, the phosphorane (5) smoothly reacted with various aldehydes in dry benzene under reflux to give the corresponding as-triazinylolefins (6a-f), in satisfactory yields. However, the reaction of 5 with ketones such as cyclohexanone and acetophenone failed to give the expected products.

Table 2. Preparation of as-Triazinylolefins (6a-f)

Compd. No.	R	mp (°C)	Yield (%)	<sup>1</sup> H-NMR J <sub>CH=CH</sub> (Hz)	Type of Stereoisomer
<u>6a</u>	Ph	145-146	70	16	E-form
<u>6b</u>	PhCH=CH	142-144	78	—	—
<u>6c</u>	MeCH=CH	146-147	62	—	—
<u>6d</u>	Me	82-84	73	16	E-form
<u>6e</u>	Me(CH <sub>2</sub> ) <sub>2</sub>	75-76	75	16	E-form
<u>6f</u>	Me(CH <sub>2</sub> ) <sub>3</sub>	150 <sup>a)</sup>	37	16	E-form

a) bp (°C) (3mmHg)

The methyl group at the 3-position of 3, like that of 2-methylpyrimidines and 2-methylpyridines, is supposed to be reactive toward Knoevenagel type condensation. In fact, the reaction of 3 with benzaldehyde under basic conditions resulted in the formation of 5,6-diphenyl-3-styryl-as-triazine, mp 145-146.5°C, which was identical with 6a.

In spite of this fact, the condensation of 3 with aliphatic aldehyde under basic conditions was unsuccessful. Therefore, the reaction of 5 with aldehydes may provide one of practical methods for the introduction of an alkenyl group into the 3-position of as-triazine ring.

Typical experiments are as follows: α-(5,6-Diphenyl-3-as-triazinyl)methylenetriphenylphosphorane (5) — A solution of PPh<sub>3</sub> (3.5 g, 13.5 mmol) in dry benzene (10 ml) was added dropwise to a solution of 3-trichloromethyl-5,6-diphenyl-as-triazine (4) (1.05 g, 3 mmol) in dry benzene (50 ml) under nitrogen. After stirring at room temperature for 72 h under nitrogen, the mixture was poured into water. The aqueous layer was separated and the benzene layer was extracted with 1% HCl solution (16 ml) for three times. The combined aqueous solution was washed with benzene and made alkaline with K<sub>2</sub>CO<sub>3</sub>. The separated red oil was

extracted with  $\text{CHCl}_3$  and the extract was dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was recrystallized from AcOEt to give 1.3 g (86 %) of 5, mp 214-215°C(decomp.), as red prisms. General procedure for the preparation of as-triazinylolefins (6a-f)<sup>4</sup> — Aldehyde (2.2 mmol) was dissolved in dry benzene (20 ml) and 5 (1.01 g, 2 mmol) was added thereto. The mixture was heated under reflux for 2.5 h and then concentrated to dryness in vacuo. The residue was purified by chromatography on a silica gel column, and then recrystallized to give as-triazinylolefins (6a-f). In the case of 6d, the reaction was carried out under ice-cooling for 12 h.

#### REFERENCES AND NOTES

1. Part 2: S. Konno, M. Yokoyama and H. Yamanaka, Heterocycles, 1982, 19, 1865.
2. T. Kato, N. Katagiri, T. Takahashi and Y. Katagiri, J. Heterocyclic Chem., 1979, 16, 1575.
3. One of the convenient method for the preparation of 3-substituted as-triazines is the reaction of amidrazones with 1,2-dicarbonyl compounds, and the other is the cyclization of the acyl hydrazones of 1,2-dicarbonyl compounds with ammonia, (H. Neunhoeffer and P. W. Wiley, "Chemistry of 1,2,3-Triazines and 1,2,4-Triazines, Tetrazines and Pentazines" in "The Chemistry of Heterocyclic Compounds" eds. by A. Weissberger and E. C. Taylor, Wiley-Interscience, New York, 1978, p 191).
4. All the compounds gave IR, <sup>1</sup>H-NMR and elemental analyses consistent with the proposed structures.

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