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### 2-Oxazolin-4-ones and their Conversion into 3-Hydroxymethyl-1,2,4triazoles

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2-Aryl-2-oxazolin-4-ones (I) react with hydrazine hydrate to yield 5-substituted-3-Hydroxymethyl-1,2,4-triazoles (II). 2-Aryl-2-oxazolin-4-ones and monosubstituted hydrazines give 1,3-disubstituted-5-hydroxymethyl-1.2,4triazoles (III). These are compared with the known 1,5-disubstituted-3-hydroxymethyl-1,2,4-triazoles (IV).

Few examples of the 2 oxazolin-4-one system (I;  $R^1$ ,  $R^2$ ,  $R^3 = H$ , alkyl, or aryl) are known, although the reaction of diazomethane with benzoyl isocyanate<sup>1</sup> and terephthaloyl'di-isocyanate<sup>2</sup> has been reported to give the oxazolinone (Ia:  $R^1 = Ph$ ,  $R^2 = R^3 = H$ ) and pphenylenebis-2-(2-oxazolin-4-one) respectively; the oxazoline (I;  $R^1 = R^2 = R^3 = Ph$ ) has been prepared by the reaction of benzoyl chloride and 4,4-diphenyl- $\Delta^2$ -1.2.3-triazolin-5-one.<sup>3</sup> A claim <sup>4</sup> that (I;  $R^1 = R^2 =$  $R^3 = Ph$ ) was formed by the reaction of benzilic acid with benzonitrile in concentrated sulphuric acid, has been shown to be incorrect.<sup>5</sup>



The reaction of acyl isocyanates with diazomethane<sup>1</sup> has been used to prepare (Ib;  $R^1 = o$ -EtOC<sub>6</sub>H<sub>4</sub>,  $R^2 =$  $R^3 = H$ ) and (Ic;  $R^1 = p - ClC_6 H_4$ ,  $R^2 = R^3 = H$ ). The reaction of phenyldiazomethane and benzoyl isocyanate gave (Id;  $R^1 = R^2 = Ph$ ,  $R^3 = H$ ) in poor yield. Diphenyldiazomethane gave no oxazolinone in an analogous reaction, benzophenone azine being the only product identified.

The unstable 2-oxazolin-4-ones were treated immediately with hydrazine hydrate or monosubstituted hydrazines; thus (Ia-d) with hydrazine hydrate yielded 3-hydroxymethyl-1,2,4-triazoles (II) [equation (1)].

Compound (IIa;  $R^1 = Ph$ ,  $R^2 = H$ ) was unambiguously synthesized from methyl benzimidoate and hydroxyacetohydrazide; it was also formed by condensation of methyl benzimidoate and ethoxyacetohydrazide, followed by cleavage of the intermediate 5-ethoxymethyl-3-phenyl-1,2,4-triazole with 55% hydriodic acid. Reaction of (Ia) with ethyl hydrazinoformate gave a low yield of (IIa) as the only product isolated. Loss of the ethoxycarbonyl group might have occurred before or after the triazole ring formation.

Reaction of (Id) with hydrazine hydrate yielded (IId:  $R^1 = R^2 = Ph$ ), identical with the alcohol formed by catalytic reduction of 5-benzoyl-3-phenyl-1,2,4-triazole.6

<sup>1</sup> J. C. Sheehan and P. T. Izzo, J. Amer. Chem. Soc., 1949, 71, 4059. <sup>2</sup> R. Neildein and R. Bottler, Ber., 1967, 100, 698. <sup>3</sup> W. Hohenlohe-Ochringen, Monatsh., 1958, 89, 58

- <sup>3</sup> K. Hohenlohe-Oehringen, Monatsh., 1958, 89, 588.

<sup>4</sup> F. R. Japp and A. Findlay, J. Chem. Soc., 1899, 75, 1027.
<sup>5</sup> C. W. Bird, J. Org. Chem., 1962, 27, 4091.
<sup>6</sup> E. J. Browne and J. B. Polya, J. Chem. Soc. (C), 1968, 824.
<sup>7</sup> A. Mustafa and A. E. A. A. Hassan, J. Amer. Chem. Soc., 704. 1957, 79, 3846.

New N-unsubstituted 3-hydroxymethyl-1,2,4-triazole are listed in Table 1.

The formation of hydroxymethyl-1,2,4-triazoles by reaction (1) is analogous to the formation of 3-o-hydroxyphenyl-1,2,4-triazoles from 1,3-benzoxazin-4-ones,7 and



of pyrazoles from  $\gamma$ -pyrones,<sup>8</sup> chromones, or thiochromones.9,10

The reaction of (Ia or c) with monosubstituted hydrazines gave products of empirical formulae consistent with any one of the isomeric structures (III), (IV), or (V). The products were not the known 1,5-di-(IV).11,12 substituted-3-hydroxymethyl-1,2,4-triazoles 5-Hydroxymethyl-1,3-diphenyl-1,2,4-triazole prepared as in equation (3), was identical with the product of the reaction of (Ia) with phenylhydrazine. The products of the reaction of (I) with monosubstituted hydrazines must thus be considered to be (III) [equation (2)]. The new 1,3-disubstituted-5-hydroxymethyl-1,2,4-triazoles are listed in Table 2.

- <sup>8</sup> C. Ainsworth and R. G. Jones, J. Amer. Chem. Soc., 1954, 76, 3172.
- <sup>9</sup> E. Koenigs and J. Freund, Ber., 1947, 80, 143.
- <sup>10</sup> W. Baker, J. B. Harborne, and W. D. Ollis, J. Chem. Soc., 1952, 1303.
  - E. J. Browne and J. B. Polya, J. Chem. Soc., 1962, 575.
     E. J. Browne and J. B. Polya, Tetrahedron, 1962, 18, 539.

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This reaction seems analogous to the formation of 1-phenyl-5-substituted-pyrazoles from  $\gamma$ -pyrones and phenylhydrazine,<sup>8</sup> and of similar reactions of chromones<sup>13</sup> or thiochromones <sup>10</sup> with this reagent. Reaction of the hydrazine NH<sub>2</sub> group must then occur at the 2-position of (I) and not at the C=O group. In contrast, 1,3-benz-oxazin-4-ones are reported <sup>7</sup> to give 4-phenylhydrazino-1,3-benzoxazines with phenylhydrazine, and not to undergo ring opening to 1,2,4-triazoles.

The i.r. spectra of (III) resembled those of (IV).<sup>12</sup> A strong symmetrical band (width *ca.* 300 cm.<sup>-1</sup>) was

methylsulphoxide at  $20^{\circ}$ . Coupling constants were in the range  $5 \cdot 5 - 6 \cdot 5$  Hz.

At higher temperatures the doublet collapsed to a singlet, and the triplet to a broad absorption of variable position. Addition of  $D_2O$  contracted the doublet to a singlet (2H) in the range 5.05—5.3, and the triplet to a singlet (1H) at higher field, corresponding to an HDO resonance. The spectrum of (IIIf) in dimethyl sulphoxide at 22° did not show splitting of the CH<sub>2</sub>OH protons. A singlet (2H) was present at  $\tau$  5.3, and on addition of  $D_2O$  a second singlet (2H) appeared at 6.1.

		Found (%)						Required (%)		
	M.p.	Yield (%)	ć	н	N	Formula	ć	H	Ŋ	
(IIa)	160-161° ª	80	61.1	5.1	24.0	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O	61.7	$5 \cdot 2$	24.0	
(IIb)	167—168 a	67	60.2	6.0	18.8	$C_{11}H_{13}N_{3}O_{2}$	60.3	6.0	19.2	
(IIc)	211—212 a	76	51.6	3.9	20·0 b	C <sub>9</sub> H <sub>8</sub> N <sub>3</sub> ClO	51.5	3.8	20·0 b	
(IId)	163—164 <i>a</i>	6	71.5	5.3	16.2	$C_{15}H_{13}N_3O$	71.7	$5 \cdot 2$	16.7	

TABLE 1

<sup>a</sup> Recrystallized from methanol-chloroform. <sup>b</sup> Found: Cl, 17.7; requires: Cl, 17.0%.

TABLE 2

			Found (%)				Required (%)		
Compound.	M.p. *	Yield (%)	б	<u>A</u>	N	Formula	<del>ر</del>	H	N
(ĪIIa)	175—176° a	80	71.6	$5 \cdot 2$	17.0	$C_{15}H_{13}N_{3}O$	71.7	$5 \cdot 2$	16.7
(IIIb)	135—136 <sup>b</sup>	32	63.5	6.0	21.9	$C_{10}H_{11}N_{3}O$	63.5	5.8	$22 \cdot 2$
(IIIc)	153—154 a	43	72.8	5.9	16.1	$C_{16}H_{15}N_{3}O$	72.5	5.7	15.8
(IIId)	201-202 a	70	53.95	$3 \cdot 6$	12.4	$C_{15}H_{12}BrN_{3}O$	$54 \cdot 4$	$3 \cdot 6$	12.7
(IIIe)	212—213 a	65	61.2	$4 \cdot 2$	18.8	$C_{15}H_{12}N_4O_3$	60.8	4.05	18.9
(IIIf)	272—273 •	75	<b>64</b> ·8	4.5	14.0	$C_{16}H_{13}N_{3}O_{3}$	65.0	4.4	14.2
(IIIg)	199—200 a	50	63.05	$4 \cdot 3$	14.80	$C_{15}H_{12}ClN_{3}O$	63.0	4.2	14.7 •
(111h)	143—144 a	39	<b>64</b> ·1	<b>4</b> ·7	14·0ª	C <sub>16</sub> H <sub>14</sub> CIN <sub>3</sub> O	64.1	4.7	14.0 4

• Recrystallized from a ethanol and b chloroform-light petroleum. Found: Cl, 12.7; required: Cl, 12.4%. d Found: Cl, 11.3; required: Cl, 11.8%.

present near 3200 cm.<sup>-1</sup> in the spectra of (III, a-e, g, h), and a weak shoulder near 3350 cm.<sup>-1</sup> in those of (IIIa, c, g, h). This band was effectively unchanged when the spectra of (IIIa or b) were determined in chloroform solution at various dilutions, suggesting intramolecular hydrogen bonding. In the spectrum of (IIIf) a strong band was present at 3340 cm.<sup>-1</sup>, with broad featureless absorption in the range 2100—3200 cm.<sup>-1</sup>. As the presence of a carboxy-group would modify the nature of the hydrogen bonding this compound has been included as a member of the triazole alcohol series (III).

<sup>1</sup>H N.m.r. spectra (data reported as  $\tau$  values) of (III, a, b, c) in deuteriochloroform at 25° showed a doublet (2H) in the range 5·1—5·3, and a triplet (1H) in the region 3·8—5·0. The position of the triplet was temperature dependent, *e.g.* one solution of (IIIa) showed the triplet at 3·18 at 0°, 4·96 at 30°, and 5·67 at 50°, with the doublet at 5·13, 5·16, and 5·17 respectively. This splitting of CH<sub>2</sub>·OH protons is not commonly observed in deuteriochloroform at ambient temperatures. It was also present in the spectrum of (IIIc) in deuteriodimethyl sulphoxide at 30°, and in that of (IIIg) in di-

<sup>13</sup> W. Baker and V. S. Butt, J. Chem. Soc., 1949, 2142.

The n.m.r. spectrum of 1,5-diphenyl-3-hydroxymethyl-1,2,4-triazole (IV;  $R^1 = R^4 = Ph$ ) in deuteriochloroform at 30° showed singlets at  $\tau$  5.18 (2H) and 5.38 (1H). At 50° the latter moved to  $\tau$  5.95, and the former was unchanged; while at 21° the bands coalesced at 5.18 (3H, s). At 0° splitting of the CH<sub>2</sub>OH protons was observed *viz.* a doublet (2H) at  $\tau$  5.17, and a triplet (1H) near  $\tau$  3.0.

Compound (IV;  $R^1 = R^4 = Ph$ ) reacted normally with acetyl chloride to give an acetate,<sup>12</sup> and with thionyl chloride to give the chloromethyl-triazole (VI). However (IIIa or b) formed the chloromethyl derivatives (VIIa or b) with either thionyl chloride or acetyl chloride. No esters were detected with the latter reagent.



<sup>1</sup>H n.m.r. data in deuteriochloroform at 30° were: (VI), 2·45-2·8 (10H), 5·27 (2H, s); (VIIa), 1·8-1·9 (2H), 2·3-2·7 (8H), 5·31 (2H, s); (VIIb), 1·9-2·02 (2H), 2·5-2·8 (3H), 5·34 (2H, s), 6·09 (3H, s). No exchangeable protons were present.

The aromatic protons in the spectra of (VI), 3-methyl-1,5-diphenyl-1,2,4-triazole and 3-hydroxymethyl-1,5-diphenyl-1,2,4-triazole form a complex multiplet in the range 2.4-2.8. In contrast a downfield shift to 1.7-2.0 of two of the aromatic protons is seen in the spectra of (VIIa or b), and also in those of (IIa) and of 1,3-diphenyl-1,2,4-triazole.

It is suggested that the interaction causing this deshielding of what are, apparently, the two H atoms of the C-phenyl group nearest the triazole ring, occurs only when these rings are coplanar. Steric hindrance effectively prevents such coplanarity in 1,5-diaryl-1,2,4-triazoles,<sup>12</sup> and the effect disappears.

Mass spectra of (VI) and (VIIa) are very similar, the parent peak being at 269, and the base peak at 91 (loss of  $C_7H_7$ ) in each case. Other main peaks common to both included 234 (loss of Cl), 193 (loss of ClC<sub>2</sub>H<sub>3</sub>N), 165 (loss of PhCNH), 103 (PhCN), and 77 (Ph). The main difference was the presence of strong peaks in the spectrum of (VI) which were very weak in that of (VIIa). These were at 166 (loss of PhCN), 132 (PhN<sub>2</sub>CNH), and 117 (PhN,C). Assignments of peak origins are tentative only, but seem consistent with the structures.

Ethyl diazoacetate and benzoyl isocyanate have been reported <sup>14</sup> to yield ethyl 1-benzoyl-5-oxo- $\Delta^2$ -1,2,3-triazole-4-carboxylate (VIII) m.p. 116-117°, but other than an analysis no evidence of the structure was given. Tautomers of (VIII), or the acyclic isomer (IX) might be considered as alternatives [equation (4)].



Repetition of the experiment gave a product, m.p. 118-119°.

The i.r. spectrum showed a band at 2150 cm.<sup>-1</sup>, characteristic of a diazo-group. Carbonyl stretching bands were present at 1665 and 1738 cm.<sup>-1</sup>. The n.m.r. spectrum in deuteriochloroform at 26° showed signals at 8.61 (3H, t), 5.62 (2H, q), 2.0-2.6 (5H), and -1.25 (1H).

Accordingly the product designated (VIII) would seem to be more correctly designated (IX). This is consistent with early work 15 showing easy opening of the 1,2,3-triazol-5-one ring to the isomeric diazocompound, which may be recyclized with sodium ethoxide.

#### EXPERIMENTAL

I.r. spectra were determined as Nujol mulls on a Perkin-Elmer spectrophotometer, model No. 221. <sup>1</sup>H N.m.r. spectra were recorded with a JEOL JNM-4-H-100 spectro-

<sup>14</sup> R. Neidlein, Ber., 1964, 97, 3476.

<sup>15</sup> O. Dimroth and, in part, H. Aickelin, B. Brahn, G. Fester, and E. Merckle, Annalen, 1910, 373, 336.

meter. Mass spectra were determined on an EAI QUAD 300 mass spectrometer.

3-Hydroxymethyl-5-phenyl-1,2,4-triazole (IIa).—(i) To compound (Ia)<sup>1</sup> freshly prepared from diazomethane and benzoyl isocyanate (from 0.1M benzamide),16 was added slowly with stirring a slight excess of 60% hydrazine hydrate. When the exothermic reaction had subsided water (10 ml.) was added, and the *alcohol* (12.6 g.) was filtered off, washed with water, and dried.

(ii) Methyl benzimidoate hydrochloride (8.6 g.) was added to a cold solution of potassium hydroxide (2.8 g.) in methanol (75 ml.), and a hot solution of hydroxyacetohydrazide (4.5 g.) in methanol (50 ml.) added at once. The mixture was heated under reflux for 1 hr. after which the solvent was removed under reduced pressure; the residue was extracted with chloroform which contained 10% of methanol (100 ml.). The extract was filtered, concentrated to 25 ml., and cooled to give (IIa) (1.5 g., 40%) identical with the product of the previous reaction.

(iii) To compound (Ia) (3.2 g.) was added a solution of ethyl hydrazinoformate (2.1 g.) in dry pyridine (20 ml.). The solution was heated for 10 min. after which the solvent was removed under reduced pressure. The residual oil dissolved in chloroform (20 ml.), the solution was filtered and cooled to yield (IIa) (0.41 g., 12%), m.p. 157-158°).

5-Hydroxymethyl-1,3-diphenyl-1,2,4-triazole (IIIa).—(i) To compound (Ia) (1.6 g.) dissolved in a slight excess of phenylhydrazine was added 50% aqueous ethanol (10 ml.); the solution was cooled in ice and the triazole was filtered off, washed with water, and dried (2.5 g., 100%), m.p. 170-174°.

(ii) Compound (Ia) (1.6 g.) in ethanol (15 ml.) was added rapidly to a solution of phenylhydrazine hydrochloride (1.45 g.) and sodium acetate (1.6 g.) in water (15 ml.). The solution was warmed for 15 min., and then filtered and cooled to yield (IIIa) (2.0 g., 80%); it was identical with the previous product.

(iii) To crude N-benzimidoyl-N'-phenylhydrazine 17 (10 g.) freshly prepared from methyl benzimidoate and phenylhydrazine, was added benzyloxyacetyl chloride 18 (8 g.); the mixture was cautiously heated to just over 100°. After the initial reaction had ceased the temperature was kept at 100° for 3 hr.; the syrup was then cooled and extracted with benzene  $(2 \times 50 \text{ ml.})$ . Evaporation of the extracts left an oil (8.8 g.), which was chromatographed on alumina in benzene. The first material eluted (4.2 g.) was recrystallized from ether and light petroleum (b.p. 40-60°) to yield the benzyl ether of (IIIa) (2.6 g., 17%) as needles, m.p. 74—75° (Found: C, 77.0; H, 5.6; N, 12.15.  $C_{22}H_{19}$ N<sub>3</sub>O requires C, 77.45; H, 5.6; N, 12.3%); n.m.r. in carbon tetrachloride at 20°: τ 1.8-1.9 (2H), 2.2-2.3 (2H), 2.5-2.8 (11H), 3.35 (2H), and 5.40 (2H).

The benzyl ether (0.79 g.), 48% hydrobromic acid (15 ml.), and glacial acetic acid (5 ml.) were heated at 80-90° for 90 min. The mixture was evaporated to dryness under reduced pressure on a water-bath; the residue was neutralized with 5% aqueous sodium carbonate and extracted with benzene (2  $\times$  25 ml.). Concentration of the solution and the addition of light petroleum gave (IIIa) (0.37 g., 64%) identical with the products from the previous reactions.

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 M. R. Atkinson and J. B. Polya, J. Chem. Soc., 1954, 3319.

<sup>18</sup> F. Benington and R. D. Morin, J. Org. Chem., 1961, 26, 194.

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5-Hydroxymethyl-1-methyl-3-phenyl-1,2,4-triazole (IIIb).---Compound (Ia) (3.2 g.) was added to a solution of methylhydrazine (1.0 g.) in dry pyridine (15 ml.). The mixture was heated on a steam-bath for 10 min. after which the solvent was evaporated off under reduced pressure. The residue was dissolved in ethanol and cooled to give the triazole (1.2 g.).

Compound (Ia) did not give identifiable products with guanidine, thiosemicarbazide, or hydroxylamine.

2(o-Ethoxyphenyl)-2-oxazolin-4-one (Ib), m.p. 88—92°, was made in 67% yield by reaction of diazomethane and o-ethoxybenzoyl isocyanate (cf. refs. 16 and 19). Attempted recrystallization from benzene lowered the m.p.

Reaction of (Ib) with a slight excess of 60% hydrazine hydrate gave the hydroxymethyltriazole (IIb) in 40% yield, calculated from *o*-ethoxybenzamide.

To p-chlorobenzoyl isocyanate,<sup>19</sup> prepared from p-chlorobenzamide (15.5 g.), was added an excess of an ethereal solution of diazomethane, with cooling. 2-(p-Chlorophenyl)-2-oxazolin-4-one (Ic) (9.1 g., 47%) was filtered off, washed twice with dry ether, and dried. The m.p. was 155—158°.

3-p-Chlorophenyl-5-hydroxymethyl-1-phenyl-1,2,4-triazole (IIIg).—Compound (Ic) (2.0 g.) was added to an excess of phenylhydrazine and the mixture was heated for 5 min. Ethanol (40 ml.) was added to the mixture which was filtered whilst hot; the filtrate was cooled to give the *product* (IIIg) (1.5 g.).

2,5-Diphenyl-2-oxazolin-4-one (Id).—To benzoyl isocyanate (from 0·1M-benzamide) in dry ether (20 ml.), was added slowly with cooling, a solution of phenyldiazomethane (15·8 g.) in dry ether (20 ml.). Nitrogen was evolved but no precipitate formed. Evaporation of the solvent left an unstable yellow oil, which was used without delay.

3-Phenyl-5-phenylhydroxymethyl-1,2,4-triazole (IId).—(i) To the crude compound (Id) prepared above, was added an excess of 99% hydrazine hydrate; the mixture was warmed on a steam-bath for 10 min. after which it was cooled and extracted with ether (50 ml.). The ether-insoluble oil was dissolved in 5% aqueous sodium hydroxide and reprecipitated with 5% aqueous hydrochloric acid. The product was recrystallized from chloroform which contained a trace of methanol (charcoal) to give the *alcohol* (IId).

(ii) To 5% palladium on charcoal (0.5 g.) in methanol (100 ml.) was added a suspension of 3-benzoyl-5-methyl-1,2,4-triazole<sup>6</sup> (2.5 g.) in methanol (100 ml.). The mixture was hydrogenated at 1 atmos. until 1.1 equivalents of hydrogen had been absorbed. Filtration and removal of the solvent left an oil, which was recrystallized as above to give an *alcohol* identical with the previous product.

3-Chloromethyl-1,5-diphenyl-1,2,4-triazole (VI).—3-Hydroxymethyl-1,5-diphenyl-1,2,4-triazole <sup>11,12</sup> (1.6 g.) and thionyl chloride (5 ml.) were heated under reflux for 6 hr. After removal of excess of reagent under reduced pressure the residue was basified with 5% aqueous sodium hydrogen carbonate; it was then extracted with benzene (2 × 10 ml.). Concentration of the extracts and addition of light petroleum precipitated unchanged alcohol (0.5 g.). Evaporation of the mother liquors gave the chloromethyl-triazole (VI) which crystallized from light petroleum (b.p. 60—80°) as waxy needles (0.7 g.), m.p. 80—81° (Found: C, 66.85; H, 4.5; Cl, 12.6; N, 15.95. C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>Cl requires C, 66.8; H, 4.5; Cl, 13.15; N, 15.6%).

5-Chloromethyl-1,3-diphenyl-1,2,4-triazole (VIIa).--(i) Compound (IIIa) (0.5 g.) was treated with an excess of acetyl chloride, with cooling and stirring. Water (5 ml.) was added to the mixture which was then neutralized with sodium hydrogen carbonate. The precipitate was filtered off, washed with water, and recrystallized from ethanol to give (VIIa; 0.22 g.) as *needles*, m.p. 145--146° (Found: C, 66.9; H, 4.4; Cl, 13.7; N, 15.75.  $C_{15}H_{12}ClN_3$  requires C, 66.8; H, 4.5; Cl, 13.15; N, 15.6%).

(ii) Reaction of (IIIa) with an excess of thionyl chloride, as for the preparation of compound (VI), gave compound (VIIa); it crystallized from benzene and light petroleum, as needles identical with those from the previous experiment.

5-Chloromethyl-1-methyl-3-phenyl-1,2,4-triazole (VIIb). Reaction of compound (IIIb) with either acetyl chloride or thionyl chloride, as for the preparation of (VIIa), gave the chloromethyl-triazole (VIIb) as needles, m.p. 110–111°, from benzene and light petroleum (b.p. 40–60°) (Found: C, 58.7; H, 4.95; Cl, 16.45; N, 19.7. O, 0.0%.  $C_{10}H_{10}$ ClN<sub>3</sub> requires C, 57.8; H, 4.85; Cl, 17.1; N, 20.2%).

3-Chloromethyl-5-phenyl-1,2,4-triazole.—Compound (IIa) (3.0 g.) and thionyl chloride (10 ml.) were heated under reflux for 4 hr.; the mixture was worked up as above to give the product (1.7 g., 51%) as prisms, m.p. 178—179°, from methanol (Found: C, 55.7; H, 4.1; Cl, 18.2; N, 21.7.  $C_{g}H_{g}ClN_{3}$  requires C, 55.8; H, 4.15; Cl, 18.3; N, 21.7%).

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<sup>19</sup> A. J. Speziale, L. R. Smith, and J. E. Fedder, *J. Org. Chem.*, 1965, **30**, 4306.