Hydrazine Derivatives. Part II.[1] Oxidation of Aldehyde *NN*-Disubstituted Hydrazones with Lead Tetra-acetate

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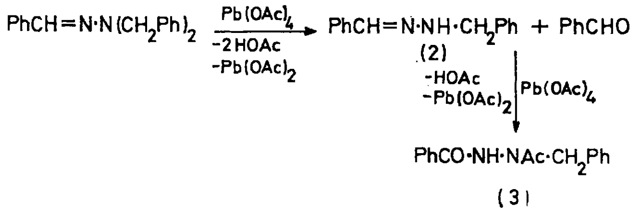
The oxidation of a number of arenecarbaldehyde *NN*-disubstituted hydrazones with lead tetra-acetate proceeds in two steps. The first involves carbon–nitrogen bond cleavage to give an aldehyde and an arenecarbaldehyde monohydrazone. The second involves further oxidation of the monohydrazone to a diacylhydrazine. The order of ease of cleavage of alkyl groups was found to be *p*-methoxybenzyl > benzyl > *p*-chlorobenzyl ⩾ methyl. A mechanism has been suggested for the cleavage reaction. The oxidation of the monohydrazone proceeds *via* a nitrilimine.

The oxidation of *N*-monosubstituted hydrazones with lead tetra-acetate has received considerable attention.[2] The mechanisms operating in the oxidations of both ketone *N*-monosubstituted hydrazones[3] and aldehyde *N*-monosubstituted hydrazones,[4] have been established. The oxidation of ketone *NN*-disubstituted hydrazones required two equivalents of lead tetra-acetate; the first equivalent brought about dealkylation to the aldehyde and monosubstituted hydrazone, and the second oxidised the monosubstituted hydrazone to an azo-acetate in the normal manner.[5] No mechanism was advanced for the dealkylation reaction. The oxidation of benzaldehyde *NN*-diphenylhydrazone gave *N*-acetyl-*N*-benzoyl-*N'N'*-diphenylhydrazine by way of an ionic mechanism; dealkylation was not possible in this case.[4] We studied the reactions of a series of arenecarbaldehyde *NN*-disubstituted hydrazones to determine if dealkylation occurs in this series, and if so, to elucidate the dealkylation mechanism.

RESULTS

The oxidation of benzaldehyde *NN*-dibenzylhydrazone (1) was studied in some detail to determine the most suitable conditions. When one equivalent of the hydrazone was added slowly to lead tetra-acetate in acetic acid at room temperature, unchanged starting material (34%), benzaldehyde (40%), and *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazine (3) (21%) were recovered. Use of two equivalents of lead tetra-acetate gave the diacylhydrazine (75%) and benzaldehyde (92%). Similar results were obtained with dichloromethane as solvent. These results indicated that the oxidation of aldehyde *NN*-disubstituted hydrazones, like their ketone analogues, proceeds by way of the monohydrazone (2).



Scheme 1

We then attempted to isolate the monosubstituted hydrazone. Lead tetra-acetete (1 equiv.) was added slowly with stirring to benzaldehyde *NN*-dibenzylhydrazone in acetic acid. Work-up yielded starting material (40%), *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazine (35%), benzaldehyde (49%), and a small quantity of benzaldehyde benzylhydrazone (2) (2%). The isolation of only a small quantity of the monohydrazone is to be expected as it reacts more rapidly with lead tetra-acetate than does the di-substituted hydrazone. An authentic sample of benzaldehyde benzylhydrazone reacted with lead tetra-acetate at $-60°$ in dichloromethane to give *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazine, whereas benzaldehyde *NN*-dibenzylhydrazone was unreactive at this temperature.

The oxidation of *p*-chlorobenzaldehyde and *p*-methylbenzaldehyde *NN*-dibenzylhydrazones readily gave the appropriate diacylhydrazines with two equivalents of lead tetra-acetate (Table). The *p*-chloro-compound required a longer reaction time at room temperature. *o*-Nitrobenzaldehyde *NN*-dibenzylhydrazone was oxidised in an attempt to extend the synthesis of 3-(substituted azo)-2,1-benzisoxazole 1-oxides.[4] The only products identified were starting material (46%), benzaldehyde (36%), and benzyl acetate (12%).* This may be due to further reaction of the benzisoxazole 1-oxide with lead tetra-acetate.

A number of benzaldehyde *NN*-dialkyl compounds were then examined to determine the ease of cleavage of various groups. The order within the *NN*-dibenzyl series was established by oxidising benzaldehyde *N*-benzyl-*N*-*p*-chlorobenzylhydrazone and benzaldehyde *N*-benzyl-*N*-*p*-methoxybenzylhydrazone and determining the proportions of arenecarbaldehyde and benzaldehyde produced. We found that a *p*-methoxybenzyl group was much more readily cleaved than a benzyl group, and the *p*-chlorobenzyl group was slightly less readily cleaved. The yields of diacyl compounds also reflect this trend (Table). The oxidation of benzaldehyde *N*-benzyl-*N*-methylhydrazone indicated that a benzyl group is cleaved more readily than a methyl group. Thus the order of ease of cleavage is *p*-methoxybenzyl > benzyl > *p*-chlorobenzyl ⩾ methyl.

The oxidations of benzaldehyde *N*-methyl-*N*-phenylhydrazone and *N*-benzyl-*N*-phenylhydrazone had to be carried our under nitrogen with excess of lead tetra-acetate because of autoxidation of the intermediate benz-

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* The further oxidation of *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazines differs from the behaviour of the *N*-phenylhydrazine derivatives previously reported (ref. 4 and W. A. F. Gladstone, *J. Chem. Soc.* (*C*), 1969, 1571). Among the products identified were benzyl acetate and benzoic acid. We are investigating this problem.

[1] Part I, J. B. Aylward, *J. Chem. Soc.* (*C*), 1969, 1663.

[2] For a review see R. N. Butler, *Chem. and Ind.*, 1968, 437.

[3] M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone, *J. Chem. Soc.* (*C*), 1967, 735.

[4] W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1969, 2587.

[5] D. C. Iffland and E. Cerda, *J. Org. Chem.*, 1963, **28**, 2769.

aldehyde phenylhydrazone produced in each case.[4,6,7] The product pattern was similar to that reported for the oxidation of benzaldehyde phenylhydrazone with lead tetra-acetate [4] except that the yields were lower. The major product in both cases was α-phenylazobenzyl acetate (4) isolated in 16% yield in the case of the *N*-methyl derivative and 20% in the case of the *N*-benzyl derivative. Benzoylazobenzene (as benzoic acid [8]) was isolated in yields of 10 and 9% respectively. *N*-Acetyl-*N'*-benzoyl-*N*-phenylhydrazine was isolated in low yields (Table). Small amounts of *N'*-benzoyl-*NN*-diphenylhydrazine and *N*-benzoyl-*NN'*-diphenylhydrazine (decomposition products of benzoylazobenzene [8]) and a trace of the azo-diacetate (5) were also identified in each case.

$\mathrm{PhCH(OAc){\cdot}N{=}NPh}$ (4)

$\mathrm{PhC(OAc)_2{\cdot}N{=}NPh}$ (5)

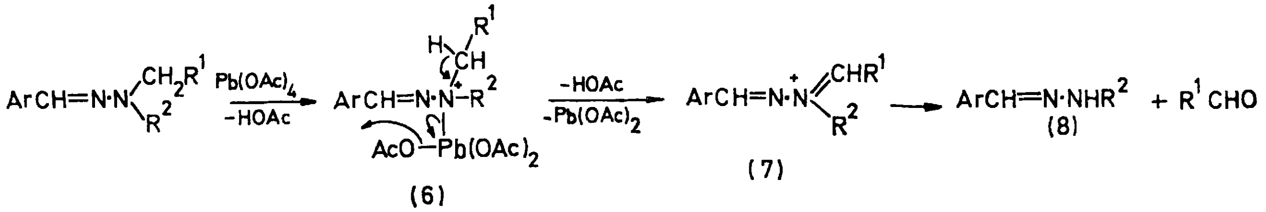
Oxidation of aldehyde *NN*-disubstituted hydrazones with lead tetra-acetate *

Hydrazone $p\text{-}XC_6H_4{\cdot}CH{:}N{\cdot}N(CH_2R^1)R^2$			Aldehyde	Diacylhydrazine
X	R^1	R^2	(%)	(%)
H	Ph	$PhCH_2$	PhCHO (92)	$X{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NAcR^2$ (75)
Me	Ph	$PhCH_2$	PhCHO (84)	$X{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NAcR^2$ (68)
Cl	Ph	$PhCH_2$	PhCHO (86)	$X{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NAcR^2$ (71)
H	$p\text{-}ClC_6H_4$	$PhCH_2$	PhCHO (46)	$PhCO{\cdot}NH{\cdot}NAcR^2$ (23)
			$p\text{-}ClC_6H_4{\cdot}CHO$ (42)	$PhCO{\cdot}NH{\cdot}NAc{\cdot}CH_2R^1$ (25)
H	$p\text{-}MeO{\cdot}C_6H_4$	$PhCH_2$	PhCHO (30)	$PhCO{\cdot}NH{\cdot}NAcR^2$ (26)
			$p\text{-}MeO{\cdot}C_6H_4{\cdot}CHO$ (62)	$PhCO{\cdot}NH{\cdot}NAc{\cdot}CH_2R^1$ (12)
H	Ph	Ph	PhCHO (79)	$PhCO{\cdot}NH{\cdot}NAcR^2$ (8) †
H	H	Ph	HCHO (—) ‡	$PhCO{\cdot}NH{\cdot}NAcR^2$ (6) †
H	Ph	Me	PhCHO (54)	$PhCO{\cdot}NH{\cdot}NAc{\cdot}CH_2R^1$ (17)
			HCHO (—) ‡	$PhCO{\cdot}NH{\cdot}NAcR^2$ (26)

* Unless otherwise indicated these reactions were carried out in acetic acid. † Reactions carried out in dichloromethane–acetic acid under nitrogen. ‡ Not estimated.

DISCUSSION

Analogy with the behaviour of benzaldehyde *NN*-diphenylhydrazone,[4] and other basic nitrogen compounds,[2,3] with lead tetra-acetate suggests that the first step in the reaction involves the formation of an organolead(IV) intermediate of type (6). The deactivating effect of the *p*-chloro-substituent in the benzaldehyde ring is similar to that observed for electron-withdrawing substituents in the benzaldehyde ring of monohydrazones, where attack also occurs at the amino-nitrogen.[4] Elimination can then occur to form the ion (7), which is similar to the dialkyliminium ion $(R_2\overset{+}{N}{=}CR_2)$ formed in dealkylation of tertiary amines with nitrous acid,[9,10] and to the species formed in the dealkylation of tertiary hydrazides with the same reagent.[11]



SCHEME 2

This step would be expected to be more favourable for a *p*-methoxybenzyl group, and less favourable for a *p*-chlorobenzyl or methyl group, relative to a benzyl group, as we have observed. This order of ease of cleavage is the same as that reported for tertiary amines [12] and may indicate that the elimination does not proceed *via* a cyclic five-membered transition state (analogous to the four-membered transition state proposed for *cis*-elimination from *N*-nitrosoammonium ions [10]) which would be expected to favour methyl elimination relative to benzyl elimination.* Acetolysis of the ion (7) would then yield the monohydrazone (8) and aldehyde.[13] Similar mechanisms probably operate in the dealkylations of *NN*-disubstituted ketone hydrazones,[5] tertiary amines,[14] 21-desoxyajmaline 17-acetate,[15] and tetrabenzyltetrazene,[16] with lead tetra-acetate.

The oxidation of aldehyde monohydrazones with lead tetra-acetate has been shown to proceed *via* a 1,3-dipolar ion.[4] Thus benzaldehyde phenylhydrazone gives

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* A more meaningful comparison can be made from a study of the cleavage of trialkylamines with lead tetra-acetate—we are investigating this.

[6] M. Busch and W. Dietz, *Ber.*, 1914, **47**, 3277; M. Busch and H. Kunder, *ibid.*, 1916, **49**, 2345.

[7] K. H. Pausacker, *J. Chem. Soc.*, 1950, 3478.

[8] S. G. Cohen and J. Nicholson, *J. Org. Chem.*, 1965, **30**, 1162.

[9] (*a*) P. A. S. Smith, 'Open-chain Nitrogen Compounds,' vol. I, Benjamin, New York, 1965, p. 33; (*b*) P. A. S. Smith and R. N. Loeppky, 19th I.U.P.A.C. Congress, London, 1963.

[10] P. A. S. Smith and R. N. Loeppky, *J. Amer. Chem. Soc.*, 1967, **89**, 1147.

[11] P. A. S. Smith and H. G. Pars, *J. Org. Chem.*, 1959, **24**, 1325.

[12] R. Wegler and W. Frank, *Ber.*, 1936, **69**, 2071.

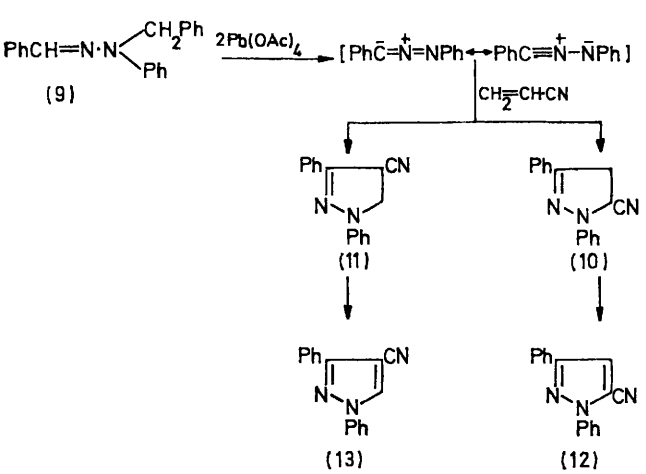
[13] E. C. Wagner, *J. Org. Chem.*, 1954, **19**, 1862.

[14] L. Horner, E. Winkelmann, K. H. Knapp, and W. Ludwig, *Chem. Ber.*, 1959, **92**, 288.

[15] M. F. Bartlett, B. F. Lambert, and W. I. Taylor, *J. Amer. Chem. Soc.*, 1964, **86**, 729.

[16] G. Koga and J. P. Anselme, *J. Amer. Chem. Soc.*, 1969, **91**, 4323.

diphenylnitrilimine, which may be trapped as its adduct with acrylonitrile. We trapped diphenylnitrilimine similarly in the oxidation of benzaldehyde *N*-benzyl-*N*-phenylhydrazone (9) with excess of lead tetra-acetate in acrylonitrile at 0° (under nitrogen).



SCHEME 3

The pyrazoles (12) and (13), further oxidation products of the pyrazolines (10) and (11),[4,17] were obtained in lower yields (41 and 0·5% respectively) than from the oxidation of benzaldehyde phenylhydrazone, possibly because of the presence of more acetic acid and benzaldehyde.

EXPERIMENTAL

Except where otherwise stated, i.r. spectra were measured for solutions in chloroform with an Infrascan H900 spectrometer, and u.v. spectra for solutions in methanol with a Perkin-Elmer 137 spectrometer. M.p.s were recorded with a Leitz model 350 microscope hot-stage apparatus. Alumina for chromatography was the Woelm neutral product, Laporte alumina was type H partially neutralised by the addition of 4% of aqueous acetic acid (10%).

Lead tetra-acetate (B.D.H. reagent grade) was recrystallised from acetic acid and dried *in vacuo* (NaOH). Dichloromethane and acrylonitrile were distilled from phosphorus pentoxide. Light petroleum had b.p. 40—60°.

Benzaldehyde benzylhydrazone, prepared by standard methods, had m.p. 64° (lit.,[18] 65°). N-*Acetyl*-N'-*benzoyl*-N-*benzylhydrazine*, prepared by the method of Gladstone,[19] had m.p. 124°, $\nu_{max.}$ 1680 and 1610 cm.$^{-1}$ (Found: C, 71·6; H, 6·0; N, 10·2. $C_{16}H_{16}N_2O_2$ requires C, 71·7; H, 6·0; N, 10·5%). N-*Acetyl*-N'-*benzoyl*-N-*methylhydrazine* had m.p. 157°, $\nu_{max.}$ 1675 and 1620 cm.$^{-1}$ (Found: C, 62·6; H, 6·4; N, 14·3. $C_{10}H_{12}N_2O_2$ requires C, 62·5; H, 6·2; N, 14·5%). 1,3-Diphenylpyrazole-5-carbonitrile, 1,5-Diphenylpyrazole-4-carbonitrile, benzyl α-phenylazoacetate, and benzyl α-acetoxy-α-phenylazoacetate were prepared as previously described.[4]

NN-Disubstituted hydrazines were prepared by nitrosation of the appropriate secondary amines followed by reduction of the nitroso-compounds with lithium aluminium hydride.[20] When the amines were not available commerically they were prepared by condensation of the appropriate primary amines with benzoyl chloride followed by reduction of the amides with lithium aluminium hydride in tetrahydrofuran. The hydrazones were prepared by condensation with the appropriate arenecarbaldehydes. The following *NN*-disubstituted hydrazones were prepared: benzaldehyde *NN*-dibenzylhydrazone, m.p. 86—87° (lit.,[21] 85°); benzaldehyde *N*-benzyl-*N*-phenylhydrazone, m.p. 110° (lit.,[22] 111°); benzaldehyde *N*-methyl-*N*-phenylhydrazone, m.p. 106—107 (lit.,[23] 104°). *Benzaldehyde* N-*benzyl*-N-p-*methoxybenzylhydrazone* had m.p. 93° (from chloroform–light petroleum) (Found: C, 79·9; H, 6·8; N, 8·5. $C_{22}H_{22}N_2O$ requires C, 80·0; H, 6·7; N, 8·5%). *Benzaldehyde* N-*benzyl*-N-p-*chlorobenzylhydrazone* had m.p. 71—72° (from ethanol) (Found: C, 75·2; H, 5·6; N, 8·6. $C_{21}H_{19}ClN_2$ requires C, 75·4; H, 5·7; N, 8·4%). p-*Methylbenzaldehyde* NN-*dibenzylhydrazone* had m.p. 125° (from ethanol) (Found: C, 84·3; H, 6·8. $C_{22}H_{22}N_2$ requires C, 84·1; H, 7·0%). p-*Chlorobenzaldehyde* NN-*dibenzylhydrazone* had m.p. 128—129° (from ethanol) (Found: C, 75·6; H, 5·7. $C_{21}H_{19}ClN_2$ requires C, 75·4; H, 5·7%). o-*Nitrobenzaldehyde* NN-*dibenzylhydrazone* had m.p. 95—96° (from acetone) (Found: C, 73·2; H, 5·6. $C_{21}H_{19}N_3O_2$ requires C, 73·0; H, 5·5%).

The following work-up procedure was used for the oxidations. The reaction mixture was poured into water and the combined ether extracts were washed with water and with sodium hydrogen carbonate to remove the excess of acids, dried ($MgSO_4$), and concentrated at aspirator pressure. Gas chromatography was used to detect, isolate, and estimate the aromatic aldehydes formed. For analysis the reactions were repeated on one tenth scale and diphenyl was used as an internal standard. Two columns were used to resolve the aldehydes, one of Apiezon L grease (10% w/w) on 80—100 mesh Celite, and one of Silicone Fluid MS 550 (10% w/w) on 80—100 mesh Celite. The arenecarbaldehydes were isolated from the silicone column and identified as their 2,4-dinitrophenylhydrazones.[24] Formaldehyde was detected in the aqueous solutions (after ether extractions) by the Tollens test and identified as its 2,4-dinitrophenylhydrazone, m.p. 166—167° (lit.,[24] 166°).

Oxidations.—(i) To lead tetra-acetate (1·48 g.) in acetic acid (50 ml.) a suspension of benzaldehyde *NN*-dibenzylhydrazone (1 g.) in acetic acid (50 ml.). was added slowly with stirring. Work-up yielded an oily product which on recrystallisation from absolute ethanol gave starting material (340 mg.). The ethanolic filtrates were evaporated to dryness and the residue gave *N*-acetyl-*N'*-benzoyl-*N*-benzylhydrazine (208 mg.), m.p. 123° (from chloroform–light petroleum), identical with an authentic sample (m.p., mixed m.p., and i.r. spectrum).

This experiment was repeated but the tetra-acetate was added to the hydrazone. The oily product was recrystal-

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[17] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc. (C)*, 1966, 1536.

[18] T. Curtius, *J. prakt. Chem.*, 1900, **62**, 96.

[19] W. A. F. Gladstone, *J. Chem. Soc. (C)*, 1969, 1571.

[20] C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Amer. Chem. Soc.*, 1955, **77**, 4100; R. L. Hinman, *ibid.*, 1956, **78**, 2463; R. L. Hinman and K. L. Hamm, *J. Org. Chem.*, 1958, **23**, 529; *J. Amer. Chem. Soc.*, 1959, **81**, 3294.

[21] T. Curtius and E. Franzen, *Ber.*, 1901, **34**, 558.

[22] A. Michaelis and B. Philips, *Annalen*, 1887, **252**, 289.

[23] E. Bamberger, *Ber.*, 1894, **27**, 373.

[24] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, 'The Systematic Identification of Organic Compounds,' New York, 1958.

lised from ethanol to yield starting material (40 mg.). The ethanolic filtrates were evaporated to dryness and the resulting oil was chromatographed on a short column. Crude benzaldehyde benzylhydrazone (35 mg.) was eluted by chloroform–light petroleum (1 : 9). Recrystallisation from aqueous ethanol gave pure benzaldehyde benzylhydrazone (20 mg.) (identical with an authentic sample). *N*-Acetyl-*N*′-benzoyl-*N*-benzylhydrazone (347 mg.) was eluted by benzene–light petroleum (4 : 1) and benzaldehyde *NN*-dibenzylhydrazone (391 mg.) by chloroform–light petroleum (2 : 2).

(ii) Lead tetra-acetate (3·0 g.) in acetic acid (50 ml.) was added slowly with stirring to benzaldehyde *NN*-dibenzylhydrazone (1 g.) in acetic acid (50 ml.). The product was recrystallised from chloroform–light petroleum to give *N*-acetyl-*N*′-benzoyl-*N*-benzylhydrazine (747 mg.).

When treated similarly, *p*-methylbenzaldehyde *NN*-dibenzylhydrazone gave N-*acetyl*-N-*benzyl*-N′-p-*methylbenzoylhydrazine* (68%), m.p. 146—147° (from light petroleum), $\nu_{max.}$ 1670 and 1625 (CO) and 3325 (NH) cm.$^{-1}$ (Found: C, 72·2; H, 6·5; N, 9·7. $C_{17}H_{18}N_2O_2$ requires C, 72·4; H, 6·4; N, 9·9%). *p*-Chlorobenzaldehyde *NN*-dibenzylhydrazone (stirred for 3 hr. for complete reaction) gave N-*acetyl*-N-*benzyl*-N′-p-*chlorobenzoylhydrazine* (71%), m.p. 154—156° (from ethanol), $\nu_{max.}$ (Nujol) 1665 and 1600 (CO) and 3320 (NH) cm.$^{-1}$ (Found: C, 63·8; H, 5·2; N, 9·06. $C_{16}H_{15}ClN_2O_2$ requires C, 63·6; H, 4·9; N, 9·3%).

Repetition of these reactions with dichloromethane as solvent gave similar results.

When *o*-nitrobenzaldehyde *NN*-dibenzylhydrazone was treated similarly the only pure product isolated was starting material (46%). Benzaldehyde (36%) and benzyl acetate (12%) were detected by gas chromatography. No pure product could be isolated from the resinous material formed.

Benzaldehyde benzylhydrazone was also oxidised at room temperature in acetic acid to give *N*-acetyl-*N*′-benzoyl-*N*-benzylhydrazine (72%). On oxidation at −60° in dichloromethane the diacylhydrazine was obtained in 81% yield. Benzaldehyde *NN*-dibenzylhydrazine was stirred for 4 hr. at −60° in dichloromethane with lead tetra-acetate without any appreciable reaction.

(iii) Lead tetra-acetate (2·68 g.) in acetic acid (50 ml.) was added slowly with stirring to a suspension of benzaldehyde *N*-benzyl-*N*-*p*-chlorobenzylhydrazone in acetic acid (50 ml.). The oily product was resolved by chromatography. A crude product (310 mg.) by elution with light petroleum–benzene (1 : 1) was recrystallised from chloroform–light petroleum to give N-*acetyl*-N′-*benzoyl*-N-p-*chlorobenzylhydrazine* (271 mg.), m.p. 159°, $\nu_{max.}$ 1675 and 1605 (CO) and 3320 (NH) cm.$^{-1}$ (Found: C, 63·3; H, 4·9; N, 9·1. $C_{16}H_{15}ClN_2O_2$ requires C, 63·5; H, 5·0; N, 9·3%). *N*-Acetyl-*N*′-benzoyl-*N*-benzylhydrazine (226 mg.), eluted by light petroleum–benzene (1 : 4) was identical with an authentic sample.

Similarly, benzaldehyde *N*-benzyl-*N*-*p*-methoxybenzylhydrazine gave *N*-acetyl-*N*′-benzoyl-*N*-benzylhydrazine (26%) (identical with an authentic sample) and *N*-acetyl-*N*′-benzoyl-*N*-*p*-methoxybenzylhydrazine (12%), m.p. 146° $\nu_{max.}$ 1685 and 1620 (CO) and 3330 (NH) cm.$^{-1}$ (Found: C, 68·5; H, 6·2; N, 9·4. $C_{17}H_{18}N_2O_3$ requires C, 68·5; H, 6·0; N, 9·4%).

The oxidation of benzaldehyde *N*-benzyl-*N*-methylhydrazone gave *N*-acetyl-*N*′-benzoyl-*N*-methylhydrazine (26%), identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample, and *N*-acetyl-*N*′-benzoyl-*N*-benzylhydrazine (17%).

(iv) The oxidation of benzaldehyde *N*-benzyl-*N*-phenylhydrazone was carried out under nitrogen in dichloromethane–acetic acid (4 : 1 v/v) as described for benzaldehyde phenylhydrazone.[4] The products isolated were benzoylazobenzene (9%) (as benzoic acid), benzyl α-phenylazoacetate (20%) and *N*-acetyl-*N*′-benzoyl-*N*-phenylhydrazine (8%) (identical with authentic samples), and small quantities of *N*-benzoyl-*NN*′-diphenylhydrazine and *N*′-benzoyl-*NN*-diphenylhydrazine (decomposition products of benzoylazobenzene [8]). A trace of benzyl α-acetoxy-α-phenylazoacetate was also identified.

Similar treatment of benzaldehyde *N*-methyl-*N*-phenylhydrazone gave benzoylazobenzene (10%) (as benzoic acid), benzyl α-phenylazoacetate (16%), *N*-acetyl-*N*′-benzoyl-*N*-phenylhydrazine (6%), and decomposition products of benzoylazobenzene.

(v) Benzaldehyde *N*-benzyl-*N*-phenylhydrazone (2 g.) in acrylonitrile (100 ml.) was added to a stirred suspension of lead tetra-acetate (12 g.) in acrylonitrile (200 ml.) at 0° under nitrogen [as in (iv)]. Work-up was carried out as described for benzaldehyde phenylhydrazone [4] and gave 1,3-diphenylpyrazole-5-carbonitrile (693 mg., 41%) and 1,3-diphenylpyrazole-4-carbonitrile (73 mg., 0·5%), identical (m.p., mixed m.p., and i.r. spectrum) with authentic samples.

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