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Studies on Pyrimidine Derivatives. XXIV.[1] Synthesis of 3-Substituted 1,2,4-Triazines by Nucleophilic Substitution

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The potassium permanganate oxidation of 3-methylthio-5,6-diphenyl-*as*-triazine in the presence of a phase-transfer catalyst afforded 3-methylsulfonyl-5,6-diphenyl-*as*-triazine. The 3-sulfonyl-*as*-triazine readily reacted not only with active methylene compounds but also with methyl or methylene ketones under basic conditions, and 5,6-diphenyl-*as*-triazines containing a functionalized carbon substituent at the 3-position were obtained. Similarly, 2-substituted 4,6-dimethylpyrimidines were synthesized by the nucleophilic substitution of 4,6-dimethyl-2-phenylsulfonylpyrimidine with various ketones.

Keywords——nucleophilic substitution; active methylene compounds; 3-chloro-5,6-diphenyl-1,2,4-triazine; 3-methylsulfonyl-5,6-diphenyl-1,2,4-triazine; 3-acylmethyl-5,6-diphenyl-1,2,4-triazines; 4,6-dimethyl-2-phenylsulfonylpyrimidine; 2-acylmethyl-4,6-dimethylpyrimidines

Investigations on pyrimidine derivatives containing a strongly electronegative group at the 4-position are not well advanced. For example, the synthesis of 4-nitropyrimidines has not yet been achieved, and the 4-cyanopyrimidines readily transform to the corresponding 4-methoxyl derivatives,[2] when they are allowed to stand in methanol under basic conditions. 1,2,4-Triazine (*as*-triazine) is regarded as a model of such pyrimidines owing to the electronic effects of the additional ring nitrogen atom. Furthermore, among various six-membered monocyclic *N*-heteroaromatics, *as*-triazines form a relatively less explored family. In particular, useful results were not obtained in the nucleophilic substitution of *as*-triazine derivatives, although the synthesis of *as*-triazines by ring-closure reactions is being actively investigated by several groups.[3-6]

Our interest was focussed on the chemistry of *as*-triazine derivatives, from the above points of view. The present paper deals with carbon-carbon bond formation at the 3-position of *as*-triazine by nucleophilic substitution, in comparison with the same type of reaction at the 2-position of pyrimidine.

Firstly, in order to determine the chemical properties of 3-chloro-5,6-diphenyl-*as*-triazine (**2**) unambiguously, some conflicting results in the literature[7] were checked as follows. This compound (**2**) was already obtained by treatment of 3-oxo-5,6-diphenyl-2,3-dihydro-*as*-triazine (**1**)[8] with phosphoryl chloride in good yield. The chloride (**2**), mp 158—159°C, was also reported to be convertible into the 3-ethoxyl derivative monohydrate (**3a'**), mp 221—222°C, by heating an ethanolic solution of **2** in the absence of bases. Since the yield of **3a'** was unspecified, we reinvestigated the above experiment and obtained the product having the reported melting point in 70% yield. However, after the product had been heated at 100°C for several days under reduced pressure, the resultant compound was identical with **1**. In contrast, the reaction of **2** with a calculated amount of sodium ethoxide in hot ethanol gave 3-ethoxy-5,6-diphenyl-*as*-triazine (**3a**), $C_{17}H_{15}N_3O$, mp 76—77°C. When excess sodium ethoxide was used, **2** was transformed into **1**, and **3a** was not obtained. In addition to this, **3a** was changed to **1** under the same conditions. Accordingly, it is suggested that alkoxyl groups at the 3-position of *as*-triazine are not very resistant to both acidic and basic conditions and are transformed into the corresponding 3-oxo compounds. In connection with the above, Sasaki *et al.*[9]

obtained the 3-methoxyl and 3-phenoxyl derivatives from **2** by the reaction with a limited amount of the corresponding sodium alkoxide.

The compound (**2**), as well as many *N*-heteroaromatics containing active halogen atoms, reacted with various amines as shown in Chart 1. In the case of hydrazine hydrate, it was reported[7] that the reaction in pyridine afforded 3-hydrazino-5,6-diphenyl-*as*-triazine (**3d**), mp 171—173°C, but the reaction conditions were not described in detail. However, the use of an equimolecular amount of hydrazine hydrate in pyridine gave *N*,*N*′-bis(5,6-diphenyl-3-*as*-triazinyl)hydrazine (**5**), mp 238°C (dec.), as a sole product. When **2** was treated with excess hydrazine hydrate in methanol, the desired compound (**3d**) was obtained in 48% yield.

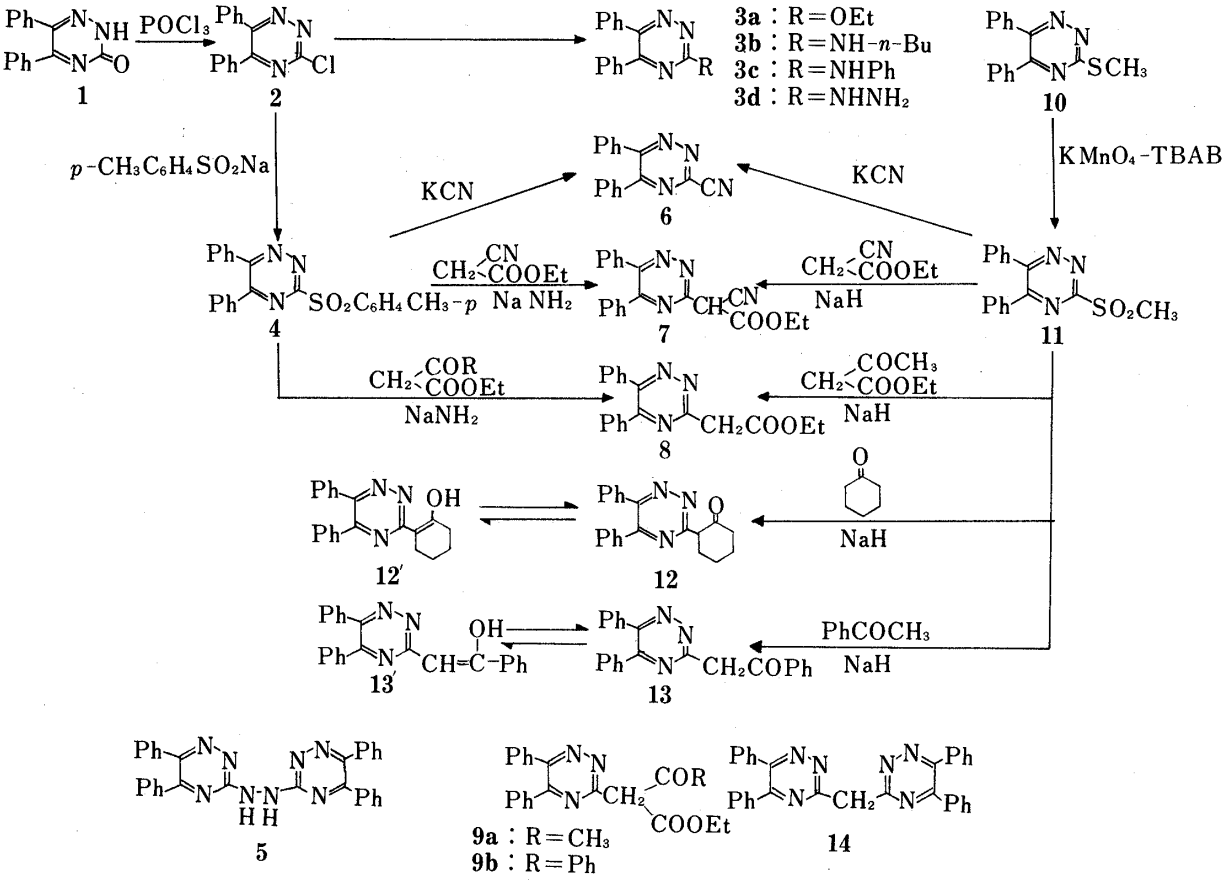

Chart 1

Secondly, the introduction of a functionalized carbon substituent into the 3-position was investigated. Since the reaction of **2** with potassium cyanide or ethyl cyanoacetate failed to give the desired compound, **2** was transformed into 5,6-diphenyl-3-(*p*-toluenesulfonyl)-*as*-triazine (**4**), mp 162.5—163°C, in 74% yield by treatment with sodium *p*-toluenesulfinate in *N*,*N*-dimethylformamide. This product (**4**) seemed to be more reactive than **2**. For example, **4** reacted with sodium ethoxide, *n*-butylamine, aniline, and hydrazine hydrate to give the corresponding 3-substituted *as*-triazine (**3a**—**d**) in better yields than those from **2**. Treatment of **4** with potassium cyanide in *N*,*N*-dimethylformamide afforded 3-cyano-5,6-diphenyl-*as*-triazine (**6**),[10] mp 156—157°C, in 75% yield. When **4** was heated with ethyl cyanoacetate in the presence of sodium amide in benzene, ethyl α-(5,6-diphenyl-3-*as*-triazinyl)-cyanoacetate (**7**), mp 235°C (dec.), was obtained in 56% yield. In contrast, the reaction of **4** with ethyl acetoacetate or ethyl benzoylacetate under conditions similar to the above

afforded the same product, ethyl 5,6-diphenyl-3-*as*-triazinylacetate (**8**), mp 123—124.5°C, which was probably formed from the *β*-keto-esters (**9a, b**) with the loss of an acyl group. Since the reaction of **4** with monoketones, such as acetophenone and cyclohexanone, under similar conditions failed, leaving groups other than the *p*-toluenesulfonyl group were examined, and the methylsulfonyl group was concluded to be better than the *p*-toluenesulfonyl group. 3-Methylthio-5,6-diphenyl-*as*-triazine (**10**),[5] easily obtained by the condensation of benzil and *S*-methylthiosemicarbazide, was oxidized with potassium permanganate in the presence of a phase-transfer catalyst, tetra-*n*-butylammonium bromide, to give 3-methylsulfonyl-5,6-diphenyl-*as*-triazine (**11**), mp 139—140°C, in 75% yield. This compound (**11**) smoothly reacted not only with potassium cyanide, ethyl cyanoacetate, and ethyl acetoacetate, but also with acetophenone and cyclohexanone. Namely, the reaction of **11** with cyclohexanone in tetrahydrofuran in the presence of sodium hydride gave 2-(5,6-diphenyl-3-*as*-triazinyl)cyclohexanone (**12**), mp 172—173°C, in 53% yield. Although the reaction of **11** with an equimolecular amount of acetophenone in the presence of sodium hydride resulted in the formation of bis-(5,6-diphenyl-3-*as*-triazinyl)methane (**14**), mp 175°C (dec.), the use of excess acetophenone gave 5,6-diphenyl-3-*as*-triazinylmethyl phenyl ketone (**13**), mp 130—132°C, as expected.

The spectral data of all the products are in good agreement with their structures illustrated in Chart 1, except for **12** and **13**. In the cases of **12** and **13**, the existence of keto-enol tautomerism due to the presence of the carbonyl group is suggested by their nuclear magnetic resonance (^{1}H-NMR) spectra. However, the tautomerism was not studied in detail in this work, because the same type of tautomerism is already well known in the corresponding quinoline[11] and pyrimidine derivatives.[12]

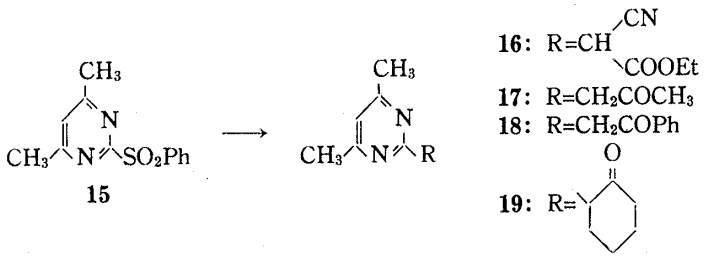

Chart 2

Finally, the nucleophilic substitution of 2-phenylsulfonyl-4,6-dimethylpyrimidine (**15**)[13] was compared with that of **4** and **11**. As shown in Chart 2, various 2-substituted pyrimidines (**16**—**19**) were synthesized by the reaction of **15** with carbonyl compounds such as ethyl cyanoacetate, acetone, acetophenone and cyclohexanone under basic conditions. These products were identical with authentic samples prepared by known methods.[12a,14–16]

Although the reason for the high reactivity of **15** toward the monoketones described above is not clear at present, the use of an appropriate sulfonyl group as a leaving group is concluded to be an effective procedure for the introduction of functionalized carbon side chains into the 3-position of *as*-triazines and the 2-position of pyrimidines.

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO IRA-1 spectrometer. Mass spectra (MS) were taken with a Hitachi M-52G spectrometer. ^{1}H-NMR spectra were taken at 60 MHz with Hitachi-Perkin-Elmer R-20 and JEOL JNM-PMX60 spectrometers. Chemical shifts are expressed as ppm downfield from tetramethylsilane (TMS) as an internal standard. The following abbreviations are used: s=singlet, t=triplet, q=quartet, m=multiplet, and b=broad. The analytical data for the products are shown in Table I.

The Reaction of 3-Chloro-5,6-diphenyl-*as*-triazine (2) with Ethanol——A solution of **2** (1.3 g, 5 mmol) in EtOH (100 ml) was heated under reflux for 48 h. The reaction mixture was concentrated under reduced pressure to give 0.9 g (70%) of 3-oxo-5,6-diphenyl-2,3-dihydro-*as*-triazine (**1**), mp 221—223°C (lit.[8] mp

224—225°C), as pale yellow prisms. IR spectral comparison showed this compound to be identical with an authentic sample.[8]

5,6-Diphenyl-3-(*p*-toluenesulfonyl)-*as*-triazine (4)——A mixture of **2** (5.0 g, 20 mmol) and sodium *p*-toluenesulfinate (6.0 g, 24 mmol) in DMF (50 ml) was heated at 50—60°C for 1.5 h with stirring. The reaction mixture was poured into water and the precipitate was collected by filtration and washed with H_2O. Recrystallization from MeOH gave 5.60 g (74%) of **4**, mp 162.5—163°C, as pale yellow needles. IR ν_{max}^{KBr} cm^{-1}: 1155, 1355.

3-Methylsulfonyl-5,6-diphenyl-*as*-triazine (11)——A solution of $KMnO_4$ (4.6 g, 30 mmol) in H_2O (150 ml) was added to a solution of 3-methylthio-5,6-diphenyl-*as*-triazine (**10**) (4.2 g, 15 mmol) [prepared according to the procedure of Paudler *et al.*[5]], tetra-*n*-butylammonium bromide (0.5 g), and AcOH (30 ml) in benzene (100 ml). The mixture was stirred at room temperature for 16 h. A sat. $NaHSO_3$ solution was added to the mixture until the purple color disappeared and the colorless solution was neutralized with solid K_2CO_3. The benzene layer was separated and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallized from AcOEt–hexane to give 3.5 g (75%) of **11**, mp 139—140°C, as pale yellow prisms. ^{1}H-NMR ($CDCl_3$): 3.50 (3H, s), 7.08—7.75 (10H, m).

3-Ethoxy-5,6-diphenyl-*as*-triazine (3a)——i) A solution of NaOEt–EtOH [prepared from metallic sodium (0.345 g, 0.015 g·atom) and abs. EtOH (150 ml)] was added to a solution of **2** (4.02 g, 15 mmol) in abs. EtOH (50 ml), and the mixture was refluxed for 0.5 h. The precipitate (NaCl) was filtered off and the filtrate was concentrated to dryness *in vacuo*. The residue was neutralized with 3 N HCl and extracted with $CHCl_3$. The $CHCl_3$ solution was dried over Na_2SO_4 and the solvent was removed. The residue was recrystallized from hexane to give 2.7 g (66%) of **3a**, mp 76—77°C, as pale yellow needles. ^{1}H-NMR ($CDCl_3$): 1.54 (3H, t, J=7 Hz), 4.71 (2H, q, J=7 Hz), 7.20—7.70 (10H, m).

ii) A solution of NaOEt–EtOH [prepared from metallic sodium (0.345 g, 0.015 g·atom) and abs. EtOH (150 ml)] was added to a solution of **4** (5.8 g, 15 mmol) in abs. EtOH (50 ml), and the mixture was stirred at room temperature for 3 h. The reaction mixture was treated according to the procedure used above to give 3.4 g (83%) of **3a**, mp 76—77°C, as pale yellow needles. This compound was identical with the sample obtained above.

3-*n*-Butylamino-5,6-diphenyl-*as*-triazine (3b)——i) A mixture of **2** (0.53 g, 2 mmol) and *n*-butylamine (0.5 g, 7 mmol) in dry benzene (30 ml) was refluxed for 0.5 h. The precipitate was collected by filtration and washed with H_2O. The crude product was recrystallized from EtOH to give 0.43 g of **3b**, mp 131—132°C, as yellow needles. The benzene layer was washed with 3 N NaOH and H_2O, and dried over K_2CO_3. After removal of the solvent, the residue was recrystallized from EtOH to give 0.07 g of **3b**, mp 131—132°C. The total yield was 0.5 g (82%). IR ν_{max}^{KBr} cm^{-1}: 3230. ^{1}H-NMR ($CDCl_3$): 0.97 (3H, t, J=6 Hz), 1.20—1.72 (4H, m), 3.60 (2H, q, J=6 Hz), 5.60—6.10 (1H, b), 7.10—7.70 (10H, m).

ii) A mixture of **4** (0.77 g, 2 mmol) and *n*-butylamine (0.5 g, 7 mmol) in dry benzene (30 ml) was refluxed for 0.5 h. The reaction mixture was treated according to the procedure used above to give 0.56 g (93%) of **3b**, mp 131—132°C, as yellow needles. This compound was identical with the sample obtained above.

3-Anilino-5,6-diphenyl-*as*-triazine (3c)——i) A mixture of **2** (0.53 g, 2 mmol) and aniline (0.37 g, 4 mmol) in dry xylene (30 ml) was refluxed for 10 h, then the reaction mixture was concentrated to dryness *in vacuo*. The residue was chromatographed on an alumina column. The first eluate with benzene gave 0.13 g (21%) of **3c**, mp 229—230°C (lit.[17] mp 230°C), as pale yellow needles (MeOH). The second eluate with benzene gave 0.36 g (68%) of starting material (**2**).

ii) A mixture of **4** (0.77 g, 2 mmol) and aniline (0.37 g, 4 mmol) in dry benzene (30 ml) was refluxed for 10 h. The reaction mixture was treated according to the procedure used above to give 0.4 g (60%) of **3c**, mp 230°C, as pale yellow needles. This compound was identical with the sample obtained above.

3-Hydrazino-5,6-diphenyl-*as*-triazine (3d)——i) A mixture of **2** (0.53 g, 2 mmol) and hydrazine hydrate (18 ml) was heated at 80°C for 2 h with stirring. The precipitate was collected by filtration and washed with H_2O. Recrystallization from MeOH gave 0.25 g (48%) of **3d**, mp 171—173°C (lit.[7] mp 171—173°C), as yellow needles.

ii) A mixture of **4** (1.16 g, 3 mmol) and hydrazine hydrate (0.3 g, 6 mmol) in MeOH (30 ml) was refluxed for 1 h. The reaction mixture was concentrated to dryness *in vacuo*. H_2O (10 ml) was added to the residue and the solution was made alkaline with K_2CO_3. The precipitate was collected by filtration and recrystallized from EtOH to give 0.5 g (64%) of **3d**, mp 172—173°C, as yellow needles. This compound was identical with the sample obtained above.

***N,N'*-Bis(5,6-diphenyl-3-*as*-triazinyl)hydrazine (5)**——A mixture of **2** (0.8 g, 3 mmol) and hydrazine hydrate (0.2 g, 4 mmol) in pyridine (5 ml) was refluxed for 1 h. The reaction mixture was poured into H_2O, and the precipitate was collected by filtration. Recrystallization from EtOH gave 0.28 g (38%) of **5**, mp 238°C (dec.), as yellow needles. IR ν_{max}^{KBr} cm^{-1}: 3220. ^{1}H-NMR (DMSO): 7.40 (s), 15.10 (s); the integrated ratio of the former signal and the latter signal was 10: 1.

3-Cyano-5,6-diphenyl-*as*-triazine (6)——i) A mixture of **4** (1.18 g, 3 mmol) and KCN (0.4 g, 6 mmol) in DMF (30 ml) was stirred at room temperature for 45 min. The reaction mixture was concentrated to dryness *in vacuo*, and a small amount of H_2O was added to the residue. The aqueous solution was extracted with $CHCl_3$, and the extract was dried over K_2CO_3. After removal of the solvent, the residue was purified

by passing it through an alumina column with benzene. Recrystallization from Et_2O–hexane gave 0.58 g (75%) of **6**, mp 156—157°C (lit.[10] mp 154—155°C), as pale yellow needles.

ii) Compound **6** was also obtained from **11** (0.62 g, 2 mmol) and KCN (0.15 g, 2.3 mmol) according to the procedure described above as pale yellow needles, mp 154—155°C. The yield was 0.3 g (58%). This compound was identical with the sample obtained above.

Ethyl α-(5,6-Diphenyl-3-*as*-triazinyl)cyanoacetate (7)——i) $NaNH_2$ (0.35 g, 9 mmol) was added to a solution of ethyl cyanoacetate (1.08 g, 9 mmol) in dry benzene (20 ml) and the mixture was stirred at room temperature for 3 h. Compound (**4**) (1.16 g, 3 mmol) was added thereto and the mixture was refluxed for 1 h. The reaction mixture was concentrated to dryness *in vacuo*, and a small amount of H_2O was added to the residue. The resulting precipitate was collected by filtration and recrystallized from AcOEt to give 0.58 g (56%) of **7**, mp 235°C (dec.), as pale yellow needles. IR ν_{max}^{KBr} cm^{-1}: 1660, 2200. ^{1}H-NMR (CF_3COOH): 1.47 (3H, t, J=7 Hz), 2.40 (1H, s), 4.46 (2H, q, J=7 Hz), 7.70—7.80 (10H, m).

ii) Compound **7** was obtained from **4** (0.94 g, 3 mmol), ethyl cyanoacetate (0.46 g, 4 mmol), and NaH (0.25 g, 5 mmol) using dry THF as a solvent according to the procedure described above, as pale yellow needles, mp 154—155°C. The yield was 0.85 g (83%). This compound was identical with the sample obtained above.

Ethyl 5,6-Diphenyl-3-*as*-triazinylacetate (8)——i) $NaNH_2$ (0.35 g, 9 mmol) was added to a solution of ethyl acetoacetate (1.17 g, 9 mmol) in dry benzene (20 ml), and the mixture was stirred at room temperature for 3 h. Compound (**4**) (1.16 g, 3 mmol) was added thereto, and the mixture was refluxed for 1 h. A small amount of H_2O was added to the reaction mixture, and then the benzene phase was separated, and dried over K_2CO_3. After removal of the solvent, the residue was recrystallized from Et_2O–hexane to give 0.5 g (52%) of **8**, mp 123—124.5°C, as pale yellow plates. IR ν_{max}^{KBr} cm^{-1}: 1730. ^{1}H-NMR (CF_3COOH): 1.45 (3H, t, J=7 Hz), 4.30—4.80 (4H, m), 7.40—8.10 (10H, m).

ii) Compound **8** was obtained from **4** (1.16 g, 3 mmol), ethyl benzoylacetate (1.73 g, 9 mmol) and $NaNH_2$ (0.35 g, 9 mmol) according to the procedure described above, as pale yellow plates, mp 123—124.5°C. The yield was 0.34 g (34%). This compound was identical with the sample obtained above.

iii) NaH (0.25 g, 5 mmol) was added to a solution of ethyl acetoacetate (0.48 g, 4 mmol) in dry THF (20 ml) and the mixture was stirred at room temperature for 1 h. Compound (**11**) (0.94 g, 3 mmol) was added thereto and the mixture was refluxed for 3 h. The reaction mixture was concentrated to dryness *in vacuo* and a small amount of H_2O was added to the residue. The aqueous solution was extracted with $CHCl_3$, and the extract was dried over K_2CO_3. After removal of the solvent, the residue was purified by passing it through a silica gel column with benzene–AcOEt (20: 1). Recrystallization from Et_2O–hexane gave 0.55 g (58%) of **8**, mp 124—125.5°C, as pale yellow plates. This compound was identical with the sample obtained above.

2-(5,6-Diphenyl-3-*as*-triazinyl)cyclohexanone (12)——Following the procedure for the preparation of **8**, treatment of **11** (0.94 g, 3 mmol) in dry THF (30 ml) with NaH (0.84 g, 17 mmol) and cyclohexanone (1.47 g, 15 mmol) gave a crude product which was purified by passing it through a silica gel column with benzene. Recrystallization from AcOEt gave 0.52 g (53%) of **12**, mp 172—173°C, as pale yellow needles. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625, 1715. ^{1}H-NMR ($CDCl_3$): 1.20—2.25 (m), 2.25—3.31 (m), 6.87—8.18 (m), the proton ratio, from low to high field, was 5: 2: 2.

5,6-Diphenyl-3-*as*-triazinylmethyl Phenyl Ketone (13)——Following the procedure for the preparation of **8**, treatment of **11** (0.94 g, 3 mmol) in dry THF (30 ml) with NaH (0.84 g, 17 mmol) and acetophenone 1.62 g, 15 mmol) gave a crude product which was purified by passing it through a silica gel column with benzene–AcOEt (20: 1). Recrystallization from AcOEt–hexane gave 0.18 g (17%) of **13**, mp 130—132°C, as brown prisms. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1690. ^{1}H-NMR ($CDCl_3$): 6.50 (1H, s), 7.05—7.74 (13H, m), 7.75—8.20 (2H, m), 13.21—14.10 (1H, b).

Bis(5,6-diphenyl-3-*as*-triazinyl)methane (14)——Following the procedure for the preparation of **8**, treatment of **11** (0.94 g, 3 mmol) in dry THF (20 ml) with NaH (0.25 g, 5 mmol) and acetophenone (0.5 g, 4.2 mmol) gave a crude product which was purified by passing it through a silica gel column with benzene–AcOEt (9: 1). Recrystallization from acetone–Et_2O gave 0.2 g (27%) of **14**, mp 175°C (dec.), as yellow prisms. ^{1}H-NMR ($CDCl_3$): 5.20 (s), 7.22—7.78 (m), the integrated ratio of the former signal and the latter signal was 10: 1. MS *m/e*: 478 (M^+).

Ethyl α-(4,6-Dimethyl-2-pyrimidinyl)cyanoacetate (16)——NaH (0.17 g, 7 mmol) was added to a solution of ethyl cyanoacetate (0.68 g, 6 mmol) in dry THF (20 ml), and the mixture was stirred at room temperature for 10 min. 4,6-Dimethyl-2-phenylsulfonylpyrimidine (**15**)[13] (0.5 g, 2 mmol) was added thereto and the mixture was heated under reflux for 1 h with stirring. A small amount of H_2O was added, and the mixture was concentrated under reduced pressure to give the residue. The residue was acidified with 10% HCl and extracted with $CHCl_3$. After removal of the solvent, this residue was purified by passing it through an alumina column with AcOEt. Recrystallization from benzene–hexane gave 0.27 g (62%) of **16**, mp 187—189°C (lit.[14] mp 192.5—193.5°C), as yellow prisms. This compound was identical with the sample prepared by an alternative route.[14]

4,6-Dimethyl-2-pyrimidinylmethyl Methyl Ketone (17)——A mixture of **15** (0.5 g, 2 mmol), acetone (2 ml) and NaH (0.1 g, 4 mmol) in dry THF (20 ml) was heated at 40°C for 1 h with stirring, and then 10%

HCl (10 ml) was added thereto. The mixture was concentrated to one-third of its original volume under reduced pressure. The residue was washed with Et_2O, made alkaline with $NaHCO_3$, and extracted with Et_2O. After removal of the solvent, the residual oil was distilled under reduced pressure to give 0.09 g (25%) of **17**, bp 91—93°C (3 mmHg), [lit.[15] bp 95°C (4 mmHg)]. This compound was identical with the sample prepared by an alternative route.[15]

4,6-Dimethyl-2-pyrimidinylmethyl Phenyl Ketone (18)——A mixture of **15** (0.5 g, 2 mmol), acetophenone (0.36 g, 3 mmol), and NaH (0.1 g, 4 mmol) in dry THF (20 ml) was refluxed for 1 h with stirring. The reaction mixture was worked up as in the case of **17** to give 0.145 g (32%) of **18**, bp 150—155°C (2 mmHg); mp 76—77°C, (lit.[16] mp 74—75.5°C), as pale yellow prisms. This compound was identical with the sample prepared by an alternative route.[16]

2-(4,6-Dimethyl-2-pyrimidinyl)cyclohexanone (19)——A mixture of **15** (0.5 g, 2 mmol), cyclohexanone (0.29 g, 2 mmol), and NaH (0.1 g, 4 mmol) in dry THF (20 ml) was refluxed for 1 h with stirring. The reaction mixture was worked up as in the case of **17** to give 0.125 g (35%) of **19**, bp 120°C (2 mmHg); mp 68—69°C (lit.[12a] mp 68—69°C), as pale yellow prisms. This compound was identical with the sample prepared by an alternative route.[12a]

Table I. Analytical Data for the Products

Compd. No.	Formula	Analysis (%) Calcd C	H	N	S	Found C	H	N	S
3a	$C_{17}H_{15}N_3O$	73.63	5.45	15.45		73.59	5.46	15.27	
3b	$C_{19}H_{20}N_4$	74.97	6.62	18.41		74.87	6.66	18.71	
4	$C_{22}H_{17}N_3O_2S$	68.21	4.21	10.85	8.26	68.17	4.23	10.78	8.47
5	$C_{30}H_{22}N_8$	72.86	4.48	22.66		72.51	4.34	22.51	
7	$C_{20}H_{16}N_4O_2$	69.75	4.68	16.27		69.45	4.79	16.04	
8	$C_{19}H_{17}N_3O_2$	71.45	5.37	13.16		71.15	5.27	13.07	
11	$C_{16}H_{13}N_3O_2S$	61.74	4.18	13.50	10.29	61.76	4.18	13.48	10.43
12	$C_{21}H_{19}N_3O$	76.57	5.81	12.76		76.29	5.78	12.62	
13	$C_{23}H_{17}N_3O$	78.61	4.88	11.96		78.77	4.64	11.96	
14	$C_{31}H_{22}N_6$	77.82	4.60	17.57		77.82	4.62	17.33	

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