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STUDIES ON *as*-TRIAZINE DERIVATIVES. III.[1] PREPARATION OF 3-ALKENYL-1,2,4-TRIAZINE DERIVATIVES BY MEANS OF WITTIG REACTION

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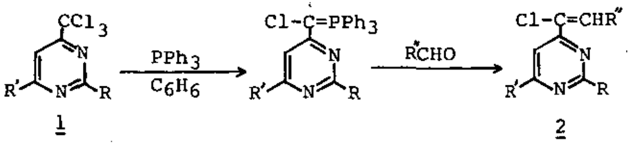
Abstract——The reaction of 3-trichloromethyl-5,6-diphenyl-1,2,4-triazine with triphenylphosphine proceeded reductively, and α-[3-(5,6-diphenyl-1,2,4-triazinyl)] methylenetriphenylphosphorane was obtained as stable, yellow prisms. The phosphorane smoothly reacted with various aldehydes in boiling benzene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

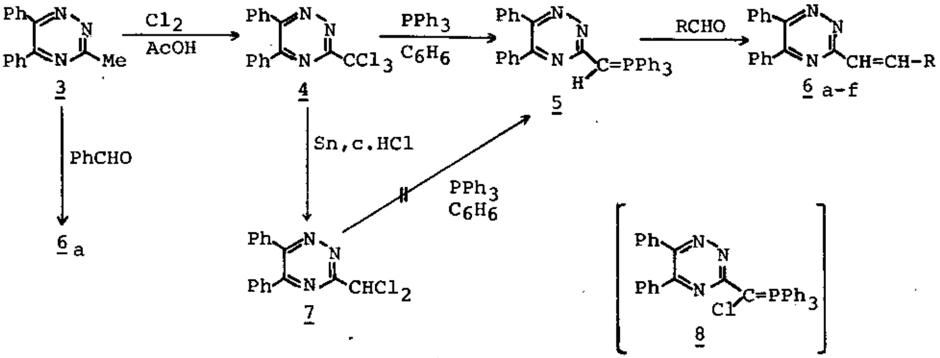
As reported in the preceding paper[1], 3-methyl-5,6-diphenyl-*as*-triazine (3) was found to be smoothly chlorinated to 3-trichloromethyl-5,6-diphenyl-*as*-triazine (4) by treatment with chlorine gas in acetic acid in the presence of sodium acetate. Recently, Kato et al. reported[2] that 4-trichloromethylpyrimidines (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.[3] 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 α-(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[1], was unchanged by treatment with triphenylphosphine under the same conditions. Accordingly, the formation of 5 is reasonably speculated to result from the reduction of α-chloro-α-(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-Triazinylmethylenetriphenylphosphorane (5)

Run	Molar Ratio		Reaction Conditions[a)]		Yield of 5
	as-Triazine	PPh_3	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 (%)	^{1}H-NMR $J_{CH=CH}$(Hz)	Type of Stereoisomer
6a	Ph	145-146	70	16	E-form
6b	PhCH=CH	142-144	78	—	—
6c	MeCH=CH	146-147	62	—	—
6d	Me	82-84	73	16	E-form
6e	$Me(CH_2)_2$	75-76	75	16	E-form
6f	$Me(CH_2)_3$	150[a]	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-stylyl-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_3 (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_2CO_3. The separated red oil was extracted with $CHCl_3$ and the extract was dried over Na_2SO_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)[4] —— 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, ^1H-NMR and elemental analyses consistent with the proposed structures.

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