343. *Synthesis of Some 1,2,4-Triazines.*

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The cyclisation of acylhydrazones of α-diketones by ammonium acetate in hot acetic acid has been applied, under controlled conditions, to the synthesis of a wide variety of 1,2,4-triazines. Some anomalous reactions have been noted. The scope of the reaction has been extended by the use of unsymmetrical α-diketones and components of the resulting mixtures of triazines have been separated and identified. Spectroscopic evidence on the structure of some dihydro-1,2,4-triazines is presented.

There are three general methods for the synthesis of fully aromatic 1,2,4-triazines containing no functional groups. Condensation of acylhydrazides with benzil in acetic acid containing ammonium acetate was used by Laakso, Robinson, and Vandrewala [1,2] to give 5,6-diphenyl-1,2,4-triazines with various aromatic and heterocyclic groups attached at position 3. A similar method was also applied by Metze and his co-workers [3,4] using a variety of aliphatic and aromatic 1,2-diketones and aliphatic, aromatic, and heterocyclic acid hydrazides, but with preliminary isolation of the 1,2-diketone monoacylhydrazones followed by ring closure with alcoholic ammonia under pressure: Metze also found that monohydrazones of aromatic (but not aliphatic) 1,2-diketones react with formamide, to give 5,6-disubstituted 1,2,4-triazines.[5]

[1] Laakso and Robinson, " Festschrift Karrer," 1948, Birkhauser, Zürich, p. 38.
[2] Laakso, Robinson, and Vandrewala, *Tetrahedron*, 1957, **1**, 103.
[3] Metze, *Chem. Ber.*, 1955, **88**, 772.
[4] (*a*) Metze, *Chem. Ber.*, 1956, **89**, 2056; (*b*) Metze and Meyer, *ibid.*, 1957, **90**, 481; (*c*) Metze and Kort, *ibid.*, 1958, **91**, 417; (*d*) Metze and Rolle, *ibid.*, p. 422.
[5] Metze, *Chem. Ber.*, 1954, **87**, 1540.

The third general method involves dehydrogenation with potassium dichromate [6] or sulphur [7] of dihydrotriazines of unknown structure which are prepared by condensation of an α-acylamino-ketone with hydrazine,[6,8] followed by ring closure. 1,2,4-Triazines of this type have also been prepared by the oxidation of 3- and 5-hydrazinotriazines with mercuric oxide,[9] or cupric salts,[2] by treatment of 3-(benzenesulphonylhydrazino)triazines with alkali,[9] and by the action of Grignard reagents on 3-chlorotriazines.[2]

In our work, synthesis of 1,2,4-triazines by the ring closure method with ammonium acetate has been successful with hydrazides of aromatic, heterocyclic, and aliphatic acids and with aromatic and aromatic-aliphatic 1,2-diketones. The rate of reaction appears to depend on the excess of ammonium acetate used, as longer times were required with the ten-fold excess used throughout this investigation than in the work of Laakso *et al.*[2] where, usually, a greater excess (and concentration) was employed. Our yellow crystalline 1,2,4-triazines, prepared from benzil, are tabulated in the Experimental section. The general method gave rise to three anomalous reactions: first, acetylation of the amino-group occurred during the preparation of 3-*p*-aminophenyl-5,6-diphenyl-1,2,4-triazine from *p*-aminobenzhydrazide, but did not occur with the *ortho*-isomer. Laakso *et al.*[2] did not obtain the *p*-acetamido-compound, presumably because of the shorter reaction time. In our hands, the acetylated derivative was still the main product when the reaction was carried out in 90% acetic acid, but acid hydrolysis readily gave the amine.

The isolation of 2,4,5-triphenylimidazole during the preparation of 3-methyl-5,6-diphenyl-1,2,4-triazine was not unexpected in view of the work of Davidson, Weiss, and Jelling [10] who obtained the imidazole from the reaction between benzil and ammonia in acetic acid.

The third anomaly occurred in the preparation of 5,6-diphenyl-1,2,4-triazine from benzil and formhydrazide; beside small yields of the expected triazine and of 3-methyl-5,6-diphenyl-1,2,4-triazine (probably formed by exchange between the hydrazide and the acetic acid as solvent), four other unidentified products were obtained. When formic acid and ammonium formate were employed as cyclising agents a high yield of bisbenzil azine was obtained. 5,6-Diphenyl-1,2,4-triazine was also prepared, along with two unidentified products, by desulphurisation of the 3-mercapto-derivative with Raney nickel, but the best method was that of Rossi [9] involving oxidation of 3-hydrazino-5,6-diphenyl-1,2,4-triazine with freshly prepared yellow mercuric oxide.

Application of the general method to unsymmetrical aromatic-aliphatic 1,2-diketones gave a mixture of the two possible isomers, even when the monoacylhydrazone of the diketone was first prepared by Metze's method.[3] Our results were not obtained by Metze who at first isolated only one isomer, but, after correspondence between us, he reported [8] the isolation of two isomers, 3,6-diphenyl-5- and 3,5-diphenyl-6-methyl-1,2,4-triazine, by manual separation of the crystals. We separated this mixture by chromatography on alumina and, in the case of 3-*p*-methoxyphenyl-6-methyl-5-phenyl- and 3-*p*-methoxyphenyl-5-methyl-6-phenyl-1,2,4-triazine, by fractional crystallisation. Metze [8] thought that the formation of isomers was due to disproportionation of the monoacylhydrazone to form the diketone and bisacylhydrazone, followed by ring closure of this bisacylhydrazone to give the unexpected isomer. This mechanism is in agreement with the results obtained by us. Laakso *et al.*[2] considered the dihydrazone to be a source of the monohydrazone as a result of hydrolytic equilibrium, and this has been demonstrated by cyclisation of benzil bisbenzoylhydrazone with ammonium acetate and acetic acid to 3,5,6-triphenyl-1,2,4-triazine, which was also obtained by Metze's method.[8] However, addition of an equivalent quantity of benzil to the reaction did not give us the increased yield of triazine which would be expected if benzhydrazide was liberated during the reaction.

[6] Sprio and Madonia, *Gazzetta*, 1957, **87**, 992.
[7] Metze, *Chem. Ber.*, 1958, **91**, 1863.
[8] Metze, Rolle, and Scherowsky, *Chem. Ber.*, 1959, **92**, 2478.
[9] Rossi, *Rend. Ist. lombardi Sci.*, Pt. I, *Classe Sci. mat. nat.*, 1955, **88**, 185.
[10] Davidson, Weiss, and Jelling, *J. Org. Chem.*, 1937, **2**, 319.

In an attempt to prepare an α-diketone monoacylhydrazone isomeric with that formed by direct condensation, *p*-methoxybenzhydrazide was condensed with α-hydroxyiminopropiophenone, to give α-hydroxyiminopropiophenone *p*-methoxybenzoylhydrazone, hydrolysis of which caused cleavage of the hydrazone in preference to that of the hydroxyimino-group. Although ring closure of benzil bisbenzoylhydrazone to the triazine was shown to occur under standard conditions adopted, a similar experiment with α-hydroxyiminopropiophenone *p*-methoxybenzoylhydrazone gave only a low yield 3-*p*-methoxyphenyl-5-methyl-6-phenyl-1,2,4-triazine; when the condensation of acylhydrazide and α-hydroxyimino-ketone and subsequent ring closure were carried out without isolation of the intermediate acylhydrazone both isomeric triazines were obtained, but in no greater yield.

The isomeric triazines obtained from unsymmetrical 1,2-diketones were identified by the unambiguous synthesis of one of them by Sprio and Madonia's method [6] from an α-acylamino-ketone of known structure and hydrazine hydrochloride, followed by dehydrogenation of the dihydrotriazine so formed. These workers employed potassium dichromate in aqueous acetic acid for dehydrogenation of dihydro-3,6-diphenyl-1,2,4-triazine in 38% yield. We were unable to improve this result by dry heating or by using aqueous potassium permanganate in acetone, but the yield of the 5-methyl analogue was increased by the last method: this also gave a good yield from dihydro-3-*p*-methoxyphenyl-5-methyl-6-phenyl-1,2,4-triazine.

The structure of the dihydrotriazines has not been clarified: the 1,2-dihydro-structure has been suggested [6] because of the ease of dehydrogenation, but Metze [7] prefers the 2,5- or 4,5-dihydro-structures as being more obvious, based on the synthetic route. The infrared spectrum of dihydro-3,6-diphenyl-1,2,4-triazine shows a maximum at 1453 cm.$^{-1}$ which is attributed to the deformation frequency of a 5-CH_2 group: this excludes the 1,2- or 2,3-dihydro-structure. A maximum at 3424 cm.$^{-1}$, and at 3448 cm.$^{-1}$ for the 5-methyl analogue, can be assigned to the NH group and therefore excludes the 5,6-dihydro-form and confirms the 2,5- or 4,5-dihydro-structure. To decide between these alternatives, methylation of the imino-group was attempted, with a view to subsequent synthesis of the two isomers. However, dimethyl sulphate in methanolic sodium methoxide under reflux was not effective and at 150° only dehydrogenation was observed.

The absorption spectra of some 1,2,4-triazines are included in the Experimental section: the ultraviolet spectrum of 3-methyl-5,6-diphenyl-1,2,4-triazine is noteworthy in being distinct from those of other methyl-diphenyl-1,2,4-triazines, which closely resemble the triphenyltriazine.

Experimental

Light petroleum had b. p. 60—80°.

3-Substituted 5,6-Diphenyl-1,2,4-triazines.—Equimolecular quantities of benzil and the acid hydrazide were dissolved in acetic acid and treated with a ten-fold excess of ammonium acetate (previously dried *in vacuo* over calcium chloride). The mixture was heated under reflux, then cooled, and the product was collected, directly or after precipitation with water, and recrystallised. The experiments and *products* are summarised in Table 1.

5,6-Diphenyl-1,2,4-triazine.—(a) *General method.* To a solution of benzil (10 g.) and formhydrazide (2·4 g.) in acetic acid (50 ml.) ammonium acetate (36 g.) was added and the mixture was heated under reflux for 4 hr. The yellow solid (0·35 g.), m. p. 205—230°, which separated was collected (cold) but could not be recrystallised owing to its extreme insolubility. The filtrate was poured into water and the yellow sticky solid (9·1 g.) was washed with water, dried, and extracted with boiling light petroleum, to leave a yellow oily residue (Z). Hydrogen chloride was passed through the cooled extract, and the precipitated hydrochlorides were collected, washed with light petroleum, and shaken with 6N-sodium hydroxide and ether until decomposed. The ether layer was separated, dried ($MgSO_4$), and evaporated. The residual oil (5·2 g.) was added in benzene (25 ml.) to an alumina column (150 g.; grade H). Elution

with benzene gave first colourless needles (25 mg.), m. p. 196—197° (from ethanol) (Found: C, 89·0; H, 5·55%), and then a fraction which gave 3-methyl-5,6-diphenyl-1,2,4-triazine (0·59 g.), m. p. 92—94°, from light petroleum. Elution with benzene–chloroform (19 : 1 and 9 : 1) gave non-crystalline material, followed (1 : 1 mixture) by a fraction

TABLE 1.

3-Substituted 5,6-diphenyl-1,2,4-triazines prepared from benzil.

No.	Ref.*	3-Subst.	Time of reaction (hr.)	AcOH (ml. per g. of Bz_2)	Yield (%)	M. p.†	Recryst. from
1	*a*	(H)	4	4	80	145° [2, 10]	EtOH
2	*b*	*p*-MeO·C_6H_4	4	2·5	75	159—160	AcOH
3	*c*	*p*-Br·C_6H_4	72	8	70	140—141	EtOH
4	*d*	*p*-Cl·C_6H_4	24	5	53	152—153 ‡	AcOH
5	*d*	*o*-NO_2·C_6H_4	4	4	56	194	AcOH
6	*d*	*m*-NO_2·C_6H_4	4	4	71	195 [2]	AcOH
7	*d*	*p*-NO_2·C_6H_4	4	4	71	201	AcOH
8	*e*	*p*-HO·C_6H_4	4	10	48	262—263 ¶	EtOAc
9	*f*	*o*-NH_2·C_6H_4	0·5	5	60	163—164	EtOH
10	*g*	*p*-NH_2·C_6H_4	0·5	5	8 [m]	218—219 [2]	Aq. MeOH
11	*g*	*p*-NHAc-C_6H_4	8	5	83 [n]	270 §	AcOH
12	*h*	Me	24	4	45	92—94 [5]	Pet [o]
13	*i*	3-Pyridyl		5	60	174—175	MeOH
14	*j*	4-Pyridyl		5	62	161—162	EtOAc
15	*k*	4-(2-Phenyl-4-quinolyl)		10	65	281—282	EtOAc

	Found (%)				Required (%)		
No.	C	H	N	Formula	C	H	N
2	78·1	5·2	10·4	$C_{22}H_{17}N_3O$	77·85	5·2	10·4
3	64·9	3·5	10·8	$C_{21}H_{14}BrN_3$	64·9	3·6	10·8
4	73·5	4·0	12·2	$C_{21}H_{14}ClN_3$	73·4	4·1	12·2
5	71·55	3·9	15·3	$C_{21}H_{14}N_4O_2$	71·2	4·0	15·8
9	77·5	5·0	17·3	$C_{21}H_{16}N_4$	77·7	5·2	16·9
13	77·1	4·5	18·3	$C_{20}H_{14}N_4$	77·4	4·45	18·1
14	77·5	4·6	18·0	,,	,,	,,	,,
15	81·9	4·4	13·3	$C_{30}H_{20}N_4$	82·5	4·6	12·8

* Prep. of hydrazide. † Refs. are to previous prepn. of the triazine. ‡ Ref. 2 gives 134—135°. ¶ Ref. 2 gives 254—255°. § Ref. 2 gives 264—265°.

Refs.: (*a*) Curtius, *J. prakt. Chem.*, 1894, **50**, 278; (*b*) Curtius and Melsbach, *ibid.*, 1910, **81**, 548; (*c*) Kahl, *Z. ver. Rübenzucht-Ind.*, 1904, 1091 (*Chem. Zentr.*, 1904, II, 1493); (*d*) Curtius and Trackmann, *J. prakt. Chem.*, 1895, **51**, 168; (*e*) Struve and Radenhauser, *ibid.*, 1895, **52**, 236; (*f*) Curtius and Melsbach, *ibid.*, 1910, **81**, 543; (*g*) Curtius, *ibid.*, 1917, **95**, 336; (*h*) Curtius and Hofmann, *ibid.*, 1896, **53**, 524; (*i*) Curtius and Mohr, *Ber.*, 1898, **31**, 2493; (*j*) Meyer and Mally, *Monatsh.*, 1912, **33**, 395; (*k*) John, *Ber.*, 1926, **59**, 1448. [l] *Benzil bis*-p-*nitrobenzoylhydrazone* (Found: C, 62·0; H, 3·9; N, 15·6. $C_{28}H_{20}N_6O_6$ requires C, 62·7; H, 3·8; N, 15·8%) was also isolated, as sparingly soluble yellow needles, m. p. 294—295°. [m] Reaction was carried out in 90% AcOH; 3-*p*-acetamidophenyl-5,6-diphenyl-1,2,4-triazine was also isolated. [n] Prep. from *p*-aminobenzhydrazide. [o] 2,3,5-Triphenylimidazole (1%), insol. in light petroleum, was also isolated.

which yielded colourless prisms (60 mg.), m. p. 211—212° (Found: C, 87·2; H, 5·8; N, 3·55%), insoluble in light petroleum, and 5,6-diphenyl-1,2,4-triazine (0·58 g.), m. p. 117° after sublimation and recrystallisation from ethanol (lit.,[2,11,5] 112—115° or 117°).

The light petroleum–hydrogen chloride liquors were shaken with alkali and evaporated, giving a yellow residue, m. p. 118—120°, which was eluted with light petroleum–benzene (1 : 1) from alumina (15 g.; grade H) as colourless needles (40 mg.) (from ligroin), m. p. 213—214° (Found: C, 90·35; H, 5·7; N, 3·5%); the mixed m. p. with product of m. p. 211—212° was 190—195°. Continued elution with benzene gave colourless needles (30 mg.), m. p. 196—197°, identical with those of the same m. p. (above), and with benzene–chloroform (1 : 1) gave colourless needles (20 mg.), m. p. 211—212°, identical with those above.

The residue (Z) was eluted from alumina (75 g.; grade H) as above but yielded only successive samples of compounds of m. p. 213—214° (15 mg.) and 211—212° (170 mg.).

(b) *From* 3-*mercapto*-5,6-*diphenyl*-1,2,4-*triazine*. This thiol (5 g.) was dissolved in boiling

[11] Ref. *a*, Table 1.

ethanol (500 ml.), Raney nickel (10 g.) was added, and the mixture set aside for 10 min. Nickel was removed and the filtrate and washings were concentrated to a brown oil (3·5 g.). This was dissolved in chloroform and extracted with N-sodium carbonate and then with 2N-hydrochloric acid. The acid extract was basified and extracted with chloroform; the chloroform removed a yellow compound which crystallised from ethyl acetate in colourless prisms (0·25 g.), m. p. 234—236° (decomp., rapid heating to 225°) (Found: C, 79·6; H, 5·4; N, 14·9%). The original chloroform solution was evaporated, and the brown oily residue was digested with light petroleum (Y) and then transferred in benzene (250 ml.) to alumina (100 g.; grade H). Elution with benzene–chloroform (4 : 1) gave 5,6-diphenyl-1,2,4-triazine (0·12 g.), m. p. 117°, and, with 3 : 1, 1 : 1, and 1 : 3 solvent mixtures, colourless needles (0·14 g.), m. p. 225—227° (Found: C, 67·9; H, 5·05; N, 16·8%), followed by colourless needles (0·13 g.), m. p. 234—236°.

The light petroleum extract (Y) was evaporated to dryness; the residue sublimed at 110—120°/0·1 mm., to give a pale yellow solid (0·55 g.) which recrystallised from aqueous ethanol to provide needles of the triazine (0·35 g.), m. p. 117° (total yield, 0·47 g., 12%).

Bisbenzil Azine.—Benzil (10·5 g.) and formhydrazide (3 g.) were heated in 90% formic acid (100 ml.) with ammonium formate (31 g.) for 4 hr. and the precipitate, m. p. 170—190°, was collected (cold), washed with water, and dried. Recrystallisation from acetic acid gave yellow needles (5·7 g.) of the ketazine, m. p. and mixed m. p. 203—204° (cf. ref. 12).

6-*Methyl*-3,5-*diphenyl*-1,2,4-*triazine.*—(*a*) A solution of methylphenylglyoxal [13] (25 g.) and benzhydrazide [11] (23 g.) in acetic acid (250 ml.) was heated under reflux for 8 hr. with ammonium acetate (130 g.). The solid (32 g.) which separated when the mixture was poured into water was collected, washed, dried, and transferred in 1 : 1 benzene–light petroleum (350 ml.) to alumina (750 g.; grade H). Elution with 1 : 1 benzene–light petroleum (2 l.) gave yellow needles of 5-methyl-3,6-diphenyl-1,2,4-triazine (6·3 g.), m. p., 123—124°, followed by uncrystallisable mixtures and finally, on elution with 1 : 1 benzene–chloroform, 6-methyl-3,5-diphenyl-1,2,4-triazine (3·3 g.), m. p. 109—110° (Found: C, 78·25; H, 5·4; N, 16·6. Calc. for $C_{16}H_{13}N_3$: C, 77·7; H, 5·3; N, 17·0%). The mother-liquors were evaporated and the residue was combined with the above oily fractions and chromatographed on alumina (500 g.; grade H). 5-Methyl-3,6-diphenyl-1,2,4-triazine (0·4 g.) was isolated by elution with 1 : 1 benzene–light petroleum and, after an oily intermediate fraction, elution with 1 : 1 benzene–chloroform gave 6-methyl-3,5-diphenyl-1,2,4-triazine (3·7 g.).

(*b*) Methylphenylglyoxal benzoylhydrazone [3] (3 g.) was heated in acetic acid (20 ml.) with ammonium acetate (8·7 g.) for 4 hr. After cooling, the mixture was worked up as in (*a*) and yielded 10% of 5-methyl-3,6- and 28% of 6-methyl-3,5-diphenyl-1,2,4-triazine.

3-p-*Methoxyphenyl*-6-*methyl*-5-*phenyl*-1,2,4-*triazine.*—Methylphenylglyoxal [13] (5 g.) and *p*-methoxybenzhydrazide (5·6 g.) were heated in acetic acid (50 ml.) with ammonium acetate (26 g.) for 8 hr. The solid (7·7 g.), m. p. 114—138°, obtained by pouring the mixture into water was collected, washed with water, dried, and extracted with light petroleum, leaving a yellow residue, m. p. 164—169°. The cold petroleum solution deposited crystals which on recrystallisation gave 3-p-*methoxyphenyl*-6-*methyl*-5-*phenyl*-1,2,4-*triazine* as yellow needles (3·75 g., 40%), m. p. 122—123° (Found: C, 73·45; H, 5·5; N, 14·6. $C_{17}H_{15}N_3O$ requires C, 73·6; H, 5·45; N, 15·15%). The residue, m. p. 164—169°, yielded 3-*p*-methoxyphenyl-5-methyl-6-phenyl-1,2,4-triazine which crystallised from methanol in yellow needles (0·5 g., 5%), m. p. and mixed m. p. 169—170°.

α-*Hydroxyiminopropiophenone* p-*Methoxybenzoylhydrazone.*—α-Hydroxyiminopropiophenone [14] (5·0 g.) and *p*-methoxybenzhydrazide [15] (5·1 g.) were heated in acetic acid (20 ml.) for 1 hr. On cooling, a colourless solid separated (3·6 g.), m. p. 178—184°, which crystallised from benzene as needles (2·1 g.), m. p. 191—192°, of α-*hydroxyiminopropiophenone* p-*methoxybenzoylhydrazone* (Found: C, 65·3; H, 5·5; N, 13·5. $C_{17}H_{17}N_3O_3$ requires C, 65·6; H, 5·5; N, 13·6%). Heating this under reflux with 0·1N-hydrochloric acid and ethanol (1 : 1) gave α-hydroxyiminopropiophenone, m. p. and mixed m. p. 114—115°.

3-p-*Methoxyphenyl*-5-*methyl*-6-*phenyl*-1,2,4-*triazine.*—(*a*) Ammonium acetate (7·1 g.) and α-hydroxyiminopropiophenone *p*-methoxybenzoylhydrazone (3 g.) were heated in acetic acid

[12] Ritter and Wiederman, *J. Amer. Chem. Soc.*, 1929, **51**, 3583.
[13] *Org. Synth.*, 1943, **23**, 1.
[14] Hartung and Munch, *J. Amer. Chem. Soc.*, 1929, **51**, 2262.
[15] Ref. *b*, Table 1.

(30 ml.) for 4 hr. The cold mixture was poured into water and the precipitate (1·05 g.), m. p. 115—128°, was collected, washed with water, and dried. Recrystallisation from ligroin gave pale yellow plates (0·35 g., 13%), m. p. 169—170°, of 3-p-*methoxyphenyl*-5-*methyl*-6-*phenyl*-1,2,4-*triazine* (Found: C, 73·9; H, 5·5; N, 14·4. $C_{17}H_{15}N_3O$ requires C, 73·6; H, 5·45; N, 15·15%).

(*b*) α-Hydroxyiminopropiophenone (5 g.) and *p*-methoxybenzhydrazide (5 g.) were heated in acetic acid (200 ml.) for 2 hr. Ammonium acetate was added to the cooled mixture and refluxing was continued for a further 8 hr. After cooling, the mixture was poured into water and the solid (5 g.), initially oily, was filtered off, washed with water, and dried. The product was extracted with boiling ligroin (charcoal) and concentrated until crystallisation occurred. This crop recrystallised from ligroin, giving yellow plates of the above triazine (0·9 g., 11%), m. p. 169—170°. The mother-liquors were concentrated and, on cooling, yellow needles, m. p. 120—125°, separated; these, on recrystallisation from methanol, gave yellow needles (0·05 g., 0·7%), m. p. 121—122°, alone or on admixture with 3-*p*-methoxyphenyl-6-methyl-5-phenyl-1,2,4-triazine.

2(or 4),5-*Dihydro*-3-p-*methoxyphenyl*-5-*methyl*-6-*phenyl*-1,2,4-*triazine*.—α-*p*-Methoxybenzamidopropiophenone (7·4 g.) and 98% hydrazine hydrate (1·5 g.) were dissolved in ethanol (75 ml.), concentrated hydrochloric acid (7·2 ml.) was added, and the solution was heated under reflux for 8 hr. The mixture was evaporated to half its volume, diluted with water, and made alkaline with ammonia. The precipitate (6·8 g.), m. p. 170—183°, was collected, washed with water, dried, and recrystallised from methanol, to give 2(or 4),5-*dihydro*-3-p-*methoxyphenyl*-5-*methyl*-6-*phenyl*-1,2,4-*triazine* (3·75 g., 50%), m. p. 196—198°, as colourless needles (Found: C, 73·0; H, 6·0; N, 16·8. $C_{17}H_{17}N_3O$ requires C, 73·1; H, 6·1; N, 15·0%).

The dihydro-compound (2 g.) in refluxing acetone (400 ml.) with 2% potassium permanganate solution, added during 2 hr., gave a solid (1·8 g.), m. p. 155—167°. This was dissolved in acetic acid and poured into water, precipitating a pale yellow solid (1·6 g.), m. p. 168—170°. Recrystallisation from methanol gave yellow plates of 3-*p*-methoxyphenyl-5-methyl-6-phenyl-1,2,4-triazine (1·45 g., 73%), m. p. 169—170°; the aqueous acetic acid liquors were made alkaline with ammonia and yielded the unchanged dihydrotriazine (0·12 g.), m. p. 194—196°.

2(or 4),5-*Dihydro*-5-*methyl*-3,6-*diphenyl*-1,2,4-*triazine*.—α-Benzamidopropiophenone [16] (10 g.) and 98% hydrazine hydrate (2 g.) were heated in ethanol (100 ml.) and concentrated hydrochloric acid (7·0 ml.) for 8 hr., cooled, diluted with water, and made alkaline with ammonia. The precipitate (9·7 g.), m. p. 162—184°, was collected, washed with water, and dried; recrystallisation from aqueous methanol gave colourless needles of the dihydrotriazine (6·8 g., 68%), m. p. 194—195° (lit.,[17] m. p. 197°) (Found: C, 77·65; H, 6·0; N, 17·5. Calc. for $C_{16}H_{15}N_3$: C, 77·1; H, 6·1; N, 16·9%).

5-*Methyl*-3,6-*diphenyl*-1,2,4-*triazine*.—(*a*) The dihydro-compound (2 g.) was dissolved in acetone (400 ml.), and 2% aqueous potassium permanganate (400 ml.) was added portionwise to the refluxing solution during 4 hr. Manganese dioxide was filtered from the hot solution and washed with acetone, and the filtrate and washings were concentrated until solid separated. The solid (1·65 g.), m. p. 119—123°, recrystallised from light petroleum to provide the triazine as yellow needles (1·45 g., 73%), m. p. 123—124° (lit.,[7] m. p. 126°) (Found: C, 77·6; H, 5·2; N, 17·2. Calc. for $C_{16}H_{13}N_3$: C, 77·7; H, 5·3; N, 17·0%).

(*b*) A solution of the dihydrotriazine (2·5 g.) in 50% aqueous acetic acid (50 ml.) was added to potassium dichromate (1 g.) in water (5 ml.). The mixture was heated under reflux for 2 hr., then cooled, and the solid (0·33 g.), m. p. 122—124°, was collected, washed with water, and dried. Recrystallisation from light petroleum gave pale yellow needles (0·3 g.), m. p. 123—124°, of the triazine. Dilution of the original filtrate yielded a mixture of triazine (0·05 g.) and unchanged dihydrotriazine (1·65 g.).

3,6-*Diphenyl*-1,2,4-*triazine*.—(*a*) The dihydrotriazine (2 g.) was dissolved in acetone (200 ml.), and 5% potassium permanganate solution (100 ml.) was added portionwise to the refluxing solution during 1 hr. Working up as above gave crystals (0·9 g.), m. p. 140—148°, that were dissolved in acetic acid, reprecipitated with water, and recrystallised from ethanol, to form yellow needles of the triazine (0·5 g., 25%), m. p. 156—157°.

[16] Lister and Robinson, *J.*, 1912, **101**, 1297.
[17] Thiele and Bailey, *Annalen*, 1898, **303**, 75.

(*b*) The dihydrotriazine (0·5 g.) was heated at 200° for 10 min., cooled, and dissolved in acetic acid. Dilution with water gave a yellow solid, m. p. 152—157°, which crystallised from ethanol as yellow needles of the triazine (0·06 g., 12%), m. p. 156—157°. The aqueous acetic acid solution contained unchanged dihydrotriazine (0·25 g.), m. p. 195—198°.

α-p-*Methoxybenzamidopropiophenone.*—A stirred suspension of α-aminopropiophenone stannichloride (21 g.) in ice-cold water (210 ml.) was treated with *p*-methoxybenzoyl chloride [18] (14·7 g.) and aqueous potassium hydroxide (63 g. in 110 ml.) with ice-cooling. Stirring was continued until the odour of the acid chloride had disappeared and the mixture was then extracted with ether. The dried ($MgSO_4$) extracts were concentrated until crystallisation occurred. The solid recrystallised from ether as colourless prisms (12 g., 64%), m. p. 114—115°, of α-p-*methoxybenzamidopropiophenone* (Found: C, 71·9; H, 5·9; N, 5·2. $C_{17}H_{17}NO_3$ requires C, 72·1; H, 6·05; N, 4·9%).

Attempted Methylation of 2(*or* 4),5-*Dihydro*-5-*methyl*-3,6-*diphenyl*-1,2,4-*triazine.*—The dihydrotriazine (1 g.) in absolute methanol (50 ml.), containing sodium (1 g.) and dimethyl sulphate (5 g.), was heated in a sealed tube at 150° for 24 hr. The methanol was evaporated and water was added to precipitate a yellow solid (0·85 g.); recrystallisation from ligroin gave colourless needles (0·38 g.), m. p. 194—195°, of the dihydrotriazine. Evaporation of the ligroin filtrate and recrystallisation of the oily residue from light petroleum gave yellow plates (0·1 g.), m. p. 123—124°, of 5-methyl-3,6-diphenyl-1,2,4-triazine. No further products could be isolated.

Spectra.—Spectra of some of the products are reported in Table 2.

TABLE 2.

Ultraviolet (in MeOH) and infrared (in $CHCl_3$) spectra.

log ε in parentheses; $\lambda_{max.}$ in mμ; i = inflexion; $\nu_{max.}$ in cm.$^{-1}$, weak unless specified.

Substituent 3	5	6	$\lambda_{max.}$	$\lambda_{max.}$	$\nu_{max.}$
1,2,4-Triazines					
Ph	Ph	Ph		281 (4·45)	
p-MeO·C_6H_4	Ph	Ph	223 (4·33)	301—302 (4·55)	
Me	Ph	Ph	217—220i (4·31)	263 (4·04), 308—310 (3·97)	
Ph	Ph	Me		263 (4·40), 300—310i (3·85)	
p-MeO·C_6H_4	Ph	Me	221 (4·15)	289 (4·49)	
Ph	Me	Ph		271 (4·40)	
p-MeO·C_6H_4	Me	Ph	223 (4·11)	295—297 (4·47)	
Ph	(H)	Ph		283—285 (4·45)	
Dihydro-1,2,4-triazines					
Ph	Me	Ph	234—235i (4·31) 241 (4·32) 312—314 (3·92)		3536m, 3448m (NH), 3350m, 2956m, 1628s, 1594m, 1493m, 1450s (Me), 1371m, 1354m, 1329s, 1306s, 1165s, 1100, 1020m, 1006, 959m, 941m, 919m, 882
Ph	(H)	Ph	233—235 (4·30) 240—242 (4·32) 308—309 (3·82)		3536m, 3424m (NH), 3020m, 1632s, 1599m, 1574m, 1493m, 1453s (CH_2), 1342s, 1320s, 1266, 1161m, 1126s, 966m, 918m
p-MeO·C_6H_4	Me	Ph	258 (4·23), 313 (4·17)		

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[18] Meyer, *Monatsh.*, 1901, **22**, 428.