119. *Union of Aryl Nuclei. Part VI. Reactions with* 1-*Aryl*-3 : 3-*dimethyltriazens.*

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1-Aryl-3 : 3-dimethyltriazens are prepared from aniline, *m*- and *p*-nitroaniline, anthranilic acid, methyl anthranilate, β-naphthylamine, 4-aminophthalimide, methyl 4-aminophthalate, and 5-aminoquinoline. Various reactions are described between these triazens and benzene, nitrobenzene, pyridine and 2-methoxynaphthalene, whereby union of the nuclei is effected according to the equation :

$$\mathrm{Ar{\cdot}N{:}N{\cdot}NMe_2 + RH + HCl \longrightarrow ArR + N_2 + NHMe_2,HCl}$$

The yields obtained are frequently good for reactions of this type, which provide further examples of amphoteric or radical substitution.

In previous communications (J., 1934, 1797, 1966; 1938, 108, 113, 699, 1386; 1940, 349, 355, 358, 372, 1279, 1284; etc.) on reactions which result in the union of aryl nuclei, yielding unsymmetrically substituted biaryls, considerable attention has been paid to the use of the diazo-hydroxides (Gomberg reaction) and the nitroso-acylarylamines. Some modifications of these reactions have recently been described in a patent specification (I.G. Farb. Akt., B.P. 513,846; cf. also U.S.P. 2,280,504), in which it is shown that water-insoluble or sparingly soluble metallic salt derivatives (*e.g.*, zinc chloride compounds) of diazo-compounds, usually in presence of aluminium or ferric chloride and free acid, react with a second component which comprises a wide variety of aromatic derivatives (excluding hydroxy- and amino-compounds). As a further improvement it is shown that the diazo-compound may be prepared *in situ* by means of nitrous gases in presence of the second component. Water-insoluble diazo-derivatives are also prepared by the action of non-coupling primary or secondary amines on the diazo-compound, thus giving rise to substituted triazens, and of particular interest are the 1-aryl-3 : 3-dialkyltriazens which form the subject of the present communication. From the numerous examples given in the specification it is clear that all these modifications conform to the general principle of "amphoteric substitution" (Grieve and Hey, J., 1934, 1797, 1966) or "radical substitution" (Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900), which has been shown to be characteristic of all reactions of this type.

1-Aryl-3 : 3-dimethyltriazens are prepared, usually in excellent yield, by the addition of an aqueous solution of the diazotised base to aqueous dimethylamine in the presence of sodium carbonate. The specification cited above refers in particular to 1-phenyl-3 : 3-dimethyltriazen, 1-(3′ : 4′-dichlorophenyl)-3 : 3-dimethyltriazen, and 1-(3′ : 4′-dimethylphenyl)-3 : 3-dimethyltriazen, prepared from aniline, 3 : 4-dichloroaniline and *o*-4-xylidine respectively. Such triazens, which may be liquids or solids, are stable in neutral or alkaline media but decompose into the diazo- and the dimethylamine salt in presence of acid. They may therefore be regarded as stabilised diazo-compounds and, as such, compounds of this type have found considerable employment in the dye industry (see Saunders, "The Aromatic Diazo Compounds," pp. 135—138). In order to form the biaryl the triazen is dissolved in an excess of the second component, and the solution heated, usually at 90—100°, while a slow current of dry hydrogen chloride (or other acidic reagent) is introduced. Under these conditions the biaryl is formed with evolution of nitrogen according to the equation :

$$\mathrm{Ar{\cdot}N{:}N{\cdot}NMe_2 + C_6H_5R + HCl \longrightarrow Ar{\cdot}C_6H_4R + N_2 + NHMe_2,HCl}$$

This reaction possesses two advantages over other methods of biaryl formation in that (*a*) in contrast to the Gomberg reaction it is effected in a homogeneous medium, and (*b*) in contrast to the nitrosoacylarylamine method it is effected at an elevated temperature, which therefore permits the use of a wider range of compounds as second components by including those which are solid at the ordinary temperature but liquid at or about 90°.

Dimethyltriazens have now been prepared from aniline, *p*-nitroaniline, *m*-nitroaniline, methyl anthranilate, anthranilic acid, β-naphthylamine, 4-aminophthalimide, methyl 4-aminophthalate, and 5-aminoquinoline, and as second components benzene, nitrobenzene, 2-methoxynaphthalene and pyridine have been used. Of these triazens, 1-phenyl-3 : 3-dimethyltriazen has been described by Baeyer and Jaeger (*Ber.*, 1875, **8**, 148) and by Heusler (*Annalen*, 1890, **260**, 249). Reactions have been carried out in the presence of hydrogen chloride and in some cases of glacial acetic acid, and in many cases the yields of biaryl are surprisingly good for reactions of this type. No examples of the use of pyridine as second component are contained in the patent specification. The results of these reactions are summarised in the following table :

No.	Base used for preparation of triazen.	Second component.	Decomposing agent.	Biaryl.	Yield of biaryl, %.
1	Aniline	Benzene	HCl	Diphenyl	25
2	,,	,,	AcOH	,,	37
3	,,	Nitrobenzene	HCl	2- and 4-Nitrodiphenyl	35
4	,,	Pyridine	,,	α-, β-, and γ-Phenylpyridine	51
5	*p*-Nitroaniline	Benzene	,,	4-Nitrodiphenyl	52
6	,,	Pyridine	,,	α-, β-, and γ-4-Nitrophenylpyridine	50
7	*m*-Nitroaniline	Benzene	,,	3-Nitrodiphenyl	53
8	,,	,,	AcOH	—	0
9	Methyl anthranilate	2-Methoxynaphthalene	HCl	Methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate	25
10	,, ,,	,, ,,	AcOH	,, ,, ,, ,,	29
11	Anthranilic acid	Benzene	HCl	—	0
12	β-Naphthylamine	,,	AcOH	2-Phenylnaphthalene	36
13	,,	Pyridine	HCl	2-Pyridylnaphthalenes	41
14	5-Aminoquinoline	Benzene	,,	5-Phenylquinoline	13
15	4-Aminophthalimide	,,	,,	4-Phenylphthalimide	v. small
16	,,	Pyridine	,,	4-Pyridylphthalimides	49
17	Methyl 4-aminophthalate	Benzene	,,	Methyl 4-phenylphthalate	66

In the formation of diphenyl the replacement of hydrogen chloride by glacial acetic acid resulted in an increased yield, but in other cases this change effected little improvement in yield and in some instances acetic acid proved to be useless as a decomposing agent, for example, in the reaction of 1-m-*nitrophenyl*-3 : 3-*dimethyltriazen* with benzene. This observation appears to indicate that the nitro-group exerts a stabilising influence on the triazen towards acids. Both 1-m- and 1-p-*nitrophenyl*-3 : 3-*dimethyltriazen* gave nitrodiphenyls in comparatively high yield and with a notable absence of tar. The use of the triazen reaction with a second component which is solid at room temperature is exemplified in the preparation of methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate, an intermediate for the preparation of 3′-hydroxy*meso*benzanthrone. This ester had been obtained in 18% yield by Heilbron, Hey, and Wilkinson (J., 1938, 699) by the action of diazotised methyl anthranilate on a chloroform solution of 2-methoxynaphthalene. Since 2-methoxynaphthalene liquifies at 72°, the use of the solvent can be dispensed with in the triazen method. The quantity of 2-methoxynaphthalene used in these experiments was small (about 2 mols.) compared with the much greater excess (15—20 mols.) used in reactions with benzene or pyridine, but in addition to the improved yield the method of working-up was considerably easier in the triazen method. In the reaction between 1-β-*naphthyl*-3 : 3-*dimethyltriazen* and pyridine a mixture of 2-pyridylnaphthalenes was obtained, from which three *isomerides* were separated by fractional crystallisation of the picrates. One of these picrates was identical with a product prepared by Dr. J. W. Haworth by the action of aqueous naphthalene-β-diazonium chloride on pyridine, and the same product was also prepared by Mr. C. W. Pritchett from the reaction of nitrosoaceto-β-naphthalide with pyridine. In both of these reactions the yields were small. In the reaction between the dimethyltriazen from 5-aminoquinoline and benzene a high proportion of 5-chloroquinoline was formed in addition to 5-*phenylquinoline*. The *dimethyltriazen* prepared from 4-aminophthalimide with pyridine gave a mixture of 4-*pyridylphthalimides*, which appeared to be identical with a similar product previously prepared by Dr. J. W. Haworth from aqueous diazotised 4-aminophthalimide and pyridine.

Both 4-aminophthalimide and methyl 4-aminophthalate were also submitted to the Gomberg reaction and its sodium acetate modification previously reported (Elks, Haworth, and Hey, J., 1940, 1284). In the reaction between diazotised 4-aminophthalimide and benzene in presence of sodium hydroxide no 4-phenylphthalimide could be isolated, probably owing to the solubility of the phthalimide in the aqueous alkaline layer (cf. Grieve and Hey, J., 1938, 108). When sodium acetate replaced sodium hydroxide, some 4-phenylphthalimide was formed but only in minute yield. On the other hand, diazotised methyl 4-aminophthalate and benzene in presence of sodium hydroxide gave methyl 4-phenylphthalate in 34% yield, but when sodium acetate replaced sodium hydroxide in this reaction the yield of methyl 4-phenylphthalate was increased to 52% (cf. Butterworth, Heilbron, Hey, and Wilkinson, J., 1938, 1386).

EXPERIMENTAL.

Preparation of 1-*Aryl*-3 : 3-*dimethyltriazens*.—Except when otherwise stated, the following general method was used for the preparation of the triazens: An aqueous solution of the diazonium chloride, prepared in the usual manner from the aromatic amine (1 mol.), was added slowly from a cooled dropping-funnel to a cooled stirred mixture of aqueous dimethylamine (33%; 160 g.) and an excess of 30% aqueous sodium carbonate over that required for the neutralisation of the acid. Stirring was continued for ½ hour, and the separated triazen then either extracted with ether or benzene or, if solid, collected by filtration. The extract was dried over caustic potash and after removal of the solvent the residual triazen was distilled under reduced pressure. The solid triazens were purified by direct crystallisation.

1-*Phenyl*-3 : 3-*dimethyltriazen*.—The triazen was prepared in 93% yield. It boiled at 125—127°/19 mm. Heusler (*loc. cit.*) recorded b. p. 113—114°/12 mm.

Reactions with benzene. (i) The triazen (20 g.), dissolved in benzene (200 c.c.), was refluxed in a flask fitted with a gas inlet tube and a calcium chloride guard-tube at the end of the condenser. A slow stream of dry hydrogen choride was passed through. When reaction was complete, hot water was added to remove dimethylamine hydrochloride and the benzene layer was separated, dried (sodium sulphate), and distilled. Evaporation to dryness of the aqueous layer gave dimethylamine hydrochloride (10 g.). After removal of most of the benzene the residue was fractionated at atmospheric pressure and chlorobenzene (2·4 g.) was collected at 130—132°, which was identified by nitration to give *p*-chloronitrobenzene, m. p. and mixed m. p. 83°. On further distillation under reduced pressure diphenyl (5·1 g.) was obtained in 25% yield, m. p. 69—70° after crystallisation from alcohol. A tarry residue (5·1 g.) remained.

(ii) In a second experiment with the triazen (17·6 g.) and benzene (175 c.c.), glacial acetic acid (25 g.) was added slowly in place of hydrogen chloride. The mixture was refluxed over-night, washed with water, and the benzene layer separated, dried, and distilled as above. Diphenyl (6·8 g.) was obtained in 37% yield, m. p. 69—70° after crystallisation from alcohol.

Reaction with nitrobenzene. Dry hydrogen chloride was passed into a solution of the triazen (23 g.) in nitrobenzene (300 c.c.) heated on the steam-bath. When evolution of nitrogen had ceased, the mixture was washed with hot water, and the nitrobenzene layer dried and distilled under reduced pressure. After removal of the nitrobenzene a mixture of nitrodiphenyls (10·6 g.) was collected at 180—200°/24 mm. in 35° yield. Crystallisation of the mixture from alcohol yielded 4-nitrodiphenyl, m. p. 112—113°, and evaporation of the mother-liquors to dryness and crystallisation of the residual oil from light petroleum (b. p. 40—60°) gave 2-nitrodiphenyl, m. p. 37—38°.

Reaction with pyridine. Dry hydrogen chloride was passed into a solution of the triazen (23 g.) in pyridine (250 c.c.) heated on the steam-bath. When reaction was complete, the mixture was allowed to cool, and the resulting solid mass treated with an excess of aqueous sodium hydroxide. The pyridine layer was separated, the aqueous alkaline layer extracted with more pyridine, and the combined pyridine extracts dried (caustic potash) and distilled. After removal of pyridine further distillation was continued under reduced pressure. Redistillation of the fraction collected above 80°/20 mm. gave a mixture of phenylpyridines (12·1 g.) at 140—150°/16 mm. in 51% yield. Fractional crystallisation of the picrates from acetone, as described by Haworth, Heilbron, and Hey (J., 1940, 349), gave α-phenylpyridine picrate, m. p. 173—175°, β-phenylpyridine picrate, m. p. 156—158°, and γ-phenylpyridine picrate, m. p. 194—196°, all undepressed by authentic specimens.

1-p-*Nitrophenyl*-3 : 3-*dimethyltriazen*, prepared in 95% yield, separated from light petroleum (b. p. 60—80°) or benzene in reddish needles, m. p. 144—145° (Found: C, 49·6; H, 5·3. $C_8H_{10}O_2N_4$ requires C, 49·5; H, 5·2%).

Reaction with benzene. A boiling solution of the triazen (15 g.) in benzene (250 c.c.) was treated with dry hydrogen chloride as described above in the preparation of diphenyl (method i). Crystallisation of the solid residue, obtained on removal of the benzene, from alcohol gave 4-nitrodiphenyl (8·0 g.) in yellow needles, m. p. 114°, in 52% yield.

Reaction with pyridine. Dry hydrogen chloride was passed for 16 hours into a solution of the triazen (25 g.) in pyridine (250 c.c.) heated on the steam-bath. When the reaction was complete, excess of aqueous sodium hydroxide was added, and the pyridine layer separated. The aqueous layer was further extracted with benzene and the combined pyridine and benzene extracts were distilled in steam to remove the solvents. Towards the end of this distillation a small quantity of *p*-chloronitrobenzene, m. p. 82—83°, collected in the condenser. The brown solid non-volatile residue (18 g.) was collected, dried, and distilled in a vacuum, a solid mixture of 4-nitrophenylpyridines (13·0 g.) being collected at 170—190°<1 mm. (yield, 50%). Separation of the isomerides by the method of Forsyth and Pyman (J., 1926, 2912) gave α-4-nitrophenylpyridine (m. p. and mixed m. p. 129—130°) and β-4-nitrophenylpyridine (m. p. and mixed m. p. 146—147°). The γ-4-nitrophenylpyridine was not obtained in a pure state.

1-m-*Nitrophenyl*-3 : 3-*dimethyltriazen* crystallised from light petroleum (b. p. 60—80°) in yellow prisms, m. p. 99—100° (Found: C, 49·7; H, 5·0. $C_8H_{10}O_2N_4$ requires C, 49·5; H, 5·2%).

Reaction with benzene. Dry hydrogen chloride was passed into a boiling solution of the triazen (60 g.) in benzene (650 c.c.), and the product worked up as in the preparation of diphenyl (method i). After removal of benzene, further distillation under reduced pressure gave 3-nitrodiphenyl (32·6 g.) in 53% yield as a yellow crystalline mass, m. p. 60° after crystallisation from alcohol. In an attempt to use glacial acetic acid in place of hydrogen chloride the greater bulk of the triazen was recovered unchanged even after boiling under reflux over-night.

1-o-*Carbomethoxyphenyl*-3 : 3-*dimethyltriazen*, prepared from diazotised methyl anthranilate, distilled at 180—182°/18 mm. as a pale yellow liquid, which, however, was not obtained analytically pure (Found: C, 59·0; H, 6·6. $C_{10}H_{13}O_2N_3$ requires C, 57·9; H, 6·3%).

Reaction with 2-*methoxynaphthalene.* Dry hydrogen chloride was passed into a solution of the crude triazen (20 g.) in molten 2-methoxynaphthalene (30 g.) heated on the water-bath. When evolution of nitrogen had ceased, the resulting cold solid mass was extracted with benzene and filtered from dimethylamine hydrochloride. After evaporation of the benzene the residue was distilled in a vacuum. The excess of 2-methoxynaphthalene was collected at 140—150°/12 mm. and methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate (7·1 g.) then distilled at 220—240°/12 mm. as a yellow oil (yield, 25%). Hydrolysis with alcoholic potassium hydroxide gave 2-methoxy-1-phenylnaphthalene-2′-carboxylic acid, m. p. and mixed m. p. 216—218°. In a second experiment with the same quantities the slow addition of glacial acetic acid (24 g.) replaced the hydrogen chloride. Heating on the water-bath was continued over-night. On working up the product as before, methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate (8·2 g.) was collected at 200°/<1 mm. (yield, 29%).

1-o-*Carboxyphenyl*-3 : 3-*dimethyltriazen* was prepared from diazotised anthranilic acid by the general method outlined above, but when the reaction was complete the mixture was made slightly acid with dilute acetic acid, and the precipitated triazen filtered off and dried. Crystallisation from benzene–ligroin gave long white needles (24 g.; yield, 74%), m. p. 124—126° (decomp.) (Found: C, 56·2; H, 5·8; N, 21·6. $C_9H_{11}O_2N_3$ requires C, 55·9; H, 5·7; N, 21·7%).

Reaction with benzene. Dry hydrogen chloride was passed into a boiling solution of the triazen (6·2 g.) in benzene (50 c.c.). The resulting solution was extracted with aqueous sodium hydroxide. Acidification of the alkaline solution deposited an acid, which on crystallisation from water gave *o*-chlorobenzoic acid (1·9 g.), m. p. and mixed m. p. 133—135°.

1-*β-Naphthyl*-3 : 3-*dimethyltriazen* crystallised from light petroleum (b. p. 60—80°), with addition of charcoal, in reddish prisms, m. p. 57—58°, the colour of which was largely removed by adsorption of alumina (Found : C, 73·1; H, 6·6. $C_{12}H_{13}N_3$ requires C, 72·3; H, 6·6%).

Reaction with benzene. Addition of glacial acetic acid (10 c.c.) to a boiling solution of the triazen (10 g.) in benzene (100 c.c.) and subsequent treatment as described in the preparation of diphenyl (method ii) gave a residue, which was distilled in a high vacuum. 2-Phenylnaphthalene (3·7 g.) was obtained, which after crystallisation from alcohol melted at 101—102°, both alone and on admixture with an authentic specimen (yield, 36%).

Reaction with pyridine. Dry hydrogen chloride was passed into a stirred solution of the triazen (20 g.) in pyridine (200 c.c.) heated on the steam-bath. The product was worked up as in the preparation of the nitrophenylpyridines. The water was decanted from the non-steam-volatile tarry solid, which was then dissolved in benzene. The benzene extract was dried (potassium hydroxide), the benzene removed, and the residue distilled in a high vacuum. A mixture of 2-pyridylnaphthalenes (8·4 g.) was collected at 185—205°/<1 mm. as a yellow oil, which solidified (yield, 41%). The product (8 g.), dissolved in hot ethyl alcohol, was added to a hot concentrated alcoholic solution of picric acid (9·5 g.). After boiling for ½ hour a solid picrate separated, which was filtered off (14 g.) and fractionally crystallised from acetone. Three isomeric *picrates* were isolated as follows : (*a*) yellow needles, m. p. 199—200° (Found : N, 13·1. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%) ; (*b*) yellow needles, m. p. 177—178° (Found : N, 12·8%) ; (*c*) yellow prisms, m. p. 216—217° (Found : N, 13·3%). The isomeride (*c*) appeared to be present to only a small extent. The free *base* generated from picrate (*a*) was obtained in small white needles, m. p. 99—100° after crystallisation from light petroleum (b. p. 40—60°) (Found : C, 87·8; H, 5·4. $C_{15}H_{11}N$ requires C, 87·8; H, 5·4%). The free *base* generated from picrate (*b*) crystallised from light petroleum (b. p. 40—60°) in clusters of needles, m. p. 69—70° (Found : C, 88·1; H, 6·4%). The m. p. of picrate (*b*) was undepressed on admixture with the compounds prepared by Dr. J. W. Haworth and Mr. C. W. Pritchett respectively as described below.

Preparation of 2-*Pyridylnaphthalenes from Diazotised β-Naphthylamine* (With J. W. HAWORTH).—The filtered diazonium chloride, prepared in the usual manner from β-naphthylamine (70 g.), was added during 2 hours to pyridine (500 c.c.) stirred at 20—25°. After standing overnight, the mixture was poured into water (2 l.) and the dark-coloured solid which separated was filtered off and dried (70 g.). A portion of this material (15 g.), which appeared to consist largely of azo by-products, was refluxed with acetic acid (400 c.c.), to which a solution of stannous chloride (100 g.) in concentrated hydrochloric acid (100 c.c.) was gradually added. The filtered solution was made alkaline and extracted with ether. The oil obtained on removal of the solvent was extracted with hot 5N-hydrochloric acid (100 c.c.). The solid hydrochloride which separated on cooling gave β-naphthylamine on basification, whereas basification of the hydrochloric acid filtrate gave a yellow solid (m. p. 35—45°), which was purified by sublimation in a vacuum. After removal of a small quantity of β-naphthylamine, a mixture of 2-*pyridylnaphthalenes* was collected as a pale yellow solid (m. p. 40—50°), readily soluble in dilute acids and most organic solvents. The crude picrate, prepared in the normal manner in alcoholic solution, melted at 150—165°, but further crystallisation from acetone raised the m. p. to 177—180° (Found : C, 58·2; H, 3·2. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires C, 58·1; H, 3·0%).

Preparation of 2-*Pyridylnaphthalenes from Nitrosoaceto-β-naphthalide* (With C. W. PRITCHETT).—Freshly prepared nitrosoaceto-β-naphthalide (20 g.), obtained by the nitrosyl chloride method described by Hey and Lawton (J., 1940, 378), was added in small portions during 20 minutes to vigorously stirred pyridine (150 c.c.). The solution became warm, but excessive heating was prevented by cooling in ice. Stirring was continued for ½ hour and evolution of nitrogen had then practically ceased. The solution was warmed to ensure completion of the reaction, and the excess of pyridine then removed by distillation with steam. A small quantity of naphthalene (0·3 g.) separated from the steam distillate. The dark red, non-volatile oil was extracted with benzene (400 c.c.) and dried. After removal of the solvent the residue was distilled at 10^{-3} mm. The distillate (5 g.) in benzene was purified by chromatographic adsorption, and the elutriate treated with alcoholic picric acid. Crystallisation of the product from acetone gave a 2-pyridylnaphthalene picrate, m. p. 177—179°.

1-(5′-*Quinolyl*)-3 : 3-*dimethyltriazen*.—This was obtained from diazotised 5-aminoquinoline in almost quantitative yield in crude form (m. p. 30—40°), but attempts to effect further purification by crystallisation were unsuccessful and an analytically pure specimen was not obtained.

Reaction with benzene. Dry hydrogen chloride was passed into a boiling solution of the crude triazen (10 g.) in benzene (100 c.c.), the mixture made alkaline with aqueous sodium hydroxide and filtered, and the benzene layer separated. The solvent was removed from the dried extract (sodium sulphate), and the residue distilled in a vacuum. Two fractions were obtained : (*a*) b. p. 90°/<1 mm. (2·9 g.), and (*b*) b. p. 160—180°/<1 mm. (1·3 g.). The former was a colourless liquid consisting of 5-chloroquinoline, part of which was converted into the *picrate*, m. p. 220—223° (from acetone) (Found : N, 14·0. $C_9H_6NCl,C_6H_3O_7N_3$ requires N, 14·3%), and part into the oxalate, which separated from alcohol in white needles, m. p. 144—145° (Found : C, 57·6; H, 3·7. Calc. for $2C_9H_6NCl,C_2H_2O_4$: C, 57·6; H, 3·4%). Claus and Kayser (*J. pr. Chem.*, 1893, **48**, 270) recorded m. p. 145° for the oxalate of 5-chloroquinoline. Fraction (*b*) solidified and after crystallisation from aqueous alcohol 5-*phenylquinoline* was obtained in white needles, m. p. 82—83° (yield, 13%) (Found : C, 88·0; H, 5·6. $C_{15}H_{11}N$ requires C, 87·8; H, 5·4%). The *picrate*, formed in the usual manner, separated from alcohol in small yellow crystals, m. p. 210—211° (Found : N, 12·9. $C_{15}H_{11}N,C_6H_3O_7N_3$ requires N, 12·9%).

1-*Phenyl*-3 : 3-*dimethyltriazen*-3′ : 4′-*dicarboxyimide*.—The filtered diazonium sulphate prepared from 4-aminophthalimide (43 g.) (Levy and Stephen, J., 1931, 80) was added slowly to a mixture of aqueous dimethylamine (26·2%; 50 g.) and excess of aqueous sodium carbonate. The precipitated solid was collected and dried. Crystallisation from pyridine gave 1-*phenyl*-3 : 3-*dimethyltriazen*-3′ : 4′-*dicarboxyimide* (40 g.), m. p. 251—253° (decomp.) (yield, 69%) (Found : C, 54·8; H, 4·8; N, 25·5. $C_{10}H_{10}O_2N_4$ requires C, 55·0; H, 4·6; N, 25·7%).

Reaction with benzene. Dry hydrogen chloride was passed for 12 hours into a vigorously stirred, boiling suspension of the triazen (19 g.) in benzene (1 l.). The solid collected (15 g.) was unchanged triazen. Evaporation of the benzene solution almost to dryness deposited a solid (1·9 g.), which was purified by vacuum sublimation. Subsequent crystallisation from alcohol gave 4-phenylphthalimide, m. p. 200—201° alone and mixed with an authentic specimen.

Reaction with pyridine. Dry hydrogen chloride was passed into a stirred solution of the triazen (18·8 g.) in pyridine (200 c.c.) heated on the steam-bath, water added, and the resulting precipitate collected (m. p. >300°). Solid sodium acetate was added to the filtrate, and the resulting precipitate collected (9·5 g.), m. p. 210—215°. After sublimation in a vacuum a mixture of 4-*pyridylphthalimides* was obtained in 49% yield, m. p. 232—242° (Found : C, 69·9; H, 3·9; N, 12·6. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6; N, 12·5%).

Preparation of 4-*Pyridylphthalimides from Diazotised* 4-*Aminophthalimide* (With J. W. HAWORTH).—The filtered diazonium sulphate, prepared from 4-aminophthalimide (24 g.), was added to pyridine (200 c.c.) at 40—50° during 2 hours. After a further ½ hour's heating, the mixture was poured into water (1500 c.c.). The yellow solid which separated was collected, dried (17 g.; yield, 54%; m. p. 205—220°), and purified by vacuum sublimation. Crystallisation from alcohol gave a mixture of 4-*pyridylphthalimides*, m. p. 238—245° (Found : C, 69·6; H, 3·9. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6%).

Methyl 1-*Phenyl*-3 : 3-*dimethyltriazen*-3′ : 4′-*dicarboxylate*.—This *triazen*, prepared from diazotised methyl 4-aminophthalate in 84% yield, crystallised from benzene–light petroleum (b. p. 60—80°) in yellow prisms. m. p. 74—75° (Found : C, 54·7; H, 5·9. $C_{12}H_{15}O_4N_3$ requires C, 54·3; H, 5·7%).

Reaction with benzene. Dry hydrogen chloride and a solution of the triazen (20 g.) in benzene (250 c.c.) being used as described under the preparation of diphenyl (method i), a residue was obtained which on distillation in a high vacuum gave a yellow oil (13·4 g.), b. p. 130—150°/*ca.* 10^{-5} mm., which solidified when cold. Recrystallisation from light petroleum (b. p. 40—60°) gave methyl 4-phenylphthalate in white needles, m. p. 62—63°, both alone and on admixture with an authentic specimen (yield, 66%). Hydrolysis with aqueous sodium hydroxide gave 4-phenylphthalic acid, m. p. and mixed m. p. 193—194°.

Preparation of 4-*Phenylphthalimide and of Methyl* 4-*Phenylphthalate by Means of the Gomberg Reaction* (cf. Elks, Haworth, and Hey, *loc. cit.*).—4-Aminophthalimide (42 g.), suspended in a mixture of hydrochloric acid (*d* 1·16; 420 c.c.) and water (420 c.c.), was diazotised at 0—3° with aqueous sodium nitrite (21 g. in 63 c.c. of water). One half of the filtered diazonium solution was added to benzene (400 c.c.), vigorously stirred at 5—10°, and treated gradually with aqueous sodium hydroxide (90 g. in 450 c.c. of water), and the other half was added to the same volume of benzene and treated similarly with aqueous sodium acetate (285 g. of the hydrate in 650 c.c. of water). Stirring was continued for 48 hours, the reaction being allowed to proceed at room temperature after the first 3 hours. The benzene layers were then separated, washed with water, and distilled. The sodium hydroxide reaction yielded only a brown residue of high m. p., but the benzene layer from the sodium acetate reaction yielded a small residue of 4-phenylphthalimide, which after crystallisation from alcohol melted at 203—204° both alone and on admixture with the product prepared by Butterworth, Heilbron, Hey, and Wilkinson (*loc. cit.*) from 4-phenylphthalic anhydride and urea (Found : C, 75·1; H, 4·1. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·1%).

Methyl 4-aminophthalate (60 g.), dissolved in a mixture of hydrochloric acid (*d* 1·16; 115 c.c.) and water (25 c.c.), was diazotised at 0° with aqueous sodium nitrite (22 g. in 44 c.c of water). The filtered diazonium solution was divided equally, added to benzene, and treated with aqueous solutions of sodium hydroxide (22 g. in 70 c.c. of water) and of sodium acetate (65 g. of the hydrate in 180 c.c. of water) as in the previous example. When the reactions were complete, the benzene layers were separated, dried, and distilled. The residues were distilled in a high vacuum (*ca.* 10^{-5} mm.) at 130—150°. The colourless distillates solidified and on crystallisation from light petroleum (b. p. 40—60°) methyl 4-phenylphthalate separated in white needles, m. p. 62—63°, both alone and on admixture with an authentic specimen. The sodium hydroxide reaction gave 13·2 g. (yield, 34%), and the sodium acetate reaction 20·3 g. (yield, 52%).

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