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# The Reaction of Some Diazoamino-compounds with Lead Tetra-acetate

### By C. M. Camaggi, M. Tiecco, and A. Tundo,\* Istituto di Chimica Organica e di Chimica Industriale dell'Università, Bologna, Italy

The dehydrogenation of some diazoamino-compounds with lead tetra-acetate in aromatic solvents has been shown to give rise to mixtures of biaryls and azo-compounds. The reaction of diazoaminobenzene, in monosubstituted benzene derivatives as solvents, gives azobenzene and mixtures of isomeric biphenyls as products. The isomer ratio for the biphenyls suggests that they are formed by substitution of intermediate phenyl radicals in the aromatic solvent. The dehydrogenation of 1,1-di-2-naphthyltriazen in benzene led to 2-phenylnaphthalene and dibenzo[a,h]phenazine as products. The latter product is also obtained from the thermal decomposition of 2-naphthyl azide. These latter results indicate the intervention of nitrenes as intermediates. The electron paramagnetic resonance spectrum of the reaction mixture of 1,3-diphenyltriazen with lead tetra-acetate exhibited a triplet with a coupling constant of about 10 gauss, which may be indicative of an intermediate triazenyl radical, which would break down to afford a phenyl radical, phenylnitrene, and nitrogen.

It has been shown by several authors that diazoaminocompounds can react homolytically under a variety of experimental conditions. Elks and Hey<sup>1</sup> found that the action of gaseous hydrogen chloride on a solution of 3,3-dimethyl-1-phenyltriazen in nitrobenzene afforded phenyl radicals which substituted in the solvent to give a mixture of isomeric biphenyls. Hardie and Thomson<sup>2</sup> and Rondestvedt and Blanchard<sup>3</sup> showed that thermal decomposition of diazoamino-compounds gave phenyl radicals. The oxidation of the 1,3-diaryltriazens (I) with potassium permanganate was studied by Theilacher and Fintelmann,<sup>4</sup> who showed that in some cases 1,3,4,6tetra-arylhexa-azadienes (III) were formed which easily decompose to the azo-compounds (IV).

We have now examined the dehydrogenation of the 1,3-diaryltriazens (I) with lead tetra-acetate with the hypothesis that the triazenyl radicals (II) formed in the first step, besides dimerizing to the hexa-azadiene (III), could also break down to nitrogen, aryl radicals (V), and arylnitrenes (VI), as indicated in the Scheme. It is well known, from experiments carried out with the aryl azides,<sup>5</sup> that arylnitrenes (VI) can dimerize to give azocompounds (IV).



In order to demonstrate the intermediate existence of aryl radicals, the reaction of 1,3-diaryltriazen (I; Ar = Ph) with lead tetra-acetate has been carried out in monosubstituted benzenes as solvent (Table 1). In all cases, besides the azobenzene, a mixture of isomeric biphenyls was obtained, the ratios of which are clearly

<sup>&</sup>lt;sup>1</sup> J. Elks and D. H. Hey, J. Chem. Soc., 1943, 441. <sup>2</sup> R. L. Hardie and R. H. Thomson, J. Chem. Soc., 1958, 1286.

<sup>&</sup>lt;sup>3</sup> G. S. Rondestvedt, H. S. Blanchard, J. Amer. Chem. Soc., 1955, 77, 1769.

<sup>&</sup>lt;sup>4</sup> W. Theilacher and E. C. Fintelmann, Chem. Ber., 1958, 91, 1597.

<sup>&</sup>lt;sup>5</sup> L. Horner, A. Christmann, and A. Gross, Chem. Ber., 1963, 96, 399.

# TABLE 1

Yields of azobenzene and biaryls and isomer ratios of monosubstituted biphenyls formed in the reaction of phenyl radicals, derived from 1,3-diphenyltriazen and lead tetra-acetate, with monosubstituted aromatic solvents

		PhN=NPh			
	Yield	ortho	meta	para	yield
$\mathbf{PhX}$	(%)	(%)	(%)	(%)	(%)
$X \approx H \dots$	40				40.9
OMe	26	65.3	19.7	15	35.5
CMe <sub>3</sub>	11.2	14.5	57.0	$28 \cdot 5$	38.5
NO2	$33 \cdot 4$	54.2	10.3	35.5	14.8

in agreement with those reported in reactions of other sources of phenyl radicals.<sup>6</sup>

PhN=N-NHPh 
$$\xrightarrow{PhOAc_1}$$
 Ph·C<sub>6</sub>H<sub>4</sub>·X( $o,m,p$ ) +  
PhN=NPh  
(X = H, OMe, CMe<sub>3</sub>, NO<sub>2</sub>)

A further indication of the intervention of aryl radicals was provided by use of carbon tetrachloride as solvent. The reaction of 1,3-di-p-tolyltriazen with lead tetraacetate in carbon tetrachloride gave p-chlorotoluene in 44.5% yield.

The dehydrogenation of some asymmetrical 1,3-diaryltriazens (VIII) with lead tetra-acetate in benzene gave a mixture of biphenyl (IX) and p-substituted biphenyl (X), and of the azo-compounds (XI)—(XIII) resulting from both aryl groups of the triazen. The

$$\begin{array}{c} PhN=N-NH\cdot C_{6}H_{4}\cdot X-p \xrightarrow{Pb(OAC)_{4}} \\ (VIII) \\ PhPh (IX) + Ph\cdot C_{6}H_{4}\cdot X-p (X) + PhN=NPh (XI) + \\ PhN=N\cdot C_{6}H_{4}\cdot X-p (XII) + \\ p-X\cdot C_{6}H_{4}\cdot N=N\cdot C_{6}H_{4}\cdot X-p (XIII) \end{array}$$

results of these experiments may be explicable on the basis of the isomerism of diazoamino-compounds.

The results so far presented do not allow a decision as to whether or not the arylnitrenes (VI) are involved in these reactions, since Theilacher and Fintelmann<sup>4</sup> have shown that the azo-compounds (IV) and (XI)—(XIII) can be formed through thermal decomposition of the hexaazadienes (III). It is, however, noteworthy that, even in those cases in which they are said to be stable and isolable,<sup>4</sup> the hexa-azadienes could not be isolated under our experimental conditions.

The dehydrogenation of 1,3-di-2-naphthyltriazen (XIV) in benzene solution provided an important result, since, in addition to the expected products 2-phenyl-naphthalene (XV) and 2,2'-azonaphthalene (XVI), we isolated dibenzo[a,h]phenazine (XVII).

Similar results were obtained from 3-2'-naphthyl-1-phenyltriazen, which on dehydrogenation with lead tetra-acetate in ethyl acetate solution afforded di-

\* Recorded by L. Lunazzi and G. Pedulli of this Institute.

benzo[a,h]phenazine (XVII) together with azobenzene, 2,2'-azonaphthalene (XVI), and naphthalene.



It seems difficult to interpret the formation of dibenzo[a,h]phenazine (XVII) through an intermediate hexa-azadiene like (III), and it probably arises from the coupling of two arylnitrenes (VI; Ar = 2-C<sub>10</sub>H<sub>7</sub>). This latter suggestion is supported by the results of the thermal decomposition of 2-naphthyl azide (XVIII). It is reported <sup>5</sup> that the thermal decomposition of aryl azides gives rise to arylnitrenes. Therefore, since the thermal decomposition of 2-naphthyl azide and the lead tetra-acetate dehydrogenation of 1,3-di-2-naphthyltriazen both give rise to a mixture of 2,2'-azonaphthalene (XVI) and dibenzo[a,h]phenazine (XVII), it is logical that in both reactions the same intermediates, the arylnitrenes, are involved.



The formation of dibenzo[a,h] phenazine (XVII) is thus indicative of arylnitrene intermediates in the dehydrogenation of 1,3-di-2-naphthyltriazen (XIV) and 3-2'naphthyl-1-phenyltriazen. The presence of arylnitrene intermediates in the lead tetra-acetate dehydrogenation of other 1,3-diaryltriazens may therefore be inferred, although we have been unable to confirm it by isolation of the appropriate phenazine derivatives.

Finally, the electron paramagnetic resonance spectrum \* of the reaction mixture between 1,3-diphenyltriazen and lead tetra-acetate in benzene solution was recorded. A triplet with a coupling constant of about 10 gauss and fine-structure was obtained which indicates a nitrogen radical, most probably the triazenyl radical (II; Ar = Ph) which, on loss of nitrogen, gives phenylnitrene.

#### EXPERIMENTAL

2-Iodonaphthalene, 2-naphthylamine, naphthalene, azobenzene, p-chlorotoluene, biphenyl, anisole, t-butylbenzene, nitrobenzene, and lead tetra-acetate were commercial

<sup>6</sup> G. H. Williams, 'Homolytic Aromatic Substitution, Pergamon, Oxford, 1960. products purified in the conventional manner. 4-Chlorobiphenyl,<sup>7</sup> 4-methylbiphenyl,<sup>8</sup> 2-phenylnaphthalene,<sup>9</sup> 4chloroazobenzene,<sup>10</sup> 4,4'-dichloroazobenzene,<sup>11</sup> 4-methylazobenzene,124,4'-dimethylazobenzenc,132,2'-azonaphthalene,14 and dibenzo [a,h] phenazine <sup>15</sup> were prepared as described in the literature.

Preparation of Triazens.-1,3-Diphenyltriazen,<sup>16</sup> 1,3-di-ptolyltriazen,<sup>17</sup> 3-p-chlorophenyl-1-phenyltriazen,<sup>18</sup> and 1phenyl-3-p-tolyltriazen 19 were prepared according to the methods described in the literature. 1,3-Di-2-naphthyltriazen was obtained from 2-naphthyl azide 20 and 2naphthylmagnesium iodide according to the procedure of Dimroth.<sup>21</sup> In a 1-l. three-necked flask equipped with a stirrer, condenser, and tap-funnel, 2-naphthyl azide (22.1 g.) was dissolved in anhydrous ether (150 c.c.). A solution of 2-napthylmagnesium iodide [prepared from 2-iodonaphthalene (33.2 g.), magnesium turnings (3.8 g.), and anhydrous ether (200 c.c.)] was added dropwise to the 5.4; N, 17.2. C<sub>16</sub>H<sub>13</sub>N<sub>3</sub> requires C, 77.55; H, 5.55; N, 17.85%).

Dehydrogenation of 1,3-Diphenyltriazen with Lead Tetraacetate in Monosubstituted Aromatic Solvents .- A solution of 1,3-diphenyltriazen (0.02 mole) in a monosubstituted aromatic solvent PhX (50 c.c.) (X = H, OMe, CMe<sub>3</sub>, NO<sub>3</sub>) was added to a suspension of lead tetra-acetate (0.02 mole) in the same solvent (50 c.c.). The mixture was kept at  $40^{\circ}$  for 3.5 hr. and then filtered. The resulting solution was washed with 10% aqueous sodium hydrogen carbonate, dried  $(Na_2SO_4)$ , and filtered through an alumina column (25  $\times$ 3.5 cm.), followed by elution with benzene (21.). The eluted solution was concentrated by distillation, and the residue (ca. 10 c.c.) was analyzed by gas-liquid chromatography using one of the following columns: A, 10% silicone oil on Celite (100-120 mesh); B, 5% polyethylene glycol 20M on Celite (80-100 mesh); C, 30% silicone oil on Celite (85-100 mesh); D,  $2\cdot5\%$  polyethylene glycol 20M on

## TABLE 2

Phenylation of monosubstituted aromatic compounds with phenyl radicals derived from 1,1-diphenyltriazen and lead tetraacetate. Quantities of reactants and yields of products as determined by gas-liquid chromatography

		DhN-N-NLIDh	Db(OAa)		Ph•C <sub>6</sub> H <sub>4</sub> •X (g.	)	
$X = H^a$	PhX	(g.) 4·15	(g.) 9.32	0-	<i>m</i> - 1·297	<i>p</i> -	PhN=NPh 0.781
OMe <sup><i>b</i></sup>		$\begin{array}{c} 4 \cdot 01 \\ 4 \cdot 08 \end{array}$	$9.11 \\ 9.17$	$0.638 \\ 0.555$	$0.193 \\ 0.167$	$0.144 \\ 0.129$	0.695
CMe <sub>3</sub> °		$4.02 \\ 4.02$	9·04 9·04	$0.072 \\ 0.055$	$0.268 \\ 0.232$	$0.138 \\ 0.113$	0.715
NO <sub>2</sub> <sup>d</sup>		4.02 4.02 4.00	$9.04 \\ 9.12 \\ 9.02$	0·714 0·657 0·580	$0.145 \\ 0.124 \\ 0.105$	0·498 0·40 0·385	0.273
	<sup>a</sup> Column A at 20	00°. <sup>b</sup> Column B	at 180°. • Col	umn C at 190	°. <sup>d</sup> Column	D at 180°.	

stirred solution of the azide at room temperature. When the addition was complete (1 hr.) the mixture was refluxed for 30 min., cooled, and poured into a cooled solution made from 25% aqueous ammonium chloride (164 c.c.) to which 25% ammonia (16.4 c.c.) had been added. The precipitate was filtered off and recrystallized from dioxan several times, to afford 1,3-di-2-naphthyltriazen (20 g.), m.p. 196-197° (decomp.) (Found: C, 80.25; H, 5.0; N, 14.6. C<sub>20</sub>H<sub>15</sub>N<sub>3</sub> requires C, 80.8; H, 5.1; N, 14.15%).

3-2'-Naphthyl-1-phenyltriazen was obtained from aniline and 2-naphthyldiazonium chloride. 2-Naphthylamine (5 g.) was dissolved in concentrated hydrochloric acid (9 c.c.) and water (50 c.c.), and the solution kept at  $5^{\circ}$  during the addition of a solution of sodium nitrite (2.9 g.) in water (50 c.c.). To this solution, neutralized with sodium acetate, was added a solution of aniline (3.8 g.) in dioxan (20 c.c.). Dilution with water precipitated 3-2'-naphthyl-1-phenyltriazen (6.5 g.), which was filtered off and obtained as needles, m.p. 150° (from dioxan) (Found: C, 77.65; H,

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- <sup>8</sup> M. Gomberg and J. C. Pernert, J. Amer. Chem. Soc., 1926, 48, 1372.
  <sup>9</sup> H. E. Carter and E. J. VanLoon, J. Amer. Chem. Soc., 1938,
- **60**, 1077
- <sup>10</sup> E. Bamberger, Ber., 1896, **29**, 103.
- <sup>11</sup> J. Burus, H. McCombie, and H. A. Scaraborough, J. Chem. Soc., 1928, 2933.
  - <sup>12</sup> C. Mills, J. Chem. Soc., 1895, 67, 925.
  - <sup>13</sup> E. Börnstein, Ber., 1901, 34, 1278.

Celite (66-100 mesh). The instrument used was a Griffin and George D6 Gas Density Balance Chromatograph, and the analytical method used was that of Phillips and Timms.<sup>22</sup> The experimental results are recorded in Table 2.

Dehydrogenation of 1,3-Di-p-tolyltriazen with Lead Tetraacetate in Carbon Tetrachloride.---1,3-Di-p-tolyltriazen (4 g.) was dissolved in carbon tetrachloride (50 c.c.), and the solution added to a suspension of lead tetra-acetate (7.88 g.) in carbon tetrachloride (50 c.c.). The mixture was kept at 40° for 22 hr. and worked up as described above. Gaschromatographic analysis (column A at 170°) of residual product showed the presence of p-chlorotoluene (1.0 g.) and 4,4'-dimethylazobenzene. The mixture was then chromatographed on an alumina column ( $40 \times 3$  cm.) using light petroleum (b.p.  $40-60^{\circ}$ ) as eluent. A colourless oil was first obtained; the boiling point of this compound (159- $161^{\circ}/760$  mm.) agreed with that of p-chlorotoluene, and its infrared spectrum was identical with that of the authentic material. Further elution with light petroleum afforded

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   <sup>15</sup> F. Reitzenstein and F. Audre, J. prakt. Chem., 1913, (2), 87, 106. <sup>16</sup> B. Fischer and H. Wimmer, *Ber.*, 1887, 20, 1581.
- - <sup>17</sup> R. Nietzki, Ber., 1877, 10, 662.
- <sup>18</sup> A. Hantzsch and F. M. Perkin, Ber., 1897, 30, 1412.
- <sup>19</sup> E. Noelting and F. Binder, Ber., 1887, 20, 3004.
- M. O. Forster and H. E. Fierz, J. Chem. Soc., 1907, 91, 1949.
   O. Dimroth, Ber., 1905, 38, 670.
   C. S. G. Phillips and P. L. Timms, J. Chromatog., 1961, 5,
- 131.

a crystalline compound, m.p.  $140-141^{\circ}$ , identified as 4,4'-dimethylazobenzene by mixed melting point and by comparison of its infrared spectrum with that of the authentic compound.

Dehydrogenation of 1-p-Chlorophenyl-3-phenyltriazen with Lead Tetra-acetate in Benzene.—1-p-Chlorophenyl-3-phenyltriazen (4 g.) was made to react with lead tetra-acetate (7.7 g.) in benzene (200 c.c.), and the mixture was filtered, concentrated, and worked up as described above. Gaschromatographic analysis of the residue (column B at 180°, and column A at 200°) showed the presence of the following compounds: biphenyl (0.5 g.), 4-chlorobiphenyl (0.95 g.), azobenzene (0.1 g.), 4-chloroazobenzene (0.36 g.), and 4,4'dichloroazobenzene (0.27 g.).

The identity of the reaction products was confirmed by column chromatography ( $70 \times 4$  cm.) on silica gel (Merck) (0.05-0.2 mm.) using cyclohexane as eluent and collecting fractions of 30 ml.; each fraction was examined by thinlayer chromatography. The products so obtained were identified by comparison of their infrared spectra with those of the authentic specimens, and by mixed melting points. The first 1500 ml. of eluate contained no products; the next fractions (300 ml.) contained a solid compound identified as 4-chlorobiphenyl, m.p. and mixed m.p. 76-77°. Fractions (1200 ml.) were then collected, and shown by t.l.c. to contain a mixture of 4-chlorobiphenyl and biphenyl; the next 150 ml. of eluate afforded pure biphenyl, m.p. and mixed m.p. 69-71°. Biphenyl and 4,4'-dichloroazobenzene were then eluted together (1000 ml.), followed by 150 ml. of solution containing pure 4,4'-dichloroazobenzene, m.p. and mixed m.p. 187-188°. A solution (2500 ml.) of 4,4'-dichloroazobenzene and 4-chloroazobenzene was collected, followed by a fraction (400 ml.) containing pure 4-chloroazobenzene, m.p. and mixed m.p. 89-90°. After 2000 ml. of solution of 4-chloroazobenzene and azobenzene, pure azobenzene was finally obtained (500 ml.), m.p. and mixed m.p. 66-67°. Further elution afforded only tars.

Dehydrogenation of 3-Phenyl-1-p-tolyltriazen with Lead Tetra-acetate in Benzene.—The reaction was carried out with 3-phenyl-1-p-tolyltriazen (4.01 g.) and lead tetra-acetate (7.8 g.) in benzene (200 c.c.), following the procedure described above. Gas-chromatographic analysis (column A at 200°) allowed the following compounds to be determined: biphenyl (0.41 g.), 4-methylbiphenyl (0.49 g.), azobenzene (0.12 g.), 4-methylazobenzene (0.26 g.), and 4,4'-dimethyl-azobenzene (0.2 g.).

The reaction mixture was then chromatographed on a silica gel column ( $70 \times 4$  cm.) using light petroleum (b.p.  $40-60^{\circ}$ ) as eluent. A mixture of biphenyl and 4-methylbiphenyl was collected together in the first 2000 ml. of eluate; the two compounds were separated by g.l.c. using a Varian Aerograph model 712 preparative gas chromatograph with a 20% silicone oil column at 230°. Biphenyl and 4-methylbiphenyl were identified by comparison of their infrared spectra with those of the authentic materials, and by mixed melting points. Further elution with a 3:1 mixture of light petroleum (b.p.  $40-60^{\circ}$ ) and benzene (2000 ml.) afforded a mixture of azobenzene and 4-methylazobenzene which were separated by g.l.c. using the above cited column at 280°. The identity of the two products was confirmed by mixed melting points and infrared

Dehydrogenation of 1,3-di-2-naphthyltriazen with Lead Tetra-acetate in Benzene.--- A solution of 1.3-di-2-naphthyltriazen (7.35 g.) in benzene (150 c.c.) was added to a suspension of lead tetra-acetate (11 g.) in benzene (100 c.c.). The solution was stirred at 40° for 15 hr., and then filtered and concentrated. The residue was chromatographed on an alumina column  $(80 \times 5 \text{ cm.})$  using light petroleum (b.p.  $40-60^{\circ}$ ) as eluent (1500 ml.), to afford 2-phenylnaphthalene (1.5 g.), m.p. and mixed m.p. 103-104°. The infrared spectrum of this compound was identical with that of the 2-phenylnaphthalene prepared independently.<sup>9</sup> Subsequent elution with a 4:1 mixture (2000 ml.) of light petroleum (b.p. 40-60°) and benzene gave 2,2'-azonaphthalene (0.1 g.), identified by mixed m.p. and by comparison of the infrared spectrum with that of the authentic material.<sup>14</sup> Finally, using a 1:2 mixture of light petroleum (b.p. 40-60°) and benzene (1500 ml.), dibenzo[a,h]phenazine (2 g.) was obtained, m.p. and mixed m.p.<sup>15</sup> 283-284° (Found: C, 86.05; H, 4.05; N, 9.9. Calc. for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>: C, 86.0; H, 3.95; N, 10.05%). The infrared and ultraviolet spectra of the reaction product and those of the synthetic dibenzo[a,h] phenazine <sup>15</sup> were identical.

Dehydrogenation of 3-2'-Naphthyl-1-phenyltriazen with Lead Tetra-acetate in Ethyl Acetate.—The reaction was carried out using 3-2'-naphthyl-1-phenyltriazen (8 g.), lead tetra-acetate (14·3 g.), and ethyl acetate (250 c.c.). The mixture was stirred at 40° for 15 hr., and then worked up as described above. Column chromatography of the residual product on an alumina column ( $80 \times 5$  cm.), using light petroleum (b.p. 40—60°) as eluent (800 ml.), gave naphthalene (0·5 g.); a 4:1 mixture of light petroleum (b.p. 40—  $60^{\circ}$ ) and benzene (1200 ml.) gave azobenzene (0·3 g.); a 1:2 light petroleum (b.p. 40— $60^{\circ}$ )-benzene mixture (1500 ml.) gave dibenzo[a,h]phenazine (1·5 g.); ether gave only tars. The products were all identified by mixed m.p. and by comparison of their infrared spectra with those of the authentic materials.

Decomposition of 2-Naphthyl Azide in Toluene.—2-Naphthyl azide (8 g.) was dissolved in toluene (200 c.c.), and the solution refluxed for 24 hr. The solvent was removed under reduced pressure, and the residue chromatographed on an alumina column ( $80 \times 5$  cm.). Elution with 1500 ml. of light petroleum (b.p. 40—60°) gave 2-naphthyl azide (3 g.); a 4:1 mixture of light petroleum (b.p. 40—60°) and benzene (1000 ml.) gave 2,2'-azonaphthalene (0·1 g.), and finally elution with 2000 ml. of a 1:2 mixture of light petroleum (b.p. 40—60°) and benzene gave dibenzo[a,h]phenazine (2 g.). Both reaction products were identified by infrared spectra and by mixed melting points.

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