

(7) *Vide* F. L. Scott, M. Ruszkiewicz and J. Reilly (forthcoming publication).

TABLE I  
 SOME HYDRAZONE DERIVATIVES

Aldehyde	Hydrazine	Form identified <sup>a</sup>	Formula	M.p., °C.	Analyses, %					
					Calculated	Found	C	H	N	
Anisaldehyde	Aminoguanidine <sup>b</sup>	Picrate	C <sub>15</sub> H <sub>15</sub> N <sub>7</sub> O <sub>8</sub>	250	..	..	23.2	..	..	23.2
Piperonal	Aminoguanidine <sup>b</sup>	Free base <sup>c</sup>	C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	184	48.2	5.3	25.6	48.3	5.1	24.6
Δ <sup>3</sup> -Cyclohexylaldehyde	Aminoguanidine <sup>b</sup>	Nitrate	C <sub>8</sub> H <sub>16</sub> N <sub>6</sub> O <sub>3</sub>	129	41.9	6.5	30.5	41.9	6.8	30.2
Δ <sup>3</sup> -Cyclohexylaldehyde	Aminoguanidine <sup>b</sup>	Picrate	C <sub>14</sub> H <sub>17</sub> N <sub>7</sub> O <sub>7</sub>	216	..	..	24.8	..	..	24.6
Anisaldehyde	Diaminoguanidine <sup>b</sup>	Free base <sup>c</sup>	C <sub>17</sub> H <sub>19</sub> N <sub>8</sub> O <sub>2</sub>	166	59.4	6.1	20.4	59.8	5.9	20.2
Cuminic aldehyde	Diaminoguanidine <sup>b</sup>	Nitrate	C <sub>21</sub> H <sub>28</sub> N <sub>6</sub> O <sub>3</sub>	145	..	..	20.4	..	..	20.4
Δ <sup>3</sup> -Cyclohexylaldehyde	Diaminoguanidine <sup>b</sup>	Picrate	C <sub>14</sub> H <sub>20</sub> N <sub>8</sub> O <sub>7</sub>	202	50.2	5.1	22.3	50.2	5.1	23.0
<i>o</i> -Nitrobenzaldehyde	Diaminoguanidine <sup>b</sup>	Nitrate	C <sub>15</sub> H <sub>14</sub> N <sub>8</sub> O <sub>7</sub>	244	43.1	3.4	26.8	42.9	3.5	26.9
<i>p</i> -Nitrobenzaldehyde	Diaminoguanidine <sup>b</sup>	Nitrate	C <sub>15</sub> H <sub>14</sub> N <sub>8</sub> O <sub>7</sub>	187	43.1	3.4	26.8	42.2	3.3	26.2
<i>m</i> -Nitrobenzaldehyde	2-Quinolylhydrazine	Free base	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub>	212	65.7	4.1	19.2	65.6	3.8	19.3

<sup>a</sup> These derivatives are either new substances or represent supplementary derivatives of previously described parent substances. <sup>b</sup> Reacted as nitrate. <sup>c</sup> Analysis corresponds to a monohydrate.

ion with benzaldehyde phenylhydrazone and -guan-ylhydrazone. The diazonium salts of sulfanilic acid, *o*-nitroaniline, *o*-nitrotoluidine, β-naphthylamine, *p*-nitroaniline and 4-chloro-*o*-toluidine also coupled with benzaldiaminoguanidine, while *m*-nitrobenzaldiaminoguanidine coupled with both diazotized aniline and *m*-nitroaniline. With heterocyclic diazonium salts specificity was evident. Thus, while benzaldiaminoguanidine coupled with diazotized 4-aminoantipyrine it did not react with 5-tetrazolyl-, 2-thiazolyl- or 2-benzthiazolyl-diazonium salts.

Similarly, benzaldehyde guanylhydrazone resisted coupling with heterocyclic diazonium salts (reacting only with diazotized 5-aminotetrazole<sup>8b</sup>) while the anisaldehyde and 2,3,5,6-tetrahydrobenzaldehydeguanylhydrazones also coupled readily with 5-diazotetrazole. Anisaldehydequinolylhydrazone coupled with phenyldiazonium chloride but was unreactive toward the tetrazolyl-diazonium salt.

Formazans, in general, are readily oxidized initially to tetrazolium salts (III) and then to tetrazoles. In this latter step either R or Ar' (*vide* III) has to be eliminated. The guanazyls oxidize by elimination of the guanyl group.<sup>8</sup>

Analogously, the iminotricarbaundecaztetraenes were now also found to be readily oxidized. With lead tetraacetate, or nitrous oxide in chloroform, they yielded the corresponding monotetrazoles in place of the possible ditetrazoles (II). With concentrated nitric acid, nitrated monotetrazoles similarly resulted, *e.g.*, 6-imino-1,3,9,11-tetraphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene gives a mixture of isomeric dinitrodiphenyltetrazoles, and 6-imino-1,11-di-*p*-nitrophenyl-3,9-diphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene also gave a dinitrodiphenyltetrazole.

Finally, as a cognate investigation, efforts were made to synthesize a further 1,5'-ditetrazole (IV) system by the alkali cyclization of 1-benzoyl-4-tetrazolylisotetrazene (V). The initial high-yield reaction product split into the corresponding benzamide and a tetrazolyl fragment after this treatment. In the presence of alkali<sup>9</sup> the tetrazene formed preferentially underwent fission rather than cyclization.

(8) Compare the ready hydrolysis of 1-guanylpurazoles, F. L. Scott and J. Reilly, *THIS JOURNAL*, **74**, 4563 (1952).

(9) Cf. O. Dimroth and G. de Montmollin, *Ber.*, **43**, 2907 (1910).

## Experimental<sup>10,11</sup>

**Hydrazone Formation.**—The guanyl- and quinolylhydrazones and the dialdehydic diaminoguanidines were prepared by refluxing the calculated quantities of aldehyde and hydrazine for a few moments in aqueous ethanolic solution. The free bases of the guanylhydrazones were isolated without isolating the nitrate but this resulted in some decomposition in the case of the diaminoguanidine compounds and separation of the intermediate salt was usually effected. The properties of some of the hydrazones concerned are summarized in Table I.

**Formazan Formation.**—Couplings were performed as previously described<sup>1</sup>; isolation of the formazan was effected by either pouring the pyridine solution into dilute hydrochloric acid solution or by dilution with water, and, if no precipitation resulted, extraction with chloroform. The chloroform solution usually deposited a tar, but on working up the dye could be isolated. A typical example of the general formazan technique is as follows.

0.01 mole of finely powdered benzylidene-5-hydrazino-tetrazole was added to a large excess (100 ml.) of 5% sodium hydroxide solution. The yellow solution which resulted was cooled to 5° and added to 0.01 mole of diazotized aniline. Immediately a deep-red color was produced and a very small amount of solid precipitated. The filtrate on neutralization with dilute acetic acid yielded a solid which, while proving only slightly soluble in water was fairly soluble in ethanol; total yield 50–60%. On careful recrystallization from ethanol-water a solid melting at 147° was obtained which was proved by analysis to be 1,3-diphenyl-5-tetrazolyl-3-monocarbapentaz-1,3-diene.

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>8</sub>: C, 57.5; H, 4.1; N, 38.3. Found: C, 57.7; H, 4.2; N, 38.2.

The properties of the other formazans are summarized in Table II.

**Oxidation of the Formazans.**—A number of different techniques were employed—concentrated nitric acid, nitrous oxide or lead tetraacetate in chloroform and finally dilute aqueous nitric acid.

(a) Three and one-half grams (0.01 mole) of finely powdered 6-imino-3,6,9-tricarbaundecaz-1,3,8,10-tetraene was added cautiously to 130 ml. of concentrated nitric acid. Even at room temperature a very gentle agitation initiated a vigorous reaction with copious evolution of nitrous fumes. After refluxing gently for 1.25 hours the mixture was allowed to stand at room temperature for several hours when a yellow solid separated. It was filtered off and washed thoroughly with boiling water to remove any soluble impurities. After a final recrystallization from nitric acid, colorless plates melting at 198° were obtained. The analysis suggests this compound was a dinitrodiphenyltetrazole.

*Anal.* Calcd. for C<sub>18</sub>H<sub>8</sub>N<sub>8</sub>O<sub>4</sub>: C, 50.0; H, 2.9; N, 26.9. Found: C, 50.1; H, 2.9; N, 26.9.

Addition of water to the filtrate yielded a further precipitate of an orange-colored solid, which on recrystallization from aqueous ethanol had a m.p. of 154°. This proved similarly to be an isomeric dinitrodiphenyltetrazole.

(10) All m.p.'s are uncorrected.

(11) All analyses are by Drs. Weiler and Strauss, Oxford, England.

TABLE II  
FORMAZANS  $\left( \text{Ar}-\text{C} \begin{array}{c} \text{N}-\text{NH}-\text{R} \\ \text{N}=\text{N}-\text{Ar}' \end{array} \right)_n$

Hydrazine	Diazotized amine <sup>a</sup>	Ar	Reaction product	R	n	M.p., °C. <sup>b</sup>	Coupling mode <sup>c</sup>	Analyses, %			
								Calculated		Found	
								C	H	C	H
N,N'-Dibenzylidenediaminoguanidine	<i>o</i> -Nitroaniline	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> - <i>o</i>	>C=NH	2	115	B	57.5	3.7	57.5	4.0
N,N'-Dibenzylidenediaminoguanidine	<i>p</i> -Nitroaniline	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> - <i>p</i>	>C=NH	2	175	A	57.5	3.7	57.4	3.6
N,N'-Dibenzylidenediaminoguanidine	<i>o</i> -Nitrotoluidine	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> -NO <sub>2</sub> - <i>o</i>	>C=NH	2	94	B	55.8	4.0	55.7	4.3
N,N'-Dibenzylidenediaminoguanidine	<i>o</i> -Nitrotoluidine	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> -NO <sub>2</sub> - <i>o</i>	>C=NH	2	108	B	58.9	5.2	59.2	5.0
N,N'-Dibenzylidenediaminoguanidine	$\beta$ -Naphthylamine	C <sub>6</sub> H <sub>5</sub>	C <sub>10</sub> H <sub>7</sub> - $\beta$	>C=NH	2	163	A	73.3	4.7	73.8	4.8
N,N'-Dibenzylidenediaminoguanidine	4-Chloro-2-toluidine	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> -Cl-4	>C=NH	2	63	B	61.1	4.4	61.0	4.8
N,N'-Dibenzylidenediaminoguanidine	4-Aminoantipyrine <sup>d</sup>	C <sub>6</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O-4	>C=NH	2	154 <sup>e</sup>	A	64.1	5.1	64.5	5.2
$\Delta^3$ -Cyclohexylidenediaminoguanidine	5-Aminotetrazole	C <sub>6</sub> H <sub>10</sub>	CHN <sub>4</sub> -5	$\begin{array}{c} \text{NH} \\ \text{—C—} \\ \text{NH}_2 \end{array}$	1	149 <sup>f</sup>	C	38.6	5.7	39.2	6.0
Anisylidenediaminoguanidine	5-Aminotetrazole	C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> - <i>p</i>	CHN <sub>4</sub> -5	$\begin{array}{c} \text{NH} \\ \text{—C—} \\ \text{NH}_2 \end{array}$	1	146 <sup>g</sup>	C	..	..	45.8 <sup>j</sup>	..
Cuminyldenediaminoguanidine	5-Aminotetrazole	C <sub>6</sub> H <sub>4</sub> -Pr <sup><math>\beta</math></sup> - <i>p</i>	CHN <sub>4</sub> -5	$\begin{array}{c} \text{NH} \\ \text{—C—} \\ \text{NH}_2 \end{array}$	1	128	A	48.0	5.3	47.9	6.2
<i>p</i> -Chlorobenzylidenediaminoguanidine	5-Aminotetrazole	C <sub>6</sub> H <sub>4</sub> -Cl- <i>p</i>	CHN <sub>4</sub> -5	$\begin{array}{c} \text{NH} \\ \text{—C—} \\ \text{NH}_2 \end{array}$	1	146	A	34.8	3.6	35.2	3.6
Benzylidene-2-quinolyldiazine	Aniline	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> (2)	1	160	A	75.2	4.8	74.5	4.9

<sup>a</sup> For references to the methods of diazotization employed, see K. H. Saunders, "The Aromatic Diazo Compounds," Arnold & Co., London, 1949. <sup>b</sup> Melting points, generally, were not sharp. They usually occurred with preliminary loss of volume and with decomposition. <sup>c</sup> Mode A represents the procedure: ethanolic solution of hydrazine + excess aqueous sodium hydroxide + diazonium salt solution. Mode B represents pyridine solution of hydrazine + [sodium carbonate neutralized] solution of diazonium salt. Mode C represents dilute acetic acid solution of hydrazine + sodium acetate + aqueous diazonium salt solution. <sup>d</sup> Except where otherwise expressed, the values in this column represent nitrogen values. <sup>e</sup> Analysis corresponds to a dihydrate. <sup>f</sup> This corresponds to the anhydrous form and is isolated in a different manner. <sup>g</sup> N,N'-Dibenzylidenediaminoguanidine did not couple, by either methods A or B, with diazotized 2-aminobenzthiazole or 5-aminotetrazole. <sup>h</sup> Analysis corresponds to a monohydrate. <sup>i</sup> Anal. Calcd. for MeO, 10.1. <sup>j</sup> Found for MeO, 10.4.

*Anal.* Calcd. as above. Found: C, 49.8; H, 2.5; N, 26.3.

The yield of each solid was about 30%. Orientation of these substances by *ad hoc* syntheses has proved difficult and will be described subsequently. Similarly when 6-imino-3,9-di-*p*-nitrophenyl-1,11-diphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene and the 3,9-di-*m*-nitrophenyl analog were treated with concentrated nitric acid they reacted less vigorously than the 3,9-diphenyl compound, but after refluxing for 1-hour periods both yielded dinitrophenyl-tetrazoles of m.p. 190°.

(b) 8.86 g. (0.02 mole) of lead tetraacetate dissolved in chloroform was added to a solution of 3.5 g. (0.01 mole) of 6-imino-1,3,9,11-tetraphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene in the same solvent. An immediate fading in color of the formazan solution resulted. The mixture was warmed gently for a few minutes before the chloroform was removed, under reduced pressure. The residue was taken up with 40 ml. absolute ethanol and all the lead precipitated by the passage of hydrochloric acid gas. Filtration, followed by thermal concentration resulted in the deposition of a white feathery material which on purification melted at 101.5–102°. Analysis showed this to be 2,5-diphenyl-tetrazole.

*Anal.* Calcd. for  $C_{13}H_{10}O_4$ : C, 70.3; H, 4.5; N, 25.2. Found: C, 70.2; H, 4.6; N, 24.4.

The yield was practically quantitative. The same reaction took place with nitrous oxide in chloroform solution. When 6-imino-3,9-diphenyl-1,11-*o*-nitro-*p*-tolyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene was oxidized by similar methods, 2-*o*-nitro-*p*-tolyl-5-phenyltetrazole of m.p. 101° was obtained.

*Anal.* Calcd. for  $C_{14}H_{11}N_5O_2$ : C, 59.7; H, 3.9. Found: C, 59.0; H, 4.4.

(c) 0.005 mole of 6-imino-3-phenyl-1-tetrazolyl-3,6-dicarbaheptaz-1,3-diene was refluxed for 10 minutes with 60 ml. of 5% nitric acid. The resulting straw-yellow solution on filtering from suspended matter was neutralized with 5% sodium hydroxide and allowed to stand at 0° for 12 hours. A slight suspension of a gray material separated, was filtered off and was not further investigated. The remaining solution was thermally concentrated and the resulting organic solid separated from inorganic contaminants by extraction with a chloroform-ethanol mixture. On concentrating, a crystalline solid was precipitated which, after recrystalliza-

tion from aqueous ethanol melted at 245–246°, yield was ca. 20%. The substance has an empirical formula of  $C_9H_{10}N_6$ .

*Anal.* Calcd. for  $C_9H_{10}N_6$ : C, 52.1; H, 4.8; N, 40.5. Found: C, 52.2; H, 4.9; N, 40.3.

A similar experiment using the anisylidene analog resulted in a solid of m.p. 265°. This also corresponds to a similar type empirical formula  $C_9H_9N_6OCH_3$ . These are being further investigated.

*Anal.* Calcd. for  $C_{10}H_{12}N_6O$ : C, 51.6; H, 5.2; N, 36.2. Found: C, 51.8; H, 5.2; N, 36.2.

The use of the dilute acid increased the extent of hydrolysis and thus the evolution of the free aldehyde. This was an undesirable side reaction, but the use of the method was necessitated by the insolubility of the tetrazolylformazans in chloroform. Refluxing a pyridine solution of such formazans with permanganate to effect the oxidation afforded anomalous results.

**Cyclization of a Tetrazolylisotetrazene.**—On adding a solution of 0.01 mole of 5-tetrazolylidiazonium nitrate to a solution of 0.01 mole of benzohydrazide in aqueous ethanolic solution in the presence of excess sodium acetate solution, a white precipitate of crude 1-benzoyl-4-tetrazolyl-isotetrazene, m.p. 94–98°, 88% yield, separated immediately. As most purification techniques resulted in decomposition of the isotetrazene, it was subjected without purification to the cyclization technique of Dimroth and de Montmollin.<sup>8</sup> Four and one-tenth grams of the well-powdered reaction product was added to 40 ml. of 5 *N* sodium hydroxide solution. An immediate yellow coloration took place. The suspension was agitated while the temperature was raised gently to 70° when ammonia vapor was given off. After filtration and subsequent crystallization from ethanol-water it was obtained as white crystals of m.p. 126°. It was shown to be benzamide by mixed melting point with an authentic sample and by analysis.

*Anal.* Calcd. for  $C_7H_7NO$ : C, 69.3; H, 5.8; N, 11.5. Found: C, 69.1; H, 5.7; N, 11.7.

Neutralization of the filtrate and extraction with ether made possible the recovery of a further yield of benzamide; total yield 20%. This experiment was repeated keeping the temperature of the alkaline suspension of tetrazene at 0° for 24 hours. Again benzamide was the main product recovered. The identification of the tetrazolyl fragment of the tetrazene fission was not pursued.

CORK, IRELAND

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

## Steric Hindrance to Coplanarity in *o*-Fluorobenzidines<sup>1a,b</sup>

BY ANDREW J. BILBO AND GEORGE M. WYMAN

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2,2'-Difluoro-, 2,2',6,6'-tetrafluoro-, 2,2'-dichloro- and 3,3'-dichlorobenzidine were synthesized by standard methods and their ultraviolet absorption spectra measured. The spectra indicate that there is an appreciable inhibition of resonance in the *o*-halogenated benzidines, probably resulting from displacement of the molecule from a coplanar configuration. The bromine water tests observed for these molecules further support this theory.

### Introduction

In conjunction with some work on conjugated polyphenyls, it was considered desirable to ascertain the steric interference with coplanarity caused by the introduction of fluorine atoms in the *o*-positions in the biphenyl structure. In contrast with the corresponding alkyl and chlorine compounds, the *o*-tetrafluorinated derivatives of biphenyl have not been successfully resolved,<sup>2</sup> although a schematic drawing of the spatial ar-

rangement of atoms in such a molecule indicates the existence of considerable steric interference between the fluorine atoms on adjacent rings, as shown in Fig. 1. In order to accommodate these "overlapping" fluorine atoms in the limited space available between the two benzene rings, it is necessary for the phenyl groups to take up non-coplanar positions by twisting about the connecting 1,1'-bond until the steric interference is removed. Since the distance of closest approach in space between two adjacent fluorine atoms in organic molecules has been reported to be 2.70 Å,<sup>3</sup> the angle of torsion of the benzene rings can be calcu-

(1) (a) The research reported in this paper was performed in part under the sponsorship of the Ordnance Corps, Department of the Army; (b) presented before the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(2) E. C. Kleiderer and R. Adams, *THIS JOURNAL*, **55**, 4219 (1933).

(3) H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950).