

## Reactions of Lead(IV). Part XXV.<sup>1</sup> Oxidation of Some Benzyl-substituted Hydrazine Derivatives

By R. O. C. Norman,\* R. Purchase, C. B. Thomas, and (in part) J. B. Aylward, Department of Chemistry The University of York, Heslington, York YO1 5DD

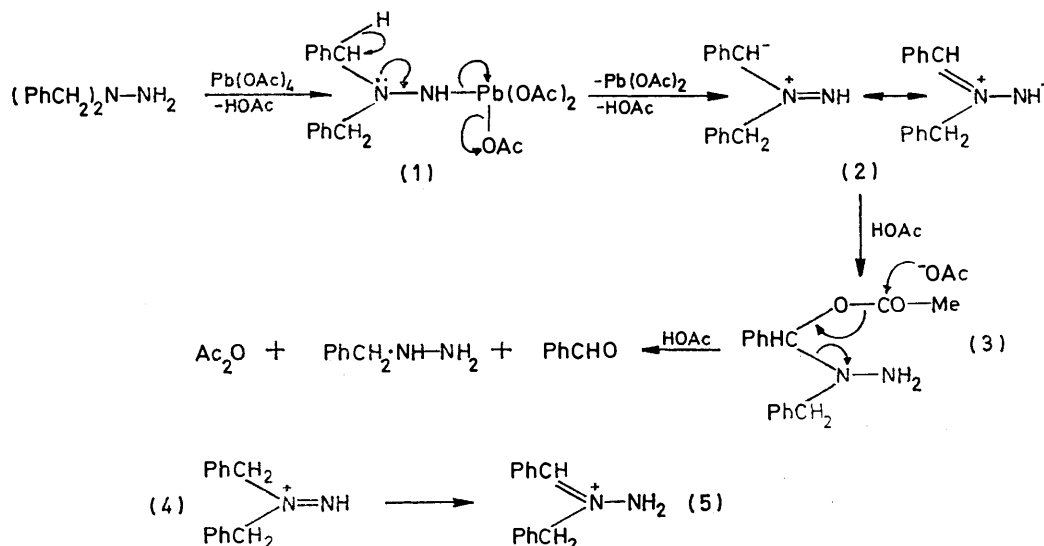
The products of oxidation of a number of benzyl-substituted hydrazine derivatives by lead tetra-acetate have been determined; in the case of *NN*-dibenzylhydrazine they depend on the way in which the reagents are mixed, and in that of *N*-acetyl-*N'*-benzylhydrazine on the temperature. There is evidence that compounds of the type  $\text{PhCH}_2\text{-NR}\cdot\text{NHR}'$  ( $\text{R}' = \text{H}$  or acyl) initially undergo oxidative debenzoylation when  $\text{R} = \text{alkyl}$  but deacylation when  $\text{R} = \text{acyl}$ .

REFERENCE has previously been made in this series to the diversity of products from the oxidation of hydrazine derivatives by lead tetra-acetate.<sup>2</sup> We now report studies of the reactions of this oxidant with other compounds derived from hydrazine, in particular those containing *N*-benzyl substituents.

*NN*-Dibenzylhydrazine.—When a dilute solution of *NN*-dibenzylhydrazine in dichloromethane–benzene was added to lead tetra-acetate (1 mol. equiv.) in the same

obtained the same results as Koga and Anselme;<sup>3</sup> in addition, we found a further product, the diacyl derivative  $\text{PhCH}_2\cdot\text{NAC}\cdot\text{NHBz}$ . Moreover, when we reduced the amount of lead tetra-acetate, we isolated tetrabenzyltetrazene; this supported the view<sup>3</sup> that this is an intermediate in the formation of benzaldehyde, benzyl azide, and dibenzylamine.

It is apparent that an intermediate from *NN*-dibenzylhydrazine and lead tetra-acetate undergoes competing



SCHEME 1

solvent at room temperature, benzaldehyde *NN*-dibenzylhydrazone was isolated. However, when the amount of lead tetra-acetate was increased to 3 mol. equiv. this product was not formed, but benzaldehyde (89%), benzyl acetate (48%), and acetic anhydride (19%) were obtained; a subsequent experiment showed that benzaldehyde was present before work-up and was not therefore a hydrolysis product. Finally, with methanol as solvent and equimolar amounts of the hydrazine and oxidant, the *NN*-dibenzylhydrazones of both benzaldehyde and formaldehyde were formed.

These results were surprising in the light of a report, which appeared while this work was in progress, that the addition of an excess of lead tetra-acetate to *NN*-dibenzylhydrazine gives benzaldehyde, benzyl azide, and dibenzylamine.<sup>3</sup> We repeated this work and

reactions; an excess of the hydrazine leads to the tetrazene and thence, by further oxidation, to products derived therefrom, whereas, in the absence of an excess of the hydrazine, the intermediate yields benzaldehyde (not by way of the tetrazene in this case), benzyl acetate, and acetic anhydride, benzaldehyde giving its *NN*-dibenzylhydrazone if more of the hydrazine is added after the oxidant has been fully consumed.

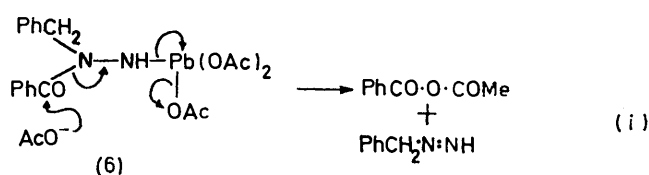
We considered first the possibility that the intermediate in question is the lead derivative (1). Thus, reaction of this species at the lead-bearing nitrogen atom with further hydrazine could yield the tetrazene and thence the tetrazene, whereas the loss of a proton from a benzylic carbon atom could give the 1,3-dipolar compound (2) from which benzaldehyde and acetic anhydride might be formed as in Scheme 1, together with

<sup>1</sup> Part XXIV, R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1972, 578.

<sup>2</sup> W. A. F. Gladstone, *J. Chem. Soc. (C)*, 1969, 1571.

<sup>3</sup> G. Koga and J.-P. Anselme, *J. Amer. Chem. Soc.*, 1969, **91**, 4323.

benzylhydrazine, which is a likely precursor of the remaining product, benzyl acetate (see later). The mediation of a 1,3-dipolar compound has precedent in lead tetra-acetate chemistry;<sup>4</sup> benzaldehyde phenylhydrazone is thought to give the dipole  $\text{PhC}\equiv\text{N}^+\text{-}\bar{\text{N}}\text{Ph}$  since, when its oxidation is carried out in the presence of acrylonitrile, the pyrazole derivatives expected from the trapping of this dipole by the nitrile are formed.<sup>4</sup> We

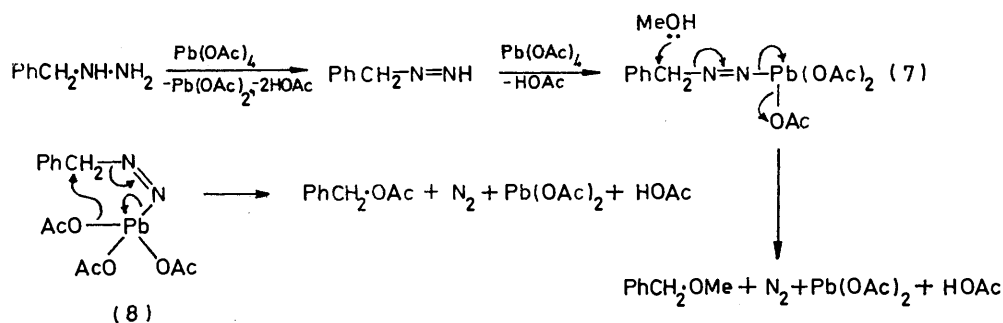


therefore carried out the oxidation of *NN*-dibenzylhydrazine by adding it slowly, in acrylonitrile solution, to a solution of the oxidant and acrylonitrile in dichloromethane; however, the same products were isolated, in

acetate ion with an intermediate (6) would yield the mixed anhydride  $\text{PhCO}\cdot\text{O}\cdot\text{COMe}$  and thence benzoic acid, leaving benzyl-di-imide, from which benzyl acetate would be expected (see later).

The tetrazene could also be formed by way of the intermediate (6) (*cf.* *NN*-dibenzylhydrazine), but it is notable that in this case the tetrazene is formed under conditions in which *NN*-dibenzylhydrazine does not give tetrazene. Two possible causes for the difference, both of which are connected with the electron-withdrawing property of the benzoyl substituent, are that *N*-benzoyl-*N*-benzylhydrazine should react less rapidly than the *NN*-dibenzyl compound with lead tetra-acetate, increasing the chance of its reacting with the intermediate (6), and that this reaction might itself be more rapid than the analogous process with the *NN*-dibenzyl compound.

*Benzylhydrazine.*—The complete oxidation of benzylhydrazine at room temperature in dichloromethane required 2 mol. equiv. of lead tetra-acetate; the product



SCHEME 2

approximately the same yields, as in the absence of the trap, and there was no trace of a heterocyclic product. Although this does not rule out the possibility that the dipolar compound (2) is an intermediate, other possibilities should be considered. One such is the species (4), which could be formed either from (1) or *via* attack of the oxidant at the tertiary nitrogen atom; this could yield the tetrazene by reaction with more of the hydrazine or the alternative products by a tautomeric shift to give (5) and thence, with acetate ion, (3). The results of our examination of related hydrazines do not enable us to clarify this aspect of the mechanism; however, they do support the view that the first benzyl group in *NN*-dibenzylhydrazine is removed in an oxidative process, to give benzaldehyde, as shown for the intermediate (3) in Scheme 1.

*N-Benzoyl-N-benzylhydrazine.*—The slow addition of this hydrazine in dichloromethane to an excess (2 mol. equiv.) of lead tetra-acetate in dichloromethane gave benzyl acetate (55%), benzoic acid, and the corresponding tetrazene (15%). Benzaldehyde was not detected, and this is consistent with the view that it is the benzoyl group which is removed first; thus, the reaction of

was benzyl acetate (78%), and it was immaterial whether the oxidant was added to the hydrazine or *vice versa*. When the reaction was carried out in methanol, benzyl acetate (63%) was again the major product, but a 27% yield of benzyl methyl ether was also obtained.

The formation of the latter product suggests that the benzylic fragment is detached from nitrogen as a carbonium ion or an incipient carbonium ion. Thus, it seems probable that oxidation leads first to benzyl-di-imide which, *via* the organo-lead intermediate (7), yields benzyl acetate or the methyl ether by nucleophilic attack (Scheme 2). However, since the acetate predominated, despite there being more available methanol than acetic acid and the former's being the stronger nucleophile,<sup>5</sup> it seems probable that benzyl acetate results from intramolecular reaction of the intermediate (7), as shown in formula (8).

*N-Acetyl-N'-benzylhydrazine.*—The addition of an equimolar amount of lead tetra-acetate to a solution of *N*-acetyl-*N'*-benzylhydrazine in dichloromethane at  $-50$  to  $-70^\circ$  gave benzaldehyde acetylhydrazone (25%). When a two-fold excess of the oxidant was used under these conditions, benzyl acetate (94%) and acetic

<sup>4</sup> W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc. (C)*, 1969, 2587.

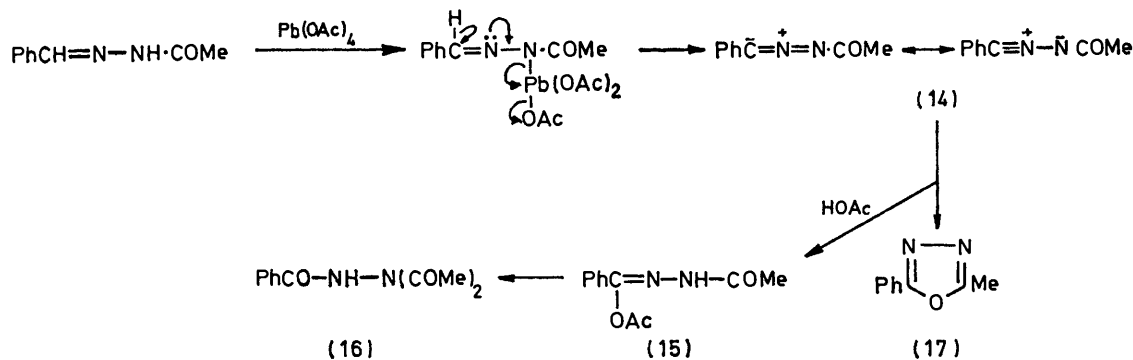
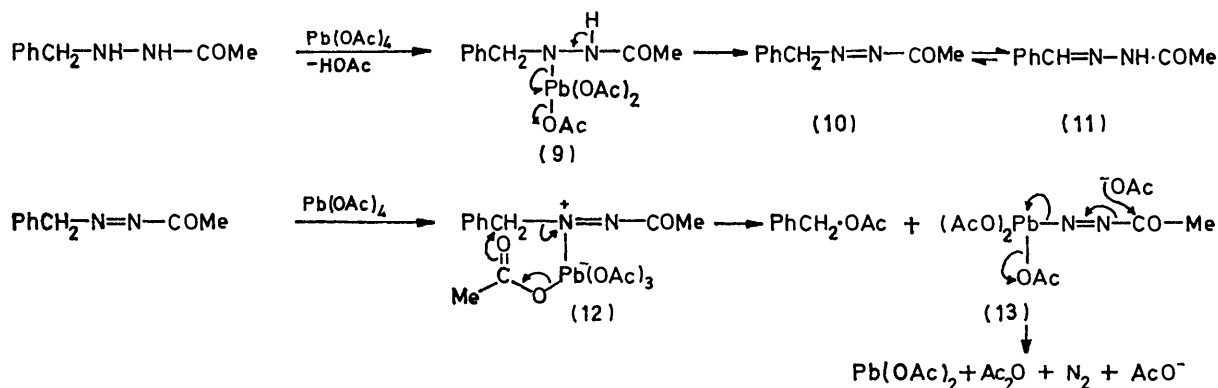
<sup>5</sup> E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1959, p. 301.

anhydride (75%) were obtained; in contrast, when the first mol. equiv. of the oxidant was added under these conditions but addition of the second was delayed until the mixture had warmed to room temperature, only small yields of these compounds were obtained (benzyl acetate, 21%; acetic anhydride, 16%), and four other products were identified: the oxadiazole (17) (23%), benzaldehyde (11%), benzylidene diacetate (9%), and *NN*-diacetyl-*N'*-benzoylhydrazine (16) (6%).

The same six products were also formed when benzaldehyde acetylhydrazone was oxidised by lead tetraacetate at room temperature, so that we interpret the course of oxidation of *N*-acetyl-*N'*-benzylhydrazine, and the dependence of the products on the conditions, as

path suggested for its formation in Scheme 3 is unexceptional. Reaction of lead(IV) is more likely to occur at the alkylated nitrogen atom, to give structure (9) as shown, than at the less nucleophilic acetylated nitrogen atom, and this should also be the case for further reaction of the azo-compound (10); we therefore infer mediation of the species (12), from which benzyl acetate can be formed as shown in Scheme 3, together with the intermediate (13), from which the other product, acetic anhydride, is to be expected.

In accord with this suggestion for the formation of benzyl acetate, benzyl methyl ether was obtained when methanol was the solvent. However, its yield, 26%, was considerably less than that of the accompanying



follows. Oxidation at low temperature gives an intermediate which, in the absence of an excess of the oxidant, yields benzaldehyde acetylhydrazone; this can be isolated or, on the addition of more oxidant, it affords the six products already mentioned. However, at least at low temperature, the rate of oxidation of the intermediate is greater than that of its conversion into benzaldehyde acetylhydrazone; thus, when it is formed in the presence of an excess of the oxidant at  $-50$  to  $-70^\circ$ , it preferentially undergoes oxidation to give benzyl acetate and acetic anhydride.

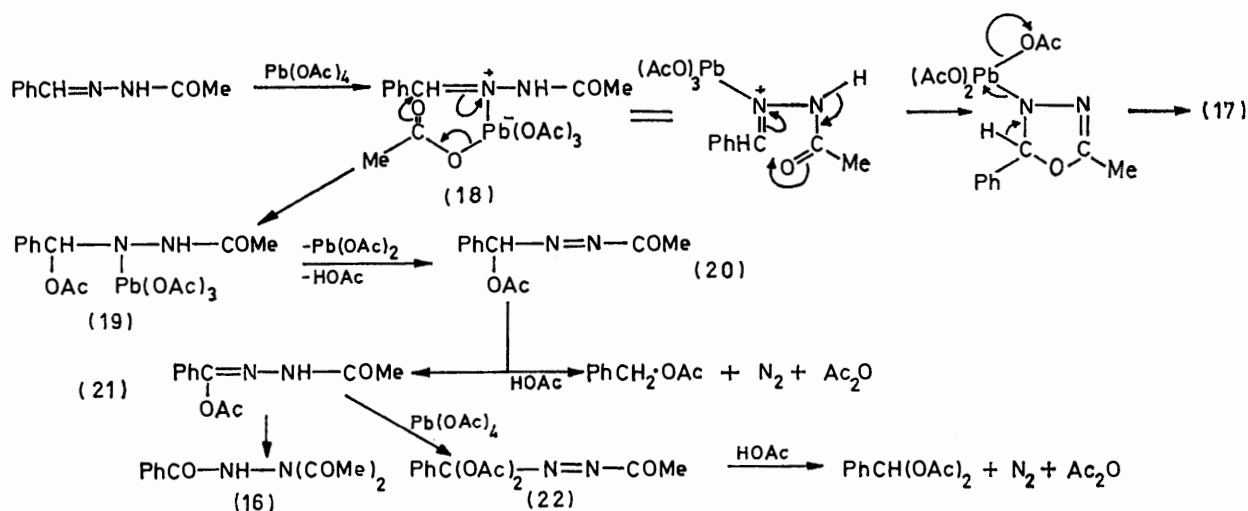
We suggest that the intermediate is the azo-compound (10). Thus, its tautomeric conversion into benzaldehyde acetylhydrazone (11) is to be expected, and the

benzyl acetate (73%), suggesting that, whereas the former product is formed by solvolysis of the intermediate (12), the latter is derived by intramolecular reaction of this species, as shown in Scheme 3 (see also Scheme 2). When oxidation was carried out in acetic [ $^2\text{H}$ ]acid, the benzyl acetate formed did not contain deuterium, showing that it does not arise in the same way as when benzaldehyde acetylhydrazone is the starting material (see later).

At first inspection, it seemed likely that the oxidation of benzaldehyde acetylhydrazone would occur in a manner similar to that of benzaldehyde phenylhydrazone, namely, by formation of the 1,3-dipolar intermediate (14) from which both the triacyl product

(16) and the oxadiazole (17) would be expected. However, oxidation of the acetylhydrazone in the presence of acrylonitrile gave the same products, in approximately the same yields, as in its absence, and there was no trace of a pyrazoline or a pyrazole (compare the oxidation of the phenylhydrazone<sup>4</sup>). Moreover, when varying amounts of acetic acid were included in the reaction mixture during oxidation of the acetylhydrazone in dichloromethane, the relative yields of the triacyl product (16) and the oxadiazole (17) were unaffected; had they been formed from the dipolar compound (14),

infer that deuterium is incorporated into an intermediate in the oxidation, a likely species being the azo-compound (20), which could yield benzyl acetate as in Scheme 5 or deuteriated benzyl acetate in acetic [<sup>2</sup>H]acid [cf. reaction (ii)]; an analogous mechanism has been adduced, involving nucleophilic displacement on intermediate diimides of the type ArN=N-COR, for the oxidation of *N*-acyl-*N'*-arylhydrazines by manganese dioxide.<sup>6</sup> Another product, benzylidene diacetate, was also found to contain one gram atom of deuterium (78%) when oxidation was carried out in acetic [<sup>2</sup>H]acid, and we

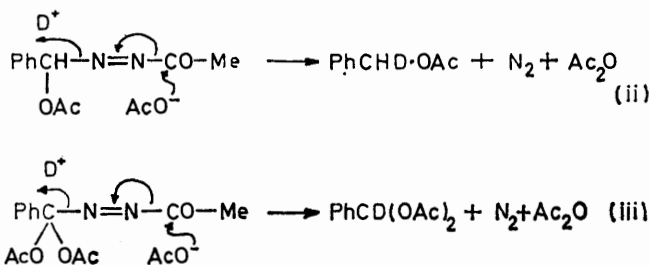


an increase in the ratio on the addition of acetic acid would have been expected (see Scheme 4).

We therefore suggest that the acetyl group in benzaldehyde acetylhydrazone so reduces the nucleophilicity of the adjacent nitrogen atom that the imino-nitrogen atom becomes the seat of attack. The intermediate (18) formed with lead tetra-acetate could cyclise to the oxadiazole (17) or yield the triacyl compound (16) [presumably by way of (19), (20), and (21), followed by rearrangement of the last; cf. formation of *N*-acetyl-*N'*-benzoyl-*N*-phenylhydrazone from benzaldehyde phenylhydrazone<sup>4</sup>] without acetic acid necessarily affecting the ratio of the yields of the two products.

The formation of benzyl acetate seemed at first difficult to account for unless benzaldehyde acetylhydrazone were to react in part by way of its azo-tautomer (10). However, this possibility was ruled out as the major pathway by our finding that, when oxidation of the acetylhydrazone was carried out in acetic [<sup>2</sup>H]acid, 71% of the benzyl acetate which was formed contained one gram atom of deuterium, whereas the benzyl acetate formed from *N*-acetyl-*N'*-benzylhydrazone [when the azo-compound (10) is thought to be the relevant intermediate] does not contain deuterium when oxidation is carried out in acetic [<sup>2</sup>H]acid; the acetylhydrazone did not itself undergo detectable exchange in acetic [<sup>2</sup>H]acid during the time allowed for oxidation. We therefore

suggest that its formation involves oxidation of the azo-compound (20) to (22) (as in Scheme 5) followed by reaction (iii) with H<sup>+</sup> or D<sup>+</sup>.



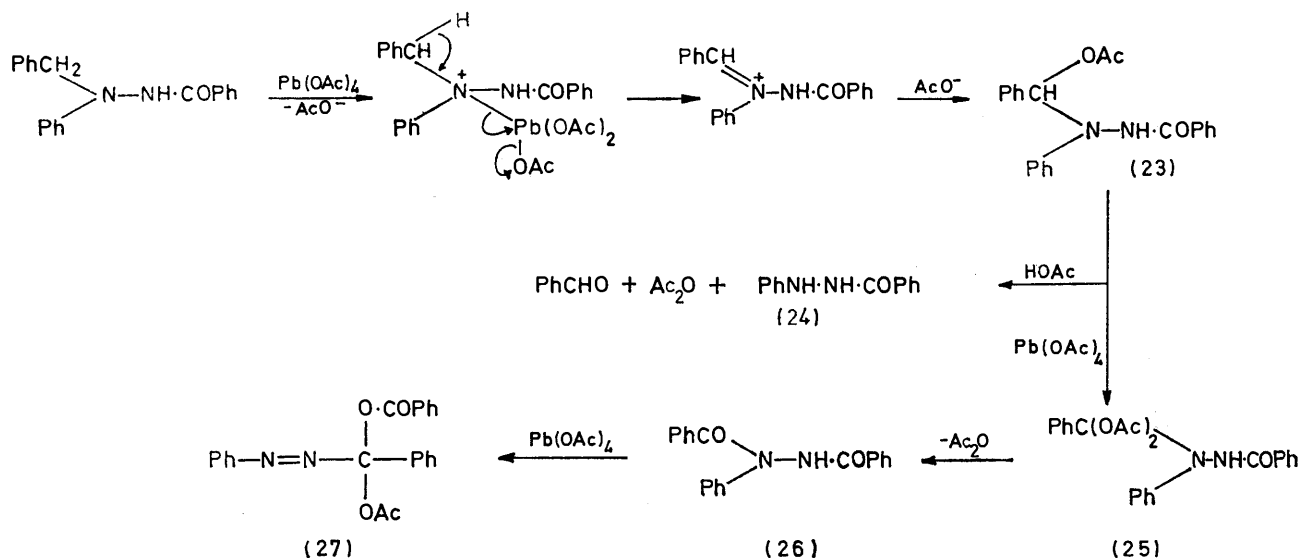
*N'*-Benzoyl-*N*-benzyl-*N*-phenylhydrazone.—When this hydrazone was oxidised with 1 mol. equiv. of lead tetraacetate, *N*-benzoyl-*N'*-phenylhydrazone (24) was obtained, together with benzaldehyde and a trace of the azoacylal (27). In contrast, when a three-fold excess of the oxidant was employed, the major products were *NN'*-dibenzoyl-*N*-phenylhydrazone (26) (15%) and the azoacylal (27) (7%); it has already been shown<sup>2</sup> that the former gives the latter under the reaction conditions. Here again, then, the inference is that an intermediate is formed which undergoes competing reactions, namely, conversion into the product (24) and further oxidation.

<sup>6</sup> R. B. Kelly, G. R. Umbreit, and W. F. Liggett, *J. Org. Chem.*, 1964, **29**, 1273.

The intermediate is likely to be (23), formed as in Scheme 6; thus, we should expect its ready conversion into *N*-benzoyl-*N'*-phenylhydrazine by reaction with acetic acid, and a second oxidation of similar type to that yielding (23) should give the intermediate (25), from which the diacyl product (26) would be expected. The formation of the product (24) demonstrates the occurrence of oxidative debenzoylation.

*N'*-Acyl-*NN*-dibenzylhydrazines.—The products of the oxidation of some members of this group are in Table 1.

acetyl-*N'*-benzylhydrazine (see earlier), and we found that *N*-benzoyl-*N'*-benzylhydrazine gave the same six products as the *NN*-dibenzyl compound, except that, as expected, the yield of benzaldehyde was very much lower in the former case (14%). Moreover, when *N'*-benzoyl-*NN*-dibenzylhydrazine was oxidised in methanol, methyl benzoate replaced benzoic acid as a product, consistent with removal of the benzoyl group from nitrogen in an intermediate such as (20; PhCO for MeCO) by reaction with methanol (giving methyl



SCHEME 6

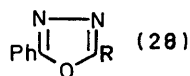
TABLE I

Products from the oxidation of  $(\text{PhCH}_2)_2\text{N}\cdot\text{NH}\cdot\text{COR}$  with  $\text{Pb}(\text{OAc})_4$  (2 mol. equiv.)

R	Solvent	Products (mol %)					
		PhCHO	PhCH <sub>2</sub> -OAc	PhCH(OAc) <sub>2</sub>	RCO <sub>2</sub> H	Ac <sub>2</sub> O	(28)
Ph	CH <sub>2</sub> Cl <sub>2</sub>	106	72	3	63	34	10 <sup>a</sup>
Ph	HOAc	108	70	<i>b</i>	63	<i>b</i>	6 <sup>a</sup>
Ph	MeOH <sup>c</sup>	101	42	<i>b</i>	66 <sup>d</sup>	<i>b</i>	3 <sup>a</sup>
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	98	79	2	79	36	2 <sup>e</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	105	63	5	36	27	12 <sup>f</sup>
Me <sup>g</sup>	CH <sub>2</sub> Cl <sub>2</sub>	103	77	11	<i>b</i>	84	7 <sup>h</sup>

<sup>a</sup> R = Ph. <sup>b</sup> Not estimated. <sup>c</sup> PhCH<sub>2</sub>-OMe (6%) also formed. <sup>d</sup> As PhCO<sub>2</sub>Me. <sup>e</sup> R = *p*-BrC<sub>6</sub>H<sub>4</sub>. <sup>f</sup> R = *p*-MeC<sub>6</sub>H<sub>4</sub>. <sup>g</sup> 3 Mol. equiv. Pb(OAc)<sub>4</sub>; a trace of PhCO·NH·NAc<sub>2</sub> was detected. <sup>h</sup> R = Me.

Yields are based on the premise that 1 mol of the hydrazine can give only 1 mol of each product; the fact that the yield of benzaldehyde is greater than 100% in several cases by amounts which exceed the experimental error in the g.l.c. estimation thus indicates that a second mol of this product can be produced.



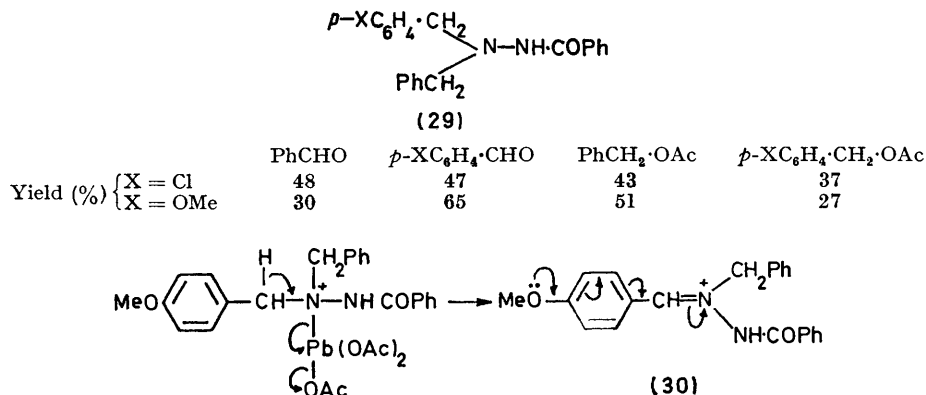
The results suggest that the first step is oxidative debenzoylation, to give benzaldehyde and the *N*-acyl-*N'*-benzylhydrazine; thus, apart from the high yield of benzaldehyde, the mixture of products from *N'*-acetyl-*NN*-dibenzylhydrazine corresponds to that from *N*-

benzoate) or acetic acid (giving the mixed anhydride and thence benzoic acid).

Oxidation of the compounds (29) gave the mixtures of aromatic aldehydes and benzylic acetates shown. Thus, there is little dependence in the oxidative debenzoylation step on the electronic character of the *para*-substituent; the small facilitating effect of the *p*-OMe group (compare yields of the *p*-methoxy- and the unsubstituted aldehydes) may be associated with developing conjugation between this substituent and the cationic centre in the transition state for formation of the intermediate (30) in the oxidative debenzoylation.

*N*-Acetyl-*N'*-acyl-*N*-benzylhydrazines.—The results for the oxidation of three members of this group are in Table 2. The nature of the products, together with the

absence of benzaldehyde, suggests that the acetyl group is cleaved from nitrogen before the benzyl group, as we have argued is the case with *N*-benzoyl-*N*-benzylhydrazine; thus, reaction of an intermediate (31) as



shown would give acetic anhydride and the azo-compound (32), reaction of which would be expected to give the other products [*cf.* reaction of the azo-compound (10) and its tautomer (11)].

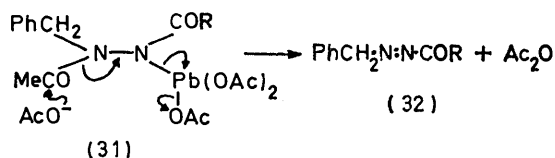


TABLE 2

Products from the oxidation of PhCH<sub>2</sub>·NAC·NH·COR with Pb(OAc)<sub>4</sub> (2 mol. equiv.) in dichloromethane

R	Products (mol %)				(28)
	PhCH <sub>2</sub> ·OAc	PhCH(OAc) <sub>2</sub>	RCO <sub>2</sub> H	Ac <sub>2</sub> O	
Ph	73	6	60	65	14 <sup>a</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	78	4	75	<i>b</i>	6 <sup>c</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	67	2	61	69	25 <sup>d</sup>

<sup>a</sup> R = Ph. <sup>b</sup> Not estimated. <sup>c</sup> R = *p*-ClC<sub>6</sub>H<sub>4</sub>. <sup>d</sup> R = *p*-MeC<sub>6</sub>H<sub>4</sub>.

## EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were recorded for solutions in deuteriochloroform on a Perkin-Elmer R10 60 MHz spectrometer. Mass spectra were determined on an A.E.I. MS 12 spectrometer which could be coupled *via* a heated capillary to a gas-liquid chromatograph. I.r. spectra were recorded on a Unicam SP 200 or SP 200G spectrometer; solid samples were in KBr discs. U.v. spectra were obtained for solutions in ethanol on a Unicam SP 800 spectrophotometer. M.p.s were recorded on a Kofler micro-hot-stage or on an Electrothermal apparatus.

G.l.c. was performed on a Pye instrument (series 104, model 24). The following columns (6 ft × ¼ in) were used (the first three phases were each on acid-washed Celite): 10% silicone oil SE 30, 10% Carbowax 20M, 10% diethylene

glycol adipate, 10% Apiezon L grease on alkali-washed Celite, and 10% Carbowax 20M on alkali-washed Celite. All quantitative measurements were carried out with biphenyl as an internal standard, except for the estimations

of acetic anhydride and benzyl methyl ether, when *p*-cymene was used. A hydrogen-inject flame-ionisation detector gave a linear response and the relationship between the quantity of a material injected and its peak area was established by analysis of authentic mixtures. Compounds analysable by g.l.c. were identified by comparison of their retention times with those of authentic materials on two g.l.c. columns together with comparison of their mass spectra, obtained by combined g.l.c.-mass spectrometry, with those of authentic materials. T.l.c. was performed on Stahl Kieselgel G or HF<sub>254</sub>, and the plates were developed in an iodine tank.

Lead tetra-acetate (B.D.H. or Fisons laboratory reagent grade), supplied as a suspension in glacial acetic acid, was sucked free of acetic acid at the pump before use; iodometric titration showed that this material contained 91% lead tetra-acetate. Dichloromethane was distilled from phosphorus pentoxide under nitrogen before use; benzene (A.R.) was dried over sodium wire. Benzaldehyde was Fisons A.R. grade material; benzyl acetate and acetic anhydride were redistilled commercial samples (Hopkin and Williams, and Harrington, respectively). Acrylonitrile (B.D.H.) was dried over molecular sieve (B.D.H., type 4A). Acetic [<sup>2</sup>H]acid was a commercial sample (Koch-Light).

*NN*-Dibenzylhydrazine and benzylhydrazine, prepared by the benzylation of aqueous hydrazine (99–100%),<sup>7</sup> had m.p. 55–57° [from light petroleum (b.p. 40–60°)] (lit.,<sup>8</sup> 55°) and b.p. 63–65° at 1 mmHg (lit.,<sup>7</sup> 103–105° at 7 mmHg), respectively, and the monohydrochloride of the latter had m.p. 111–112° (from ethanol-ether) (lit.,<sup>9</sup> 109–111°). Benzaldehyde *NN*-dibenzylhydrazone, prepared from the hydrazine and benzaldehyde at room temperature, had m.p. 83–84° [from light petroleum (b.p. 60–80°)] (lit.,<sup>10</sup> 85°). Benzaldehyde benzylhydrazone, prepared by the method of Carpino,<sup>11</sup> had m.p. 63–65° (decomp.) [lit.,<sup>11</sup> 70–73.5° (decomp.)]. *N*-Benzoyl-*N*-benzylhydrazine, prepared from benzoyl chloride and benzylhydrazine,<sup>12</sup> had m.p. 69–71° (from ether) (lit.,<sup>12</sup> 68–72°).

<sup>7</sup> G. B. Kline and S. H. Cox, *J. Org. Chem.*, 1961, **26**, 1854.

<sup>8</sup> T. Curtius and H. Franzen, *Ber.*, 1901, **34**, 552.

<sup>9</sup> J. H. Biel, A. E. Drukker, T. F. Mitchell, E. P. Sprengeler, P. A. Nuhfer, A. C. Conway, and A. Horita, *J. Amer. Chem. Soc.*, 1959, **81**, 2805.

<sup>10</sup> L. A. Carpino, *J. Amer. Chem. Soc.*, 1963, **85**, 2144.

<sup>11</sup> C. S. Rooney, E. J. Cragoe, C. C. Porter, and J. M. Sprague, *J. Medicin. Chem.*, 1962, **5**, 155.

Benzaldehyde acetylhydrazone, prepared from benzaldehyde and acetylhydrazine,<sup>13</sup> had m.p. 137—140° (from carbon tetrachloride) (lit.,<sup>13</sup> 134°). *N*-Acetyl-*N'*-benzylhydrazine, prepared by the hydrogenation<sup>14</sup> of benzaldehyde acetylhydrazone, had m.p. 80—82° [from benzene-light petroleum (b.p. 60—80°) (2.5 : 1)] (lit.,<sup>14</sup> 81—82°). *N*-Benzoyl-*N'*-benzylhydrazine, prepared by the hydrogenation of benzaldehyde benzoylhydrazone,<sup>15</sup> had m.p. 115—117° [from benzene-light petroleum (b.p. 60—80°) (7 : 3)] (lit.,<sup>15</sup> 115°). 2-Methyl-5-phenyl-1,3,4-oxadiazole, prepared from *N*-benzoylhydrazine<sup>18</sup> and warm (75°) acetic anhydride containing a few drops of conc. sulphuric acid, had m.p. 70° (from water) (lit.,<sup>16</sup> 67°), *m/e* 160 (*M*<sup>+</sup>, 100%), 159, 118 (*M* - CH<sub>2</sub>CO), 105, 104, 103, 90, 77, 63, 51, and 43. 2,5-Diphenyl-1,3,4-oxadiazole was available from a previous study.<sup>4</sup> The following oxadiazoles were prepared from the oxidation of the appropriate benzaldehyde *para*-substituted benzoylhydrazones with lead tetra-acetate: <sup>4</sup> 2-*p*-chlorophenyl-5-phenyl-1,3,4-oxadiazole, m.p. 161—163° (lit.,<sup>17</sup> 162°), 2-*p*-bromophenyl-5-phenyl-1,3,4-oxadiazole, m.p. 164—165° (lit.,<sup>17</sup> 167°), and 2-phenyl-5-*p*-tolyl-1,3,4-oxadiazole, m.p. 128° (lit.,<sup>18</sup> 126°).

*NN*-Diacetyl-*N'*-benzoylhydrazine, prepared from *N*-benzoylhydrazine in refluxing (30 min) acetic anhydride, had m.p. 150—152° (from water) (lit.,<sup>19</sup> 152°). Benzylidene diacetate, prepared by the slow addition of benzaldehyde to acetic anhydride containing a few drops of boron trifluoride-ether complex, had m.p. 44—46° (from ether) (lit.,<sup>20</sup> 46°). *N'*-Benzoyl-*N*-benzyl-*N*-phenylhydrazine, prepared from benzoyl chloride and *N*-benzyl-*N*-phenylhydrazine<sup>21</sup> in dry ether containing triethylamine, had m.p. 141—143° (from carbon tetrachloride) (lit.,<sup>22</sup> 140°). *N*-Benzoyl-*N'*-phenylhydrazine, prepared from equimolar amounts of phenylhydrazine and benzoyl chloride in pyridine, had m.p. 170° (lit.,<sup>23</sup> 168°). *NN'*-Dibenzoyl-*N*-phenylhydrazine, prepared from phenylhydrazine and benzoyl chloride (2 mol. equiv.) in pyridine, had m.p. 178—179° (lit.,<sup>22</sup> 178°).

*N'*-Acyl-*NN*-dibenzylhydrazines were prepared from *NN*-dibenzylhydrazine and the appropriate acid chlorides in ether, and the products were recrystallised from aqueous ethanol unless stated otherwise. In the preparation of *N'*-acetyl-*NN*-dibenzylhydrazine, triethylamine was included in the reaction mixture. *N'*-Benzoyl-*NN*-dibenzylhydrazine had m.p. 171—172° (lit.,<sup>24</sup> 166—168°); *NN*-dibenzyl-*N'*-*p*-bromobenzoylhydrazine had m.p. 174—176° (Found: C, 63.9; H, 4.8; N, 6.9. C<sub>21</sub>H<sub>19</sub>BrN<sub>2</sub>O requires C, 63.8; H, 4.8; N, 7.1%), *v*<sub>max</sub> 1645 and 3250 cm<sup>-1</sup>; *NN*-dibenzyl-*N'*-*p*-toluoylhydrazine had m.p. 163—165° (Found: C, 79.7; H, 6.5; N, 8.7. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O requires C, 80.0; H, 6.7; N, 8.5%), *v*<sub>max</sub> 1630 and 3350 cm<sup>-1</sup>; *N'*-acetyl-*NN*-dibenzylhydrazine had m.p. 110—111° [from light petroleum (b.p. 60—80°)] (lit.,<sup>25</sup> 108°).

*N*-Benzyl-*N*-*p*-methoxybenzylhydrazine and *N*-benzyl-*N*-*p*-chlorobenzylhydrazine were prepared from the appropriate *N*-benzoyl- (*para*-substituted benzyl)amine by successive treatment with lithium aluminium hydride,<sup>26</sup>

nitrous acid,<sup>27</sup> and lithium aluminium hydride.<sup>27</sup> Benzoylation gave *N'*-benzoyl-*N*-benzyl-*N*-*p*-methoxybenzylhydrazine, m.p. 161—162° (Found: C, 76.3; H, 6.5; N, 8.3. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.3; H, 6.4; N, 8.1%), *v*<sub>max</sub> 1635 and 3350 cm<sup>-1</sup>, and *N'*-benzoyl-*N*-benzyl-*N*-*p*-chlorobenzylhydrazine, m.p. 164—165° (Found: C, 72.1; H, 5.5; N, 7.8. C<sub>21</sub>H<sub>19</sub>ClN<sub>2</sub>O requires C, 71.9; H, 5.5; N, 8.0%), *v*<sub>max</sub> 1640 and 3300 cm<sup>-1</sup>.

*N*-Acetyl-*N'*-acyl-*N*-benzylhydrazines were available from previous work.<sup>28</sup>

*Oxidations*.—All oxidations were carried out at room temperature unless stated otherwise. Reaction mixtures were mechanically or magnetically stirred, and were worked up by filtering off the insoluble lead(II) salts at the pump and washing the filtrate with sodium hydrogen carbonate solution, dilute hydrazine nitrate solution (if an excess of oxidant was present), and water. If the concentration of acetic anhydride was to be determined (on the 10% Carbowax 20M column coated on acid-washed Celite), then the alkali wash was omitted. The organic solution was dried (MgSO<sub>4</sub>) and evaporated.

*Oxidation of NN-dibenzylhydrazine*. (i) *NN*-Dibenzylhydrazine (2.1 g, 0.01 mol) in benzene (25 ml) and dichloromethane (50 ml) was added to a solution of lead tetra-acetate (4.5 g, *ca.* 0.01 mol) in benzene (50 ml) and dichloromethane (50 ml) during 4 h. The mixture was stirred a further 30 min then worked up to give a semi-solid which was mixed with cold methanol to precipitate benzaldehyde *NN*-dibenzylhydrazine (0.25 g) [from light petroleum (b.p. 60—80°)], identical (m.p. and mixed m.p.) with authentic material.

(ii) Lead tetra-acetate (25 g) in dichloromethane (100 ml) was added to a solution of *NN*-dibenzylhydrazine (10.5 g) in dichloromethane (100 ml) during 2 h at 5—10°. Work-up yielded tetrabenzyltetrazene (5.7 g, 54%), m.p. 96—98° [from light petroleum (b.p. 60—80°)] (lit.,<sup>10</sup> 100°), *τ* 2.9 (20H, m, ArH) and 5.7 (8H, s, PhCH<sub>2</sub>).

(iii) *NN*-Dibenzylhydrazine (2.1 g) in dichloromethane (150 ml) was added to a vigorously stirred solution of lead tetra-acetate (15 g, *ca.* 0.03 mol) and acetic acid (10 ml) in dichloromethane (100 ml) under nitrogen during 3.5 h. The mixture was stirred overnight and then worked up to give an oil. G.l.c. analysis showed the presence of benzaldehyde (89%), benzyl acetate (48%), and acetic anhydride (19.5%). Addition of a 2,4-dinitrophenylhydrazine solution to the product yielded the benzaldehyde hydrazone, m.p. and mixed m.p. 238—239° (lit.,<sup>20</sup> 237°).

(iv) Lead tetra-acetate (10 g) in dichloromethane (40 ml) was added to a solution of *NN*-dibenzylhydrazine (2.12 g) in dichloromethane (25 ml) during 2.25 h. Work-up gave an oil (1.9 g), analysis of which by g.l.c. and mass spectrometry, revealed three products, benzyl azide, benzaldehyde, and benzyl acetate. Addition of ether-light petroleum (b.p. 40—60°) precipitated *N*-acetyl-*N*-benzyl-*N'*-benzoyl-

<sup>21</sup> H. E. Fierz-David, L. Blangey, and H. Kaul, *Helv. Chim. Acta*, 1946, **29**, 1765.

<sup>22</sup> H. Franzen, *Ber.*, 1909, **42**, 2465.

<sup>23</sup> F. Just, *Ber.*, 1886, **19**, 1203.

<sup>24</sup> Beilstein, 'Handbuch der Organischen Chemie,' vol. 15, p. 540.

<sup>25</sup> A. N. Kost and R. S. Sagitullin, *Zhur. obshchei Khim.*, 1957, **27**, 3338 (*Chem. Abs.*, 1958, **52**, 9071).

<sup>26</sup> V. M. Mićović and M. Lj. Mihailević, *J. Org. Chem.*, 1953, **18**, 1190.

<sup>27</sup> C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Amer. Chem. Soc.*, 1955, **77**, 4100.

<sup>28</sup> J. B. Aylward, *J. Chem. Soc. (C)*, 1970, 1494.

<sup>13</sup> T. Curtius and H. Franzen, *Ber.*, 1902, **35**, 3236.

<sup>14</sup> A. N. Kurtz and C. Niemann, *J. Org. Chem.*, 1961, **26**, 1843.

<sup>15</sup> J. S. Aggarwal, N. L. Darbari, and J. N. Ráy, *J. Chem. Soc.*, 1929, 1941.

<sup>16</sup> R. Stollé, *Ber.*, 1912, **45**, 273.

<sup>17</sup> A. P. Grekov, L. N. Kulakova, and O. P. Shvaika, *Zhur. obshchei Khim.*, 1959, **29**, 3054.

<sup>18</sup> R. Stollé and E. Munch, *J. prakt. Chem.*, 1904, **70**, 417.

<sup>19</sup> G. Heller, *J. prakt. Chem.*, 1929, **120**, 52.

<sup>20</sup> 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

hydrazine (ca. 50 mg), m.p. 121—123° [from light petroleum (b.p. 60—80°)—benzene (1 : 1)], identical (m.p., mixed m.p., n.m.r. and i.r. spectra) with the solid product obtained from the lead tetra-acetate oxidation of benzaldehyde dibenzylhydrazine<sup>28</sup> and benzaldehyde benzylhydrazine.<sup>28</sup> The aqueous liquors obtained from the initial work-up were basified and saturated with sodium chloride. Extraction with ether and evaporation of the dried (MgSO<sub>4</sub>) ether solution left an oil which contained dibenzylamine (g.l.c. and mass spectrometry).

(v)<sup>29</sup> *NN*-Dibenzylhydrazine (2.1 g) in methanol (25 ml) and dichloromethane (50 ml) was added during 3 h to a vigorously stirred solution of lead tetra-acetate (4.5 g) in methanol (50 ml) and dichloromethane (50 ml). Work-up gave an oil which was chromatographed on alumina (Spence, type H) with light petroleum (b.p. 40—60°) to give benzaldehyde *NN*-dibenzylhydrazine (0.87 g) and formaldehyde *NN*-dibenzylhydrazine (0.76 g), m.p. 40—41° (from ethanol at -78°) (Found: C, 80.6; H, 7.5; N, 11.8. C<sub>15</sub>H<sub>16</sub>N<sub>2</sub> requires C, 80.3; H, 7.2; N, 12.5%).

(vi) *NN*-Dibenzylhydrazine (2.5 g) in acrylonitrile (70 ml) was added to a solution of lead tetra-acetate (15 g; washed free of absorbed acetic acid with anhydrous ether) in acrylonitrile (180 ml) during 3.5 h, under nitrogen. Work-up gave a semi-solid which was mixed with cold methanol to precipitate benzaldehyde *NN*-dibenzylhydrazine (0.5 g), m.p. and mixed m.p. 83—84°. Evaporation of the methanolic solution gave a further crop of the hydrazine, and an oil which did not show a cyanide absorption band in its i.r. spectrum.

*Oxidation of N-benzoyl-N-benzylhydrazine.* *N*-Benzoyl-*N*-benzylhydrazine (2.3 g, 0.01 mol) in dichloromethane (100 ml) was added to a solution of lead tetra-acetate (11 g, ca. 0.02 mol) in dichloromethane (100 ml) under nitrogen during 3.5 h. Work-up gave a semi-solid which, on mixing with light petroleum (b.p. 40—60°), afforded 1,4-dibenzoyl-1,4-dibenzyltetrazene (0.35 g, 15%), m.p. 208—210° (from benzene) (Found: C, 74.85; H, 5.4; N, 12.45. C<sub>28</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub> requires C, 75.0; H, 5.4; N, 12.5%),  $\tau$  2.6 (10H, s, ArH), ca. 2.8 (6H, m, ArH), 3.3 (4H, m, *ortho*-protons), and 5.0 (4H, s, ArCH<sub>2</sub>), *m/e* ca. 450 (M<sup>+</sup>), 329, 193, 142, 141, 127, 105 (100%), 91, and 77. The light petroleum filtrate obtained during work-up was evaporated to leave an oil (2.3 g) which contained benzyl acetate (55%). The oil was stirred with aqueous sodium hydrogen carbonate and extracted into ether. Acidification of the aqueous solution gave benzoic acid (30 mg), m.p. and mixed m.p. 123°.

*Oxidation of benzylhydrazine.* (i) Lead tetra-acetate (11 g) in dichloromethane (45 ml) was added to a solution of benzylhydrazine (1.2 g) in dichloromethane (10 ml) under nitrogen during 1 h. Work-up gave an oil (1.7 g) which contained benzyl acetate (78%) and a trace of dibenzyl. If the oxidation was performed with benzene as co-solvent, a trace of diphenylmethane was detected. Benzyl acetate was the predominant product when the addition procedure was reversed, *i.e.* when benzylhydrazine was added to lead tetra-acetate (2 mol) in dichloromethane.

(ii) Lead tetra-acetate (11 g) in dichloromethane (30 ml) was added to a solution of benzylhydrazine (1.2 g) in methanol (15 ml) and dichloromethane (40 ml) under nitrogen during 1 h. Work-up gave an oil (1.7 g) which contained benzyl acetate (63%) and benzyl methyl ether<sup>30</sup> (27%).

*Oxidation of N-acetyl-N'-benzylhydrazine.* (i) Lead tetra-

acetate (5.2 g) in dichloromethane (50 ml) was added to a solution of *N*-acetyl-*N'*-benzylhydrazine (1.64 g) in dichloromethane (75 ml) under nitrogen at -50 to -70°. The mixture was stirred for 1 h at -50°, then allowed to warm to room temperature, and stirred overnight. Work-up gave benzaldehyde acetylhydrazine (0.4 g, 25%), m.p. and mixed m.p. 140—142°.

(ii) Lead tetra-acetate (11 g) in dichloromethane (75 ml) was added to a solution of *N*-acetyl-*N'*-benzylhydrazine (1.64 g) in dichloromethane (75 ml) under nitrogen at -50 to -70° during 10 min. The mixture was stirred for a further 2.5 h at -78°, then allowed to warm to room temperature, and worked up to give an oil (2.84 g) which contained benzyl acetate (94%) and acetic anhydride (75.5%).

(iii) Lead tetra-acetate (11 g) in dichloromethane (35 ml) was added to a solution of *N*-acetyl-*N'*-benzylhydrazine (3.28 g) in dichloromethane (50 ml) during 15 min at -50 to -70° under nitrogen. The mixture was stirred for 1 h at -50°, allowed to warm to room temperature, and stirred overnight. More lead tetra-acetate (11 g) in dichloromethane (60 ml) was then added during 30 min at room temperature. Work-up gave an oil which was mixed with light petroleum (b.p. 40—60°) to give *NN*-diacetyl-*N'*-benzoylhydrazine (0.26 g), identical (m.p., mixed m.p., and i.r. spectrum) with authentic material. Evaporation of the light petroleum solution, obtained after removal of solid product, gave an oil (3.1 g), which g.l.c. analysis and mass spectrometry showed to contain acetic anhydride (16%), benzaldehyde (11%), benzyl acetate (21%), benzylidene diacetate (9%), and 2-methyl-5-phenyl-1,3,4-oxadiazole (23%).

(iv) Lead tetra-acetate (5.2 g) in dichloromethane (35 ml) was added to a solution of *N*-acetyl-*N'*-benzylhydrazine (0.82 g) in dichloromethane (30 ml) and methanol (10 ml) under nitrogen at -60°. The mixture was allowed to warm to room temperature during 3 h, then worked up to give an oil (1.1 g) which contained benzyl acetate (73%) and benzyl methyl ether (26%).

(v) Lead tetra-acetate [1.5 g; dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>)] in dichloromethane (20 ml) was added to a solution of *N*-acetyl-*N'*-benzylhydrazine (0.33 g) in dichloromethane (20 ml) and acetic [<sup>2</sup>H]acid (10 g) under nitrogen at -78° during 5 min. The mixture was stirred for 1.5 h at -78°, then allowed to warm to room temperature during 2 h, and worked up. The benzyl acetate produced was examined by mass spectrometry; no deuterium had been incorporated into the product.

*Oxidation of benzaldehyde acetylhydrazine.* (i) Lead tetra-acetate (8.0 g) in dichloromethane (60 ml) was added to a solution of benzaldehyde acetylhydrazine (1.62 g) in dichloromethane (45 ml) under nitrogen during 45 min. Work-up gave a semi-solid which, on addition of light petroleum (b.p. 40—60°), precipitated *NN*-diacetyl-*N'*-benzoylhydrazine (0.3 g, 15%), identical (m.p., mixed m.p., and i.r. spectrum) with authentic material. The light petroleum solution was evaporated to leave an oil which g.l.c. analysis showed to contain benzaldehyde (6%), benzyl acetate (3%), acetic anhydride (8%), benzylidene diacetate (16%), and 2-methyl-5-phenyl-1,3,4-oxadiazole (18%).

<sup>29</sup> M. J. Harrison, D.Phil. Thesis, York, 1967.

<sup>30</sup> W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, jun., and L. C. Gibbons, *J. Amer. Chem. Soc.*, 1947, **69**, 2451.



(ii) Lead tetra-acetate [8.0 g; dried ( $P_2O_5$ ) *in vacuo*] in dichloromethane (65 ml) was added to a solution of benzaldehyde acetylhydrazone (1.62 g) in dichloromethane (65 ml) containing suspended calcium carbonate (20 g), during 2 h. Work-up afforded *inter alia* *NN*-diacetyl-*N'*-benzoylhydrazine (0.3 g) and 2-methyl-5-phenyl-1,3,4-oxadiazole (23%). A duplicate experiment yielded *NN*-diacetyl-*N'*-benzoylhydrazine (0.28 g) and 2-methyl-5-phenyl-1,3,4-oxadiazole (25%).

(iii) Lead tetra-acetate (8.0 g) in dichloromethane (60 ml) was added to a solution of benzaldehyde acetylhydrazone (1.62 g) in dichloromethane (60 ml) and glacial acetic acid (5 ml) during 2 h. Work-up afforded *inter alia* *NN*-diacetyl-*N'*-benzoylhydrazine (0.28 g) and 2-methyl-5-phenyl-1,3,4-oxadiazole (23%).

(iv) Benzaldehyde acetylhydrazone (1.62 g) in acrylonitrile (70 ml) was added to a solution of lead tetra-acetate in acrylonitrile (150 ml) during 2 h at 0° under nitrogen. Work-up yielded *NN*-diacetyl-*N'*-benzoylhydrazine (0.3 g) and an oil which did not show a cyanide absorption band in its i.r. spectrum.

(v) Lead tetra-acetate [1.5 g; dried ( $P_2O_5$ ) *in vacuo*] in dichloromethane (20 ml) and acetic [ $^2H$ ]acid (2 ml) was added to a solution of benzaldehyde acetylhydrazone (0.324 g) in dichloromethane (20 ml) and acetic [ $^2H$ ]acid (8 ml) at -30° in a nitrogen atmosphere during 15 min. The mixture was stirred for 2 h after the addition, allowed to warm to room temperature, and worked up to give an oil which was examined by g.l.c. and mass spectrometry. The percentage uptake of 1 g atom of deuterium per mol of benzyl acetate and benzylidene diacetate respectively was estimated; benzyl acetate incorporated 71% g atom deuterium per mol and benzylidene diacetate incorporated 78% g atom deuterium per mol. The n.m.r. spectrum of benzaldehyde acetylhydrazone in acetic [ $^2H$ ]acid showed that no exchange occurs between the methine hydrogen atom of the hydrazone ( $\tau$  2.1) during the time allowed for the oxidation.

*Oxidation of N'-benzoyl-N-benzyl-N-phenylhydrazine.* (i) Lead tetra-acetate (11 g) in dichloromethane (150 ml) was added to a solution of *N'*-benzoyl-*N*-benzyl-*N*-phenylhydrazine (6.04 g, 0.02 mol) in dichloromethane (100 ml) during 2.5 h. Work-up gave an oil which, on mixing with light petroleum (b.p. 40–60°), precipitated impure starting material (2.7 g). The light petroleum solution obtained after removing the insoluble material was evaporated *in vacuo* and the residue was mixed with light petroleum (b.p. 40–60°) to yield a solid which, after two recrystallisations from benzene, gave *N*-benzoyl-*N'*-phenylhydrazine (0.26 g), m.p. and mixed m.p. 171°. Evaporation of the light petroleum mother liquors left a semi-solid which contained benzaldehyde and  $\alpha$ -phenylazobenzylidene acetate benzoate (g.l.c. and t.l.c.).

(ii) Lead tetra-acetate [11 g; washed free of absorbed acetic acid with dry light petroleum (b.p. 60–80°)] in dichloromethane (150 ml) was added to a solution of *N'*-benzoyl-*N*-benzyl-*N*-phenylhydrazine (3 g) in dichloromethane (75 ml) during 1.5 h. More oxidant (5 g) was then added in small portions during 15 min, and the mixture was stirred for a further 20 min and then worked up to give an oil. Trituration of this oil with light petroleum (b.p. 60–80°) afforded a solid (2.6 g) which was mixed with cold benzene. The benzene-insoluble product (0.5 g) was recrystallised twice from ethanol-water (7 : 3) to give *NN'*-

dibenzoyl-*N*-phenylhydrazine, identical (m.p., mixed m.p., and i.r. spectrum) with authentic material. The benzene solution, obtained after removal of the last product, was evaporated to leave an oil which solidified on triturating with light petroleum (b.p. 40–60°). Chromatography on silica with benzene yielded  $\alpha$ -phenylazobenzylidene acetate benzoate (0.26 g) as a pale yellow solid, m.p. 128–129° (from methanol) (lit.,<sup>2</sup> 126–127°) (Found: C, 70.9; H, 5.0; N, 7.7. Calc. for  $C_{22}H_{19}N_2O_4$ : C, 70.6; H, 4.8; N, 7.5%),  $\lambda_{max}$  279 nm (lit.,<sup>2</sup> 276),  $\nu_{max}$  1720 and 1760  $cm^{-1}$  (lit.,<sup>2</sup> 1730 and 1775  $cm^{-1}$ ).

*Oxidation of N'-acetyl-NN-dibenzylhydrazine.* (i) Lead tetra-acetate (15 g) in dichloromethane (75 ml) was added to a solution of *N'*-acetyl-*NN*-dibenzylhydrazine (2.54 g) in dichloromethane (75 ml) during 2 h. Work-up afforded an oil which was analysed by g.l.c. and mass spectrometry (Table 1).

(ii) Lead tetra-acetate [15 g; dried ( $P_2O_5$ ) *in vacuo*] in dichloromethane (80 ml) was added to a solution of *N'*-acetyl-*NN*-dibenzylhydrazine (2.54 g) in dichloromethane (70 ml) during 45 min. The mixture was worked up to give an oil. The volatile components of the product were removed *in vacuo* (3.0 mmHg) at 100°, and the residue was mixed with carbon tetrachloride-light petroleum (b.p. 40–60°) to precipitate *NN*-diacetyl-*N'*-benzoylhydrazine (15 mg), identical (m.p., mixed m.p., and i.r. spectrum) with authentic material.

*Oxidation of N'-aroyl-NN-dibenzylhydrazines.* A typical procedure was as follows. Lead tetra-acetate (8 g) in dichloromethane (30 ml) was added to a solution of *N'*-benzoyl-*NN*-dibenzylhydrazine (5 g) in dichloromethane (30 ml) during 30 min. The mixture was poured into water and the ether extract was washed with dilute hydrazine hydrate solution, sodium hydrogen carbonate solution, and water, dried ( $MgSO_4$ ), and evaporated to give an oil which contained benzaldehyde (106%), benzyl acetate (72%), benzylidene diacetate (3%), and acetic anhydride (34%). The product was heated briefly with ethanol (10 ml) under reflux to precipitate (on cooling) 2,5-diphenyl-1,3,4-oxadiazole (350 mg), identical (m.p., mixed m.p., and i.r. spectrum) with authentic material. The aqueous sodium hydrogen carbonate solution (obtained during work-up) was acidified (HCl) and extracted with ether. Work-up of the extract yielded benzoic acid (1.24 g).

The other *N'*-aroyl-*NN*-dibenzylhydrazines in Table 1 and the hydrazides (29) were similarly treated.

*Oxidation of N-benzoyl-N'-benzylhydrazine.*—Lead tetra-acetate (2 mol. equiv.) was added to a solution of *N*-benzoyl-*N'*-benzylhydrazine in dichloromethane. The mixture was worked up as described for the oxidation of *N'*-aroyl-*NN*-dibenzylhydrazines to give a product containing benzaldehyde (14%), acetic anhydride, benzyl acetate (24%), benzylidene diacetate (2%), 2,5-diphenyl-1,3,4-oxadiazole (33%), and benzoic acid (20%).

*Oxidation of N-acetyl-N'-acyl-N-benzylhydrazines.* A typical experiment was as follows. Lead tetra-acetate (9.4 g) in dichloromethane (40 ml) was added to *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazine (5 g) in dichloromethane (30 ml) during 30 min. The mixture was worked up as described for the oxidation of *N'*-aroyl-*NN*-dibenzylhydrazines to give the products shown in Table 2. The two other *N*-acetyl-*N'*-acyl-*N*-benzylhydrazines were similarly treated.

We thank the S.R.C. for a Studentship (to R. P.).