109. *Triazoles. Part VI.** 1,5-*Diaryl*-1,2,4-*triazole*-3-*aldehydes.*

By Mrs. E. J. Browne and J. B. Polya.

1,5-Diaryl-1,2,4-triazole-3-aldehydes have been prepared from the esters or hydrazides of the corresponding acids obtained by the rearrangement of 4-arylazo-2-aryloxazolin-5-ones in the presence of basic reagents. Some of the acyclic intermediates formed in the course of such rearrangements have been isolated.

Aldehydes derived from 1,2,3-triazoles [1,2] have been known for some time,[3] but free aldehydes of 1,2,4-triazoles were not prepared until recently [4] and only two such derivatives have been recorded. The phenylhydrazone of 5-hydroxy-1-phenyl-1,2,4-triazole-3-aldehyde was one of the products of the little investigated reaction between chloroacetylurethane or chloroacetylurea and phenylhydrazine,[5] and the ozonolysis of monoacetylated 5-hydroxy-3-styryl-1,2,4-triazole [6] gave an aldehyde, isolated as the dinitrophenylhydrazone.[7]

The pure 1,5-diaryl-1,2,4-triazole-3-aldehydes are stable and easy to handle, but evolve irritant vapours when warmed. In reaction mixtures the aldehydes are sensitive to heat and basic reagents, and their rapid isolation is essential. Two kinds of preparation could be considered in principle: substitution of 1,5-diaryl-1,2,4-triazoles by groups readily converted into the aldehyde group; and rearrangement or cyclisation to triazoles of substances already provided with this group. Although the 1,2,4-triazole nucleus is

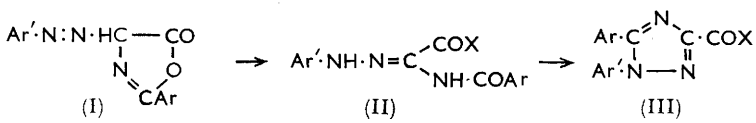
* Part V, *J.*, 1954, 4508.

[1] Hüttel, *Ber.*, 1941, **74**, 1680.
[2] Henkel and Weygand, *Ber.*, 1943, **76**, 812.
[3] Jonas and von Pechmann, *Annalen*, 1891, **262**, 277.
[4] Browne and Polya, *Chem. and Ind.*, 1960, 1085, 1086.
[5] Frerichs and Beckurts, *Arch. Pharm.*, 1899, **237**, 346; *J.*, 1899, **76**, 808.
[6] Young and Annable, *J.*, 1897, **71**, 200.
[7] E. A. Parkes, Ph.D. Thesis, University of Tasmania, 1953, pp. 57—59.

regarded as π-excessive,[8] it has sufficient π deficient character to resist both electrophilic and nucleophilic substitution. Hence the first alternative appeared unpromising. The only known method of this nature, the preparation of 3-hydroxymethyl-1,2,4-triazole by Jones and Ainsworth,[9] presents difficulties which are avoided in the second alternative.

3-Methyl-1,2,4-triazoles are accessible but their oxidation is difficult to control. The resulting acids are readily decarboxylated; further decomposition, presumably ring cleavage, also occurs, judging from the substantial loss of the expected decarboxylated triazoles. The 3-methyl group of 1,2,4-triazoles is not reactive enough to permit condensation except when the triazole is quaternised.[10] Both 1,2,4-triazole and 3-methyl-1,2,4-triazole are readily tritylated, probably in the 1-position,[11] and the latter substance is quaternised by methyl iodide, theoretically in the 4-position.[10] The quaternary iodide did not form a Schiff's base by Kröhnke's method;[12] 4,4'-bisdimethylaminoazoxybenzene was the only product isolated from this reaction mixture.

Aldehydes were prepared from esters and hydrazides of 1,5-diaryl-1,2,4-triazole-3-carboxylic acids, obtained by basic rearrangement of arylazoaryloxazolinones,[4] which had been satisfactory in the preparation of other 3-substituted 1,5-diaryl-1,2,4-triazoles.[13]



(I) (II) (III)

No.	Ar	Ar′	No.	Ar	Ar′	No.	X	No.	X
-1	Ph	Ph	-6	Ph	p-C_6H_4Br	a	O^-	e	$NH{\cdot}NH{\cdot}CO{\cdot}NH_2$
-2	Ph	o-C_6H_4Me	-7	p-C_6H_4Br	Ph	b	OMe	f	NHPh
-3	Ph	m-C_6H_4Me	-8	Ph	p-$NO_2{\cdot}C_6H_4$	c	NH_2	g	NHEt
-4	Ph	p-C_6H_4Me	-9	Ph	2-$C_{10}H_7$	d	$NH{\cdot}NH_2$	h	N_3
-5	Ph	p-$MeO{\cdot}C_6H_4$							

Kuskov[14] prepared some 4-arylazo-2-phenyloxazolin-5-ones, " azlactones " (I-1, I-4, and I-8) and ascribed acyclic structures (IIc) to their products of rearrangement with methanolic ammonia. Sawdey[15] showed that methanolic ammonia or potassium hydroxide converts oxazolinone (I-1) into the triazole-amide (III-1c) or the triazole anion (III-1a), respectively. According to Sawdey rearrangement of the oxazolinone (I) could occur through the acyclic ester (IIb), followed by cyclisation to the triazole ester (IIIb), which is ammonolysed or hydrolysed to the final product. Extension of Sawdey's work to a number of azlactones (Table 1) and basic reagents supports Sawdey's suggestions, but also provides evidence for the existence of a second mechanism.

The rearrangement does not occur in solutions acid to litmus. In weakly alkaline methanol the azlactone ring opens to give the acyclic ester (IIb), which resists hydrolysis but is readily cyclised to the triazole ester (IIIb); this is very sensitive to hydrolysis. Hence the formation of triazolecarboxylic acid (IIIa) is favoured in strongly alkaline solution. Acyclic acids (IIa) cannot be obtained, as cyclisation of their esters (IIb) precedes hydrolysis. Even the acyclic esters cannot be isolated except when the rate of cyclisation is slow (II-2b and II-3b).

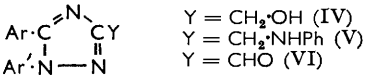
The acyclic intermediates (II) (Table 2) are yellow, labile compounds which can be distinguished from the colourless, stable triazoles (III) (Table 3) by their melting points and by the low solubility of the intermediates in organic solvents. Attempts to recrystallise the intermediates brought about decomposition or at least partial cyclisation. Thus

[8] Albert, " Heterocyclic Chemistry," Athlone Press, London, 1959, pp. 136, 164.
[9] Jones and Ainsworth, *J. Amer. Chem. Soc.*, 1955, **77**, 1538.
[10] Duffin, Kendall, and Waddington, *J.*, 1959, 3799.
[11] Atkinson and Polya, *J.*, 1954, 141, 3319.
[12] Kröhnke, *Ber.*, 1938, **71**, 2583.
[13] Asker and Elagroudi, *J. Org. Chem.*, 1961, **26**, 1440.
[14] Kuskov, *Zhur. obshchei Khim.*, 1951, **21**, 152.
[15] Sawdey, *J. Amer. Chem. Soc.*, 1957, **79**, 1955.

an analytical sample could be prepared in one case only (II-2b) in which cyclisation was exceptionally slow. The three sharp ultraviolet absorption bands of the intermediates, reminiscent of the spectra of azo-dyes, are easily distinguished from the two triazole bands, which are shallow, broad, and at lower wavelengths.

Acyclic amides (IIc) were obtained in two cases only (from I-2 and I-3). All azlactones, with the exception of (I-1), gave acyclic hydrazides (IId); all but two of these (II-3 and II-9) were cyclised by warming them with dilute aqueous sodium carbonate. The hydrazides (IIId) of triazolecarboxylic acids were prepared also by reaction of the triazole-esters (IIIb) with hydrazine. On the other hand the oxazolinone (I-1) with semicarbazide or aniline gave the expected triazoles (III-1e and III-1f, respectively), neither of which could be prepared from the triazole-ester (III-1b). Evidently these rearrangements did not involve Sawdey's mechanism. Since the relatively stable acyclic ester (II-2b) could not be converted into the acyclic hydrazide without cyclisation and extensive decomposition, the formation of the cyclic hydrazide (III-2d) could, but need not, take place by Sawdey's mechanism. In the cases of the triazole-hydrazides which could be prepared from the acyclic analogues the alternative mechanism is postulated.

Secondary and tertiary amines, urethane, thiosemicarbazide, guanidine, and aminoguanidine did not react with the most readily cyclised azlactone (I-1); attempts to force such reactions afforded triazole-acids (IIIa) or -esters (IIIb). The hydrazides of the triazolecarboxylic acids can be converted into stable azides (IIIh) and other derivatives. Rearrangements proceeded most smoothly when leading to triazoles substituted on $N_{(1)}$ by *p*-tolyl, *p*-methoxyphenyl, or phenyl, and least satisfactorily when the substituents were 2-naphthyl or *m*-tolyl on $N_{(1)}$ or *p*-bromophenyl on $C_{(5)}$.



The triazole-esters (IIb) were reduced to 3-hydroxymethyltriazoles (IV) (Table 4) by lithium aluminium hydride in ether. Reduction of the acyclic esters (II-2b and II-3b) occurred with, or immediately after, cyclisation. The secondary triazole-amide (III-1f) was reduced to the expected secondary amine (V) by lithium aluminium hydride, but reduction of the analogue (III-1g) failed.

The triazole-aldehydes (VI) and their derivatives (Table 5) were obtained by the oxidation of the alcohols (IV) with lead tetra-acetate in benzene; old preparations of lead tetra-acetate gave better results than fresh ones. Less satisfactory was oxidation with *N*-bromosuccinimide; only traces of aldehyde were obtained by oxidation with manganese dioxide. The aldehydes could be estimated by the oxime method; they were characterised as 2,4-dinitrophenylhydrazones, semicarbazones, or oximes. None of these derivatives could be hydrolysed to the free aldehydes, which were prepared by decomposing Girard-T derivatives with formaldehyde [16] and hydrochloric acid in the presence of chloroform.

Although their derivatives were obtained thereby in satisfactory yields, the free aldehydes could not be prepared by Kalb and Gross's method,[17] or by the related McFadyen–Stevens reaction [18] or its modification with powdered glass.[19]

The aldehydes gave the expected triazolylacrylic acids in Döbner or Perkin reactions. Unlike the acidic 1,2,3-triazole-aldehydes which are stable in alkaline solution,[1,20] the 1,2,4-triazole-aldehydes undergo the Cannizzaro dismutation reaction.

The ultraviolet absorption spectra of the aldehydes consist of a broad band ($\lambda_{max.}$ 243—261 mμ; log ε 4·0—4·3) and an even less distinct band or shoulder ($\lambda_{max.}$ 219—228

[16] Teitelbaum, *J. Org. Chem.*, 1958, **23**, 646.
[17] Kalb and Gross, *Ber.*, 1926, **59**, 727.
[18] McFadyen and Stevens, *J.*, 1936, 584.
[19] Newman and Caflisch, *J. Amer. Chem. Soc.*, 1958, **80**, 862.
[20] Hüttel and Gebhardt, *Annalen*, 1947, **558**, 34.

mμ; log ε 4·17—4·44). The alcohols have similar spectra (with the exception of IV-1 which occurs in isomeric forms and will be considered elsewhere). The spectra of acids, esters, and hydrazides show little contrast. The broad bands suggest the superimposition of isolated chromophores brought about either through lack of coplanarity of the aryl groups and the triazole nucleus or through the uncoupling of 5-aryl group and the hetero-aromatic system. The difference between the spectrum of 1,5-diphenyl-1,2,4-triazole [21] and those considered at present and the argument that substitution in the " unhindered " 3-position is unlikely to affect the coplanarity of the molecule make the second hypothesis more probable. The infrared spectra of 1,2,4-triazoles are beyond the scope of the present paper. Characteristic bands of the triazole aldehydes are shown in Table 6. Weak C–H stretching bands [22] are located mostly in the region between 2900 and 2700 cm.$^{-1}$. A strong and a weak band slightly displaced in either direction beyond the region of carbonyl stretching bands usual for aromatic and β-unsaturated aldehydes [23] strengthen the hypothesis suggested by the ultraviolet spectra.

Experimental

Representative experiments are described; further details and analyses appear in the Tables. Light petroleum had b. p. 40—60°.

The difficulty of obtaining accurate nitrogen analyses on triazoles containing bromine will be considered elsewhere.

4-p-*Methoxyphenylazo*-2-*phenyloxazolin*-5-*one* (I-5). A solution of *p*-anisidine (12·3 g.) in glacial acetic acid (75 ml.) and concentrated hydrochloric acid (22 ml.) was cooled in an ice–salt bath and diazotised with pentyl nitrite (13 g.). Freshly fused sodium acetate (20 g.) was added, followed by a freshly prepared solution of hippuric acid (20 g.) in acetic anhydride (80 ml.), which was added rapidly, with stirring below 15°. The mixture was cooled to 0—4°; The crude *product* was almost completely precipitated within 2 hr.; it was dried by suction, and was either recrystallised for analysis or used directly although contaminated with inorganic salts and acetic acid.

Table 1.

2-Aryl-4-arylazo-oxazolin-5-ones (I).

				Yield	Found (%)				Required (%)		
No.	Ar	Ar′	M. p.*	(%)	C	H	N	Formula	C	H	N
I-1 [14]	Ph	Ph	201—203° [a, c, h]	70	—	—	—		—	—	—
I-2 [13]	Ph	*p*-C_6H_4Me	161—162 [d, i]	30	68·6	4·7	14·9	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·1
I-3	Ph	*m*-C_6H_4Me	188—191 [b, d, i]	18	69·1	4·9	15·1	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·1
I-4 [14]	Ph	*p*-C_6H_4Me	209—211 [e, i]	68	—	—	—		—	—	—
I-5	Ph	*p*-$MeO{\cdot}C_6H_4$	201—203 [c, j]	45	64·9	4·4	14·1	$C_{16}H_{13}N_3O_3$	65·1	4·4	14·2
I-6	Ph	*p*-C_6H_4Br	247—248 [a, f, h]	40	52·4	2·9	11·6	$C_{15}H_{10}BrN_3O_2$	52·3	2·9	12·2
I-7	*p*-C_6H_4Br	Ph	260—261 [a, f, h]	42	51·5	3·0	11·4	$C_{15}H_{10}BrN_3O_2$	52·3	2·9	12·2
I-8 [14]	Ph	*p*-$NO_2{\cdot}C_6H_4$	314—317 [g, i]	30	—	—	—		—	—	—
I-9 [13]	Ph	2-$C_{10}H_7$	229—230 [b, f, k]	35	71·5	4·2	12·7	$C_{19}H_{13}N_3O_2$	72·3	4·2	13·3

* With decomp. [a] Needles. [b] Plates. [c] From acetone. [d] From benzene–light petroleum. [e] From benzene. [f] From chloroform–light petroleum. [g] From dioxan. [h] Yellow. [i] Orange. Crimson. [k] Red.

Methyl N-*Benzoyloxamate* o-*Tolylhydrazone* (II-2b). Crude 2-phenyl-4-*o*-tolylazo-oxazolin-5-one (I-2) (10 g.) was suspended in methanol (120 ml.). The mixture was made faintly alkaline to litmus by addition of aqueous potassium hydroxide solution (20 ml.), then warmed for 10 min., the orange colour disappearing. After dilution with water and cooling, pale yellow needles (~3 g.) of the *product* were precipitated and, recrystallised from chloroform–light petroleum, had m. p. 136—138° (Found: C, 66·2; H, 5·6; N, 13·5. $C_{17}H_{17}N_3O_3$ requires C, 65·6; H, 5·5; N, 13·5%).

[21] Atkinson, Parkes, and Polya, *J.*, 1954, 4256.
[22] Pinchas, *Analyt. Chem.*, 1955, **27**, 2.
[23] Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194; Hunsberger, *ibid.*, 1950, **72**, 5626.

TABLE 2.

N-Benzoyloxamic acid arylhydrazone derivatives (II).

(Ultraviolet absorption spectra in methanol; $\lambda_{max.}$ in mμ.)

No.	Ar′	Deriv.	M. p.*	$\lambda_{max.}$ (log ε)
II-2b	*o*-C_6H_4Me	Me ester	136—138° [a, b, h]	230, 290, 336 (4·22, 3·82, 4·01)
c	,,	Amide	184—189 [h]	
d	,,	Hydrazide	180—184 [h]	234, 281, 342 (4·19, 3·75, 3·93)
II-3b	*m*-C_6H_4Me	Me ester	181—184 [a, h]	230, 290, 332 (4·18, 3·77, 4·20)
c	,,	Amide	166—168 [i]	
d	,,	Hydrazide	191—193 [a, h]	
II-4d	*p*-C_6H_4Me	,,	157—159 [b, h]	233, 293, 337 (4·30, 3·95, 4·18)
II-5d	*p*-MeO·C_6H_4	,,	158—162 [a, h]	
II-6d	*p*-C_6H_4Br	,,	175—180 [h]	
II-7d	Ph †	,,	158—160 [h]	
II-8d	*p*-NO_2·C_6H_4	,,	170—176 [h]	
II-9d	2-$C_{10}H_7$	,,	168—171 [h]	

* With decomp. † *N*-*p*-Bromobenzoyl (not *N*-benzoyl). [a–i] See Table 1.

TABLE 3.

1,5-Diaryl-1,2,4-triazole-3-carboxylic acids and their derivatives (III).

					Found (%)				Required (%)		
No.	Ar	Ar′	X	M. p.	C	H	N	Formula	C	H	N
III-1a [15]	Ph	Ph	OH	177—178°*	—	—	—		—	—	—
b [15]			OMe	158—159 [d]	—	—	—		—	—	—
c [15]			NH_2	198—199	—	—	—		—	—	—
d			NH·NH_2	185—186 [e]	64·8	5·0	24·9	$C_{15}H_{13}N_5O$	64·5	4·7	25·1
e			NH·NH·CO·NH_2	198—200 [m]	59·1	4·6	25·6	$C_{16}H_{14}N_6O_2$	59·6	4·4	26·1
f			NHPh	255—256 [f]	72·5	4·7	15·6	$C_{21}H_{16}N_6O,\frac{1}{2}H_2O$	72·2	4·9	16·0
g			NHEt	195—196 [l]	70·6	5·7	19·1	$C_{17}H_{16}N_4O$	69·8	5·5	19·2
h			N_3	124—125 *[l]	62·1	3·7	28·4	$C_{15}H_{10}N_8O$	62·1	3·5	28·9
III-2a	Ph	*o*-C_6H_4Me	OH	171—172 *[f]	67·9	4·7	14·9	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·1
b			OMe	92—94 [d]	69·7	5·2	14·3	$C_{17}H_{15}N_3O_2$	69·6	5·2	14·3
d			NH·NH_2	152—153 [d]	65·9	5·3	23·6	$C_{16}H_{15}N_5O$	65·5	5·3	23·9
III-3a	Ph	*m*-C_6H_4Me	OH	182—183*[f]	68·3	4·7	14·8	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·1
b			OMe	127—128 [f]	70·2	5·3	14·4	$C_{17}H_{15}N_3O_2$	69·6	5·2	14·3
III-4a	Ph	*p*-C_6H_4Me	OH	177—178*[f]	68·3	4·7	14·9	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·1
b			OMe	132—133 [d]	69·6	5·1	14·3	$C_{17}H_{15}N_3O_2$	69·6	5·2	14·3
c			NH_2	155—156 [d]	70·8	5·2	18·8	$C_{16}H_{14}N_4O,\frac{1}{4}C_6H_6$	71·0	5·3	18·4
d			NH·NH_2	149—150·5 [f]	65·5	4·9	23·6	$C_{16}H_{15}N_5O$	65·5	5·1	23·9
IV-5a	Ph	*p*-MeO·C_6H_4	OH	176—177 *[f]	65·0	4·6	13·8	$C_{16}H_{13}N_3O_3$	65·1	4·4	14·2
b			OMe	106—107	65·9	4·8	13·5	$C_{17}H_{15}N_3O_3$	66·0	4·9	13·6
c			NH_2	183—184 [f]	65·2	4·7	18·4	$C_{16}H_{14}N_4O_2$	65·8	4·7	18·8
d			NH·NH_2	165—167 [f]	61·8	5·0	22·3	$C_{16}H_{15}N_5O_2$	62·6	4·8	22·4
h			N_3	107—108 [d]	60·5	4·0	25·9	$C_{16}H_{12}N_8O_2$	60·0	3·8	26·2
III-6a	Ph	*p*-C_6H_4Br	OH	179—180 *[d]	52·2	3·0		$C_{15}H_{10}BrN_3O_2$	52·3	2·9	
b			OMe	138—139 [f]	53·9	3·5		$C_{16}H_{12}BrN_3O_2$ †	54·2	3·4	
c			NH_2	176·5—178	52·0	3·4		$C_{15}H_{11}BrN_4O$	52·5	3·2	
d			NH·NH_2	175—177	50·2	3·4	19·4	$C_{15}H_{12}BrN_5O$	50·3	3·4	19·5
III-7b	*p*-C_6H_4Br	Ph	OMe	157—159 [d]	53·7	3·6	11·4	$C_{16}H_{12}BrN_3O_2$	54·2	3·4	11·6
d			NH·NH_2	159—161 [d]	51·2	3·5	18·6	$C_{15}H_{12}BrN_5O$	50·3	3·4	19·5
IV-8b	Ph	*p*-NO_2°C_6H_4	OMe	179—181	59·7	4·0	17·2	$C_{16}H_{12}N_4O_4$	59·7	3·7	17·1
d			NH·NH_2	201—203 [f]	55·3	4·1	25·7	$C_{15}H_{12}N_6O_3$	55·5	3·7	25·9
III 9a	Ph	2-$C_{10}H_7$	OH	193—194 *[f]	71·8	4·2	13·3	$C_{19}H_{13}N_3O_2$	72·3	4·2	13·3

* With decomp. † Found: Br, 22·8. Reqd.: Br, 22·1%.
[a–f] See Table 1. [l] From aq. MeOH. [m] From aq. EtOH.

TABLE 4.

1,5-Diaryl-3-hydroxymethyl-1,2,4-triazoles (IV).

				Yield	Found (%)				Required (%)		
No.	Ar	Ar′	M. p.*	(%)	C	H	N	Formula	C	H	N
IV-1	Ph	Ph	153—154°	80	71·8	5·2	15·9	$C_{15}H_{13}N_3O$	71·7	5·2	16·7
IV-2	Ph	*o*-C_6H_4Me	136—138	45	72·4	5·6	15·9	$C_{16}H_{15}N_3O$	72·4	5·7	15·8
IV-3	Ph	*m*-C_6H_4Me	159—161	70	72·9	5·8	15·3	$C_{16}H_{15}N_3O$	72·4	5·7	15·8
IV-4	Ph	*p*-C_6H_4Me	151·5—152·5	85	72·6	5·6	15·7	$C_{16}H_{15}N_3O$	72·4	5·7	15·8
IV-5	Ph	*p*-MeO·C_6H_4	152—153	80	68·8	5·4	14·6	$C_{16}H_{15}N_3O_2$	68·3	5·4	14·9
IV-6	Ph	*p*-C_6H_4Br	164—165	65	54·9	3·9		$C_{15}H_{12}BrN_3O$ †	54·6	3·6	
IV-7	*p*-C_6H_4Br	Ph	133—135	55	54·8	3·8	12·2	$C_{15}H_{12}BrN_3O$	54·6	3·6	12·7

* Recryst. from benzene–light petroleum (b. p. 40—60°). † Found: Br, 23·8. Reqd.: Br, 24·2%.

TABLE 5.

1,5-Diaryl-1,2,4-triazole-3-aldehydes (VI) and their derivatives.

No.	Compound & yield	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
VI-1	Ar = Ar′ = Ph								
	Aldehyde (50%)	144—145° [d]	72·5	4·7	16·6	$C_{15}H_{11}N_3O$	72·3	4·5	16·8
	Oxime	162—170 [f]	67·9	4·7	21·0	$C_{15}H_{12}N_4O$	68·1	4·6	21·2
	Semicarbazone	222—223 [f]	62·1	4·6	26·4	$C_{16}H_{14}N_6O$	62·7	4·6	27·4
	2,4-Dinitrophenylhydrazone	247—249 [f] (232°?)	58·2	3·6	22·2	$C_{21}H_{15}N_7O_4$	58·7	3·5	22·8
	1-(1,5-Diphenyl-1,2,4,-triazol-3-ylmethylene)-2-(1,5-diphenyl-1,2,4,-triazol-3-ylcarbonyl)hydrazine	232—233, [m] 247—249	69·9	4·3	21·9	$C_{30}H_{22}N_8O$	70·6	4·3	21·9
VI-2	Ar = Ph, Ar′ = *o*-C_6H_4Me								
	Aldehyde (10%)	80—82 [d]	73·3	4·9	16·1	$C_{16}H_{13}N_3O$	73·0	5·0	16·0
	2,4-Dinitrophenylhydrazone	230—232, [f] 256—258	58·5	4·0	21·0	$C_{22}H_{17}N_7O_4,\frac{1}{2}H_2O$	58·4	4·0	21·7
VI-3	Ar = Ph, Ar′ = *m*-C_6H_4Me								
	Aldehyde (15%)	98—100 [d]	72·8	5·0	15·8	$C_{16}H_{13}N_3O$	73·0	5·0	16·0
VI-4	Ar = Ph, Ar′ = *p*-C_6H_4Me								
	Aldehyde (45%)	92—93 [d]	73·2	5·3	16·1	$C_{16}H_{13}N_3O$	73·0	5·0	16·0
	Semicarbazone	226—227 [m]	63·5	5·2	25·8	$C_{17}H_{16}N_6O$	63·7	5·0	26·2
	2,4-Dinitrophenylhydrazone	235—236 [d]	59·6	3·9	21·6	$C_{22}H_{17}N_7O_4$	59·6	3·9	22·1
VI-5	Ar = Ph, Ar′ = *p*-MeO·C_6H_4								
	Aldehyde (40%)	93—94 [d]	68·7	4·7	14·5	$C_{16}H_{13}N_3O_2$	68·8	4·7	14·1
	2,4-Dinitrophenylhydrazone	227—228 [d]	60·7	4·2	19·4	$C_{22}H_{17}N_7O_5,\frac{1}{2}C_6H_6$	60·3	4·1	19·7
VI-6	Ar = Ph, Ar′ = *p*-C_6H_4Br								
	Aldehyde (50%)	128—130 [d]	55·4	3·2	12·1	$C_{15}H_{10}BrN_3O$	54·9	3·1	12·8
	Oxime	173—175 [f]	52·9	3·4		$C_{15}H_{11}BrN_4O$ *	52·5	3·2	
	Semicarbazone	235—236 [f]	49·6	3·5		$C_{16}H_{13}BrN_6O$ †	49·9	3·4	
	2,4-Dinitrophenylhydrazone	223—224, and 252—254 [f]	50·2	2·7	18·8	$C_{21}H_{14}BrN_7O_4$	49·6	2·8	19·3
VI-7	Ar = *p*-C_6H_4Br, Ar′ = Ph								
	Aldehyde (20%)	88—89 [n]	55·2	3·2	12·2	$C_{15}H_{10}BrN_3O$	54·9	3·1	12·8

* Found: Br, 24·2. Reqd.: Br, 24·3%. † Found: Br, 21·6. Reqd.: Br, 20·8%.
[d, f, m] See Table 1. [n] From ether–light petroleum.

TABLE 6.

Infrared absorption bands (cm.$^{-1}$) of 1,5-diaryl-1,2,4-triazole-3-aldehydes (KBr discs; Perkin-Elmer double-beam spectrophotometer no. 221).

No.	Ar	Ar′	C=O stretching		C–H stretching
VI-1	Ph	Ph	1740	1680(sh)w	2840, 2820, 2780, 2720vw, 2680vw
VI-2	Ph	*o*-C_6H_4Me	1717	1670w	2960, 2925, 2860m, 2790
VI-3	Ph	*m*-C_6H_4Me	1706	1685m	2925, 2870, 2810
VI-4	Ph	*p*-C_6H_4Me	1720, 1711	—	2920, 2840m, 2790, 2720vw, 2680vw
VI-5	Ph	*p*-MeO·C_6H_4	1710	1682wm	3020, 2970, 2940, 2910vw, 2875, 2840m, 2780
VI-6	Ph	*p*-C_6H_4Br	1710	1670(sh)w	2840, 2790
VI-7	*p*-C_6H_4Br	Ph	1710	1670w	2850

Phenyl-1-p-*tolyl*-1,2,4-*triazole*-3-*carboxylic Acid* (III-4a) *and its Methyl Ester* (III-4b).—Crude 2-phenyl-4-*p*-tolylazo-oxazolin-5-one (I-4) (12 g.), suspended in methanol (150 ml.), was treated as in the preceding experiment. The *ester* (6 g.), recrystallised from benzene–light petroleum, had m. p. 132—133°. After the azlactone in methanol had been made alkaline to litmus, then warmed for 5 min. and freed from most of the methanol by evaporation, cautious acidification of the mixture with concentrated hydrochloric acid gave the *acid* (6 g.), m. p. 177—178° (from chloroform–light petroleum). At intermediate alkalinities both acid and ester were obtained. The ester was allowed to separate from the alkaline mixture, then acidification of the filtrate gave the acid.

5-Phenyl-1-p-tolyl-1,2,4-triazole-3-carboxylic Acid Hydrazide (III-4d).—The crude azlactone (I-4) (7 g.) was suspended in methanol (100 ml.) and treated with 85% hydrazine hydrate in excess; the original deep orange colour was discharged and a yellow precipitate formed [4 g.; m. p. 156—160° (slight decomp.)]. This was heated with 2N-aqueous sodium carbonate (20 ml.) for 2—3 min.; the material dissolved and the colour was discharged. On cooling, buff crystals of the *hydrazide* (3·5 g.), m. p. 149—150·5° (from chloroform–light petroleum; charcoal), were precipitated. Alternatively the pure azlactone (2·3 g.) was suspended in methanol (50 ml.) and treated with a slight excess of 85% hydrazine hydrate in the cold. After 5 min. water (10 ml.) and 2N-sodium carbonate (1—2 ml.) were added and the mixture warmed for 2—3 min. Filtration, evaporation, and cooling gave the hydrazide (1·8 g., 75%), identical with the preceding preparation and the product prepared by the following method. The triazole-ester (III-4b) (0·3 g.) in ethanol (10 ml.) and 85% hydrazine hydrate (2 ml.) were heated under reflux for 1 hr. Concentration of the mixture and dilution with water gave the hydrazide (0·25 g., 83%), m. p. 149—150°.

5-Phenyl-1-p-tolyl-1,2,4-triazole-3-carboxyamide (III-4c).—To the azlactone (I-4) (0·50 g.) suspended in methanol (20 ml.), concentrated aqueous ammonia (10 ml.) was added. The mixture was heated for 5 min. The nearly colourless solution was concentrated and adjusted to pH 8 with concentrated hydrochloric acid and extracted with chloroform. Acidification of the aqueous phase gave a few mg. of the triazolecarboxylic acid (III-4a). The chloroform extract was evaporated to dryness and the residual *amide* recrystallised three times from benzene–light petroleum; it had m. p. 155—156° (0·17 g., 37%).

1,5-Diphenyl-1,2,4-triazole-3-carbonylsemicarbazide (III-1e). The crude azlactone (I-1) (2 g.) was suspended in methanol (50 ml.) and water (5 ml.). Semicarbazide hydrochloride (6 g.) was added in portions, neutralised (to litmus) after each addition with sodium hydrogen carbonate, and the whole was heated under reflux for 30 min. After concentration, dilution with water, and cooling, the *semicarbazide* (1·7 g.) that was recrystallised from aqueous alcohol had m. p. 198—200°. It did not depress the m. p. of the semicarbazide made by treatment of the hydrazide (III-1d) (0·3 g.) in glacial acetic acid (10 ml.) with sodium cyanate in excess.

1,5-Diphenyl-1,2,4-triazole-3-carboxyanilide (III-1f) *and 3-Anilinomethyl-1,5-diphenyl-1,2,4-triazole* (V).—The crude azlactone (I-1) (2 g.) in methanol (25 ml.) was boiled with aniline (0·8 g.) for 75 min., to discharge the yellow colour. The *anilide* was filtered off, washed with water, and recrystallised from chloroform–light petroleum (charcoal); the m. p. was 255—256° (0·7 g.).

The anilide (1 g.) was boiled with lithium aluminium hydride (0·25 g.) in ether (50 ml.) for 5 hr., then left at room temperature overnight. 80% Aqueous methanol (3 ml.) was added; filtration and evaporation of the filtrate gave a crude powder (0·7 g.). Fractional crystallisation from ethanol gave unchanged amide (0·2 g.) and white crystals of *3-anilinomethyl-1,5-diphenyl-1,2,4-triazole* (0·3 g.), m. p. 151—152° (Found: C, 77·6; H, 5·7; N, 17·2. $C_{21}H_{18}N_4$ requires C, 77·3; H, 5·6; N, 17·2%).

1,5-Diphenyl-1,2,4-triazole-3-carbonyl Azide (III-1h).—Sodium nitrite (1·5 g.) in water (15 ml.) was added to a solution of the acid hydrazide (III-1d) (4·7 g.) in acetic acid (50 ml.) and 2N-hydrochloric acid (15 ml.) at 0—5°. After 5 min. the mixture was diluted with water. The *azide* precipitated was collected, washed with water, recrystallised from aqueous methanol, and dried at 60° in a vacuum [4·5 g.; 92%; m. p. 124—125° (decomp.)].

3-Hydroxymethyl-5-phenyl-1-p-tolyl-1,2,4-triazole (IV-4).—A suspension of the triazole-ester (III-4b) (3·7 g.) in ether (50 ml.) was added to lithium aluminium hydride (0·5 g.) in ether (150 ml.). The mixture was boiled under reflux for 5 hr., then treated with 10% aqueous methanol (10 ml.) and boiled for 20—30 min. The inorganic material was filtered off and washed with methanol. The combined methanolic filtrates were concentrated to 15—20 ml. Dilution with water gave a precipitate of the *alcohol* (3·0 g.), m. p. 151·5—152·5° (from benzene–light petroleum).

5-Phenyl-1-p-tolyl-1,2,4-triazole-3-aldehyde (VI-4).—The alcohol (IV-4) (1·0 g.) and lead tetra-acetate (2·5 g.) were boiled under reflux in sodium-dried benzene (30 ml.) for 6 hr. The excess of reagent was destroyed by boiling for 15 min. more with a few drops of ethylene glycol. The mixture was filtered and evaporated to a syrup which was dissolved immediately in absolute ethanol (20 ml.) containing glacial acetic acid (1 ml.). Girard-T reagent (0·7 g.) was added and the mixture was boiled under reflux for 1 hr. Most of the ethanol was evaporated and water (50 ml.) added, with sufficient sodium hydrogen carbonate to neutralise the acetic acid. Repeated extraction with chloroform removed non-aldehydic material. The residual clear

aqueous solution was treated with 40% aqueous formaldehyde (15 ml.), concentrated hydrochloric acid (3 ml.), and chloroform (20 ml.). The mixture was heated gently for 3—5 min. After separation of the phases the aqueous phase was warmed and extracted with a second portion of chloroform (20 ml.). The combined chloroform solutions were evaporated to dryness. The residual *aldehyde* solidified on treatment with cold ether and was recrystallised from benzene–light petroleum (0·42 g.), then having m. p. 92—93°.

1,5-*Diphenyl*-1,2,4-*triazole*-3-*aldehyde* (VI-1).—(i) N-*Bromosuccinimide method.* The alcohol (IV-1) (0·6 g.) and *N*-bromosuccinimide (0·6 g.) in carbon tetrachloride (10 ml.) and benzene (10 ml.) were boiled under reflux for 90 min. The deep orange solution was cooled, filtered, and evaporated to dryness on a water-bath. The lachrymatory residue was boiled for 10 min. with 2N-hydrochloric acid (10 ml.). The mixture was filtered hot. The filtrate was treated with 2,4-dinitrophenylhydrazine reagent and gave the *dinitrophenylhydrazone* (0·3 g., 30%), m. p. 247—249° (with a possible change of phase around 232°).

(ii) *Kalb–Gross method.* The hydrazide (III-1d) (2·0 g.) in ethanol (30 ml.) was added in a thin stream with rapid stirring to a solution of potassium ferricyanide (4·8 g.) in a mixture of 20% aqueous ethanol (80 ml.) and 8% aqueous ammonia (20 ml.). After nitrogen evolution had ceased (30—60 sec.) the mixture was acidified with hydrochloric acid and treated with a solution of 2,4-dinitrophenylhydrazine (0·6 g.) in ethanol (20 ml.) containing concentrated hydrochloric acid (1 ml.). After 20 min. the hydrazone (0·75 g., 24%), identical with that obtained by method (i), was obtained.

(iii) *McFadyen–Stevens method.* The hydrazide (II-1d) (3·2 g.) in dry pyridine (15 ml.) was cooled in ice; benzenesulphonyl chloride (2·1 g.) was added dropwise with stirring in 15 min. After 30 min. at room temperature water was added dropwise. The precipitate when washed with water and recrystallised from chloroform–light petroleum had m. p. 239—241° (2·7 g., 56%) (Found: C, 60·2; H, 4·3; N, 16·0. $C_{21}H_{17}N_5O_3S$ requires C, 60·1; H, 4·1; N, 16·7%).

The *sulphonylhydrazide* (1·1 g.) and powdered soft glass (0·6 g.) were heated in ethylene glycol (10 ml.) at 160—165°. Anhydrous sodium carbonate (0·14 g.) was added with rapid stirring. When the vigorous evolution of nitrogen had ceased (2—3 min.) the mixture was rapidly cooled to room temperature and treated with ethanol (30 ml.), followed immediately by a solution of 2,4-dinitrophenylhydrazine (0·5 g.) in 50% aqueous ethanol (10 ml.) containing a few drops of concentrated hydrochloric acid. After 20 min. the dinitrophenylhydrazone (0·48 g., 42%) was filtered off; it was identical with the samples prepared by the other methods.

β-(5-*Phenyl*-1-p-*tolyl*-1,2,4-*triazol*-3-*yl*)*acrylic Acid.*—Dry 5-phenyl-1-*p*-tolyl-1,2,4-triazole-3-aldehyde (VI-4) (0·6 g.) and malonic acid (0·5 g.) in dry pyridine (15 ml.) containing piperidine (3 drops) were boiled under reflux for 7 hr. until the slow evolution of gas had almost ceased. The solution was concentrated to 5 ml., poured into water (70 ml.), and acidified with hydrochloric acid. The precipitate was extracted with sodium hydrogen carbonate solution. The *acid* was reprecipitated with hydrochloric acid and, recrystallised from benzene–light petroleum (charcoal), had m. p. 203—204° (0·18 g., 27%) (Found: C, 70·8; H, 5·0; N, 13·3. $C_{18}H_{15}N_3O_2$ requires C, 70·8; H, 5·0; N, 13·8%).

The same method was used to prepare (in similar yields) β-(1,5-*diphenyl*-1,2,4-*triazol*-3-*yl*)*acrylic acid*, m. p. 201—202° (Found: C, 70·4; H, 4·7; N, 14·4. $C_{17}H_{13}N_3O_2$ requires C, 70·1; H, 4·5; N, 14·4%), and β-(1-p-*methoxyphenyl*-5-*phenyl*-1,2,4-*triazol*-3-*yl*)*acrylic acid*, m. p. 187—188° (Found: C, 67·3; H, 4·8; N, 12·6. $C_{18}H_{15}N_3O_3$ requires C, 67·3; H, 4·7; N, 13·1%).

3-*Methyl*-1-*trityl*-1,2,4-*triazole*.—3-Methyl-1,2,4-triazole was prepared from 5-amino-3-methyl-1,2,4-triazole [24] by diazotisation in the presence of hypophosphorous acid.[25] Dry methyltriazole (2·0 g.) in absolute methanol (15 ml.) was treated with sodium (0·5 g.). The methanol was evaporated and the residue first dried at 85°, then boiled under reflux with dry benzene (30 ml.) and triphenylmethyl chloride (6·0 g.) for 2 hr. The solution was filtered and the residue washed with warm benzene. The combined benzene extracts were concentrated until cooling and addition of ether gave the *derivative* as cream needles or prisms (3·7 g., 54%), m. p. 195—196° (Found: C, 81·3; H, 5·9; N, 13·8. $C_{22}H_{19}N_3$ requires C, 81·2; H, 5·9; N, 12·9%). In another preparation a *compound*, m. p. 135—136°, was obtained as prisms (5·5 g., 51%) (Found: C, 84·5; H, 6·0; N, 7·5; O, 2·3. $C_{22}H_{19}N_3,Ph_3C{\cdot}OH$ requires C, 84·1;

[24] Thiele and Heidenreich, *Ber.*, 1893, **26**, 2598.
[25] Henry and Finnegan, *J. Amer. Chem. Soc.*, 1954, **76**, 290.

H, 6·0; N, 7·2; O, 2·7%). Mild treatment of the adduct in ethanolic hydrochloric acid gave free triphenylmethanol.

Tritylation of 1,2,4-triazole in the same manner gave white prisms (from benzene–ether), m. p. 210—211° (Found: C, 81·2; H, 5·4; N, 13·7. $C_{21}H_{17}N_3$ requires C, 81·0; H, 5·5; N, 13·5%).

Methyltrityltriazole (3·25 g.) in sodium-dried benzene (30 ml.) and methyl iodide (3 g.) were boiled under reflux for 4 hr. Bronze plates of *methiodide*, m. p. >185—190° (decomp.) (Found: I, 27·5. $C_{23}H_{22}N_3I$ requires I, 27·2%), were obtained (1·38 g.), or in a higher yield (2·1 g., 44%) when the filtered reaction mixture was treated with more methyl iodide.

This iodide (2·0 g.) in absolute methanol (30 ml.) containing piperidine (3 drops) was boiled under reflux with *p*-nitrosodimethylaniline (0·66 g.) for 5 hr. On cooling, black plates (0·3 g.) of 4,4′-bisdimethylaminoazoxybenzene,[26] m. p. 236—238° (from light petroleum), were obtained (Found: C, 67·9; H, 7·0; N, 19·7. Calc. for $C_{16}H_{20}N_4O$: C, 67·6; H, 7·0; N, 19·7%). Evaporation of the filtered methanol solution gave a black tar.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF TASMANIA,
HOBART.

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[26] Schraube, *Ber.*, 1875, **8**, 616.