Reaction of Lead Tetra-acetate with Aldehyde Nitrophenylhydrazones

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Oxidation of aliphatic aldehyde 2-nitrophenyl- or 2,4-dinitrophenyl-hydrazones with lead tetra-acetate is exceptional, giving azo-acetates containing α-hydrogen atoms as major products. Lesser yields of the expected diacylhydrazine products are also formed in a competing reaction. The yields of these diacylhydrazines increase, at the expense of the azo-acetates, with increasing chain length of the aliphatic substituent at the methine carbon atom of the hydrazone. Aliphatic aldehyde 4-nitrophenylhydrazones and benzaldehyde 2-nitro- and 2,4-dinitro-phenylhydrazones behave normally, giving diacylhydrazines.

OXIDATION of aldehyde hydrazones with lead tetra-acetate (LTA) in acetic acid solution normally gives N-acyl-N'-acetylhydrazines *via* nitrilimine intermediates, whereas with ketone hydrazones azo-acetates are the normal products.[1] Although a wide range of aldehyde hydrazones has been treated with LTA, aldehyde 2,4-dinitrophenylhydrazones have previously been considered to be inert to the reagent [2] and oxidation of such compounds by LTA has not been reported.[1] Also, although oxidation of N-unsubstituted hydrazones by LTA has been investigated in detail,[3,4] the reaction with a C-unsubstituted system, derived from formaldehyde, has not been reported to date.[1] Recently,[5] it was found that treatment of formaldehyde 2,4-dinitrophenylhydrazone with bromine yielded 2,4-dinitrobromobenzene. This reaction contrasts sharply with the normal reaction between aldehyde hydrazones and halogens [6] and since oxidations of hydrazone systems by LTA sometimes parallel those by halogens the comparable reaction with LTA was of interest. We now report the oxidation by LTA of a range of aldehyde

mono- and di-nitrophenylhydrazones including some formaldehyde hydrazones.[7]

RESULTS AND DISCUSSION

(i) *2,4-Dinitrophenylhydrazones.*—When the aliphatic 2,4-dinitrophenylhydrazones (1a—e) (Table 1) were treated with LTA (1·1 mol. equiv.) in acetic acid for 1 h at 80°, followed by 16 h at ambient temperature, reactions readily occurred and the main products were the unexpected azo-acetates (2a—e). Despite the wide range of aldehyde hydrazones which has been treated with LTA,[1] only a single azo-acetate with one α-hydrogen atom has previously been encountered (in low yield) in oxidations of aldehyde hydrazones by LTA, namely α-phenylazobenzyl acetate.[2] Compound (2a), obtained in the present work, has two α-hydrogen atoms and is the only such compound isolated from LTA–hydrazone oxidations to date. Its formation is of particular interest when compared with the breakdown of the hydrazone chain which occurred when compound (1a) was oxidised with bromine.[5] With the hydrazones (1b—e) low yields of the corresponding diacylhydrazines (3b—e) (Table 1), formed by the competing nitrilimine

[1] For reviews see R. N. Butler, F. L. Scott, and T. A. F. O'Mahony, *Chem. Rev.*, 1973, **73**, 93; R. N. Butler, *Chem. and Ind.*, 1968, 437.

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

[3] D. H. R. Barton, J. F. McGhie, and P. L. Batten, *J. Chem. Soc.* (C), 1970, 1033.

[4] A. Stojilkovic, N. Orbovic, S. Sredojevic, and M. Lj. Mihailovic, *Tetrahedron*, 1970, **26**, 1101.

[5] M. M. El-Abadelah and Y. Abu-Odeh, *Chem. and Ind.*, 1972, 934.

[6] For reviews see J. Buckingham, *Quart. Rev.*, 1969, **23**, 37; R. N. Butler and F. L. Scott, *Chem. and Ind.*, 1970, 1216.

[7] A preliminary report of the work with formaldehyde and benzaldehyde 2,4-dinitrophenylhydrazones has been published: R. N. Butler, *Chem. and Ind.*, 1973, 1066.

pathway which is the normal reaction of aldehyde hydrazones, were also isolated. Control reactions showed that the compounds (3) were formed independently and not from further reactions of compounds (2). The relative amounts of the products (2) and (3) varied with the nature of the substituent R at the methine carbon atom of the parent hydrazone (1). In the case R = H the diacylhydrazine (3a) was not encountered but a low yield (3·5%) of the N-formyl derivative (7e), which may have resulted from deacetylation of compound (3a), was obtained. Thereafter the yield of the compounds (3) increased from 5 to *ca.* 30% as the length of the carbon chain in the substituent R increased from one to seven atoms (Table 1). When the substituent R was aromatic, *e.g.* compound (1f), the main product was the diacylhydrazine (3f) and no azo-acetate was encountered. In this reaction with benz-

a decomposition fragment was preferred over solvent addition. The reaction with the aliphatic 2-nitrophenylhydrazones (6a and b) closely paralleled those of the corresponding 2,4-dinitrophenylhydrazones (1b and c), giving high yields of the azo-acetates (2f and g) along with low yields of the diacylhydrazines (3i and j). The behaviour of the aromatic aldehyde 2-nitrophenylhydrazone (6c) also paralleled that of the corresponding 2,4-dinitrophenylhydrazone (1f). The diacylhydrazine (3k) was the main product, extensive decomposition occurred, and no azo-acetate was detected.

These results showed that the exceptional behaviour of the aliphatic 2,4-dinitrophenylhydrazones is due to two combining factors: (i) the presence of a 2-nitrosubstituent in the N-phenyl ring, and (ii) the presence of an alkyl group at the methine carbon atom. Either factor alone is not sufficient to orient the reaction in

TABLE 1

Oxidation of nitrophenylhydrazones by LTA

$$\text{ArNH–N=CHR} \longrightarrow \overset{\overset{\displaystyle R}{|}}{\text{Ar–N=N–CH}_A}\text{–OAc} + \text{ArNAc–NH–COR}$$

(1), (4), or (6)   (2)   (3)

Ar	R	Cpd.	Cpd.	Yield (%)	M.p. (°C)	Cpd.	Yield (%)	M.p. (°C)
(i) 2,4(NO$_2$)$_2$C$_6$H$_3$	H	(1a)	(2a)	90	44—46	(3a)	b	
	Me	(1b)	(2b)	85	52—55	(3b)	5 c	205—207
	Et	(1c)	(2c)	74	54—56	(3c)	14 c	204—206
	Pr^n	(1d)	(2d)	66	(Oil)	(3d)	19	140—142
	n-Heptyl	(1e)	(2e)	59	30—32	(3e)	29	100—101
	Ph	(1f)				(3f)	40 c,d	160—162
(ii) 4-(NO$_2$)C$_6$H$_4$	H	(4a) a						
	Me	(4b)				(3g)	70 c	185—187
	Et	(4c)				(3h)	61 c	132—134 e
(iii) 2-(NO$_2$)C$_6$H$_4$	Me	(6a)	(2f)	78	(Oil)	(3i)	6 c	133—135
	Et	(6b)	(2g)	76	(Oil)	(3j)	10 c	123—125
	Ph	(6c)				(3k)	48 c,d	143—145

a Gave the triazole (5).   b The N-formyl compound (7e) was obtained in 3·5% yield.   c Various quantities of yellow-green gums were also isolated.   d Spectra of the gums showed no azo-acetate absorptions.   e Lit.,[2] m.p. 121—123°.

aldehyde 2,4-dinitrophenylhydrazone a considerable amount of decomposition occurred yielding resins which accompanied compound (3f). The spectra of these resins showed no azo-acetate characteristics.

(ii) *2-Nitro- and 4-Nitro-phenylhydrazones.*—In order to assess the influence of each of the two nitro-substituents in the parent hydrazones (1) a number of mononitrophenylhydrazones were examined. The aliphatic 4-nitrophenylhydrazones (4b and c) behaved normally, giving the expected products (3g and h, respectively) from solvent trapping of nitrilimine intermediates. The presence of a nitrilimine intermediate in the oxidation of compound (4c) by LTA has previously been established [2] by carrying out the reaction in the presence of acrylonitrile. These reactions of compounds (4b and c) in acetic acid parallel those of aromatic aldehyde 4-nitrophenylhydrazones on which we have previously reported.[8] With formaldehyde 4-nitrophenylhydrazone (4a) a large-scale decomposition was encountered and the main product was the triazole (5), which also appears to be derived from a nitrilimine although this may not be entirely free since addition of

favour of azo-acetate formation. The increased tendency towards the diacylhydrazine pathway as the aliphatic substituent at the methine carbon atom is increased in length or changed to aromatic is probably

(5)

(7)

a; R = Me , X = Y = NO$_2$
b; R = Me , X = H, Y = NO$_2$
c; R = Ph, X = Y = NO$_2$
d; R = Me, X = NO$_2$, Y = H
e; R = H, X = Y = NO$_2$

due to enhanced stability at the positive end of the intermediate nitrilimine from which the diacylhydrazines are derived. We believe that the 2-nitro-substituent effect identified here, for the first time, has important

[8] F. L. Scott and R. N. Butler, *J. Chem. Soc.* (C), 1966, 1202.

mechanistic significance and will lead to an unequivocal identification of the initial site of attack by the reagent. Kinetic and other mechanistic studies are being carried out to elucidate this point and will be reported elsewhere.

(iii) *Structure Determinations.*—The structure of the azo-acetates (2) was established from spectroscopic data: (*a*) i.r. spectra showed $>$C=O and -C-O-C- stretching bands at *ca.* 1755 and 1210 cm^{-1}, respectively and had no N-H or O-H absorptions; (*b*) u.v. spectra showed characteristic [9,10] azo-acetate absorptions at $\lambda_{max.}$ (MeOH) 260—270 nm (log ε 3·94—4·14); (*c*) ^{1}H n.m.r. data were as expected. The important signals of H$_A$ are given in Table 2. The diacylhydrazines (3) showed amide carbonyl doublets at 1660—1710 and N-H stretching at 3200—3300 cm^{-1}. These compounds also showed all the expected ^{1}H n.m.r. signals. The shifts of the NAc protons and the *ortho*-protons H$_o$ are given in Table 2. These *ortho*-protons are particularly deshielded due to the presence of the nearby carbonyl group: a useful phenomenon, which we have commented on previously,[8] for structural determination. The representative compounds (3b, g, and f) were also prepared by acetylation of the respective compounds (7a—c). Compound (3i) was also prepared by direct diacetylation of 2-nitrophenylhydrazine with acetyl chloride. The structure of compound (5) was suggested by its spectra and was proved by unequivocal preparation according to a literature procedure.[11,12]

EXPERIMENTAL

M.p.s were measured with a Gallenkamp apparatus. I.r. spectra were measured for either films or KBr discs with Perkin-Elmer 377 and 457 spectrophotometers. U.v. spectra were measured for solutions in methanol with a Unicam SP 800 spectrophotometer. N.m.r. spectra were measured with a JEOL JNM-MH-100 spectrometer. The hydrazone substrates were prepared by standard procedures.[13]

(i) *Oxidation of 2,4-Dinitrophenylhydrazones* (1).—The following are typical examples.

(a) *Formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazones.* A solution of the formaldehyde hydrazone (1a) (1 g) in glacial acetic acid (60 ml) containing acetic anhydride (1 ml) was treated with LTA (2·33 g) and stirred for 30 min at ambient temperature, then 1 h at 80—85°, and a further 16 h at ambient temperature. After removal of lead salt the solution was made up to 300 ml with water and extracted with ether (6 × 120 ml). The combined extracts, after careful washing with water (2 × 250 ml) (washings W) and dilute aqueous sodium carbonate (250 ml) (excess of which tended to decompose the product to a deep red gum), were evaporated slowly and yielded yellow needles of 2,4-*dinitrophenylazomethyl acetate* (2a) (1·15 g, 90%), m.p. 42—44°. Careful rapid recrystallisation from slightly warmed aqueous ethanol raised the m.p. to 44—46° (Found: C, 40·15; H, 2·9; N, 20·5. C$_9$H$_8$N$_4$O$_6$ requires

C, 40·3; H, 3·0; N, 20·9%); $\nu_{max.}$ 1758 (ester C=O) and 1210 cm^{-1} (-C-O-C-) (no N-H or O-H bands); $\lambda_{max.}$ (MeOH) 266 (log ε 4·01), 344 (3·49), and 236 nm (4·05); τ (CDCl$_3$) 7·79 (3H, Ac), 3·94 (2H, CH$_2$), 1·19, 1·44, and 1·59 (2H, aromatic), and 2·52 (d, *J* 9 Hz, H$_o$). When the washings (W) were evaporated under reduced pressure, yellow crystals (3·5%) of *N'*-2,4-dinitrophenylformohydrazide (7e) (m.p. 186—188°) separated [$\nu_{max.}$ 3320 (sharp) and 3250br (NH), and 1660 cm^{-1} (C:O); τ 1·56 (HCO), aromatic 2,4-dinitrophenyl pattern, and 2·60 (H$_o$)]. Compound (7e) was also prepared in 92% yield by treating 2,4-dinitrophenylhydrazine with formic acid (90% w/w).

When a solution of compound (2a) in 95% ethanol was sealed and stirred in the dark for 5 days, removal of the solvent yielded a green-yellow gum [$\lambda_{max.}$ (MeOH) 321 nm] contaminated with ethyl acetate. When a solution of compound (2a) (106 mg) in concentrated hydrochloric acid (10 ml) was heated under reflux for 40 min, cooled, and treated with water (8 ml) and methanol (8 ml) followed by benzaldehyde (1 ml) in methanol (3 ml), benzaldehyde 2,4-dinitrophenylhydrazone (89%) separated.

A similar oxidation by LTA of acetaldehyde 2,4-dinitrophenylhydrazone (1b), in which the ethereal extracts were washed with water (washings A) but not with sodium carbonate solution, yielded 1-(2,4-*dinitrophenylazo*)*ethyl acetate* (2b) as a deep red-brown oil (85%). This slowly solidified to a sticky brown solid (m.p. 52—55°) (Found: C, 42·9; H, 3·8; N, 19·5. C$_{10}$H$_{10}$N$_4$O$_6$ requires C, 42·55; H, 3·55; N, 19·85%); $\lambda_{max.}$ (MeOH) 267 and 343w,sh nm; $\nu_{max.}$ 1755 (C=O) and 1220 cm^{-1} (-C-O-C-) (no N-H or O-H bands); τ (CDCl$_3$) 8·35 (3H, d, *J* 7 Hz, *Me*CH), 7·8 (3H, s, Ac), 3·64 [1H, q, *J* 7 Hz, MeC*H*(OAc)-N=N], and aromatic signals (3H) identical with those of compound (2a).

The water washings (A) were evaporated under reduced pressure at *ca.* 50° until crystals (65 mg, 5%) of *NN'*-*diacetyl*-N-2,4-*dinitrophenylhydrazine* (3b) (m.p. 205—207°; from 95% ethanol) separated (Found: C, 42·4; H, 3·3; N, 19·8%), $\nu_{max.}$ 3240 (NH) and 1660 and 1690 cm^{-1} (C:O, doublet); τ 7·92 (AcNH), 7·81 (AcNAr), aromatic 2,4-dinitrophenyl pattern and 2·22 (d, *J* 8 Hz, H$_o$) [downfield shift of 0·56 p.p.m. in H$_o$ signal on introduction of acetyl group into compound (7a)]. Further evaporation of the water washings (A) yielded only a green gum (53 mg).

Compound (3b) was also prepared by prolonged stirring of compound (7a) in 50% v/v acetic acid–acetyl chloride.

With the hydrazones of the higher aldehydes the diacylhydrazines (3) did not separate into the water washings but were deposited from the ethereal solutions as mixtures with the azo-acetates (2). These mixtures were separated by one of two procedures: (i) swirling the residue in small quantities of cold ether when the azo-acetate dissolved and the diacylhydrazine remained insoluble, or (ii) leaching the residue in a Soxhlet apparatus with pentane (at 30—40°); the azo-acetates again dissolved.

When the azo-acetates (2c and e) were treated under conditions identical with those for the oxidations with LTA, no diacylhydrazines were formed and the azo-acetates were recovered quantitatively. This showed that these azo-acetates, which were accompanied by the highest yields of diacylhydrazines, did not change to the latter materials under the reaction conditions.

[9] D. C. Iffland, L. Salisbury, and J. Schafer, *J. Amer. Chem. Soc.*, 1961, **83**, 747.

[10] J. Bornstein and L. Skarlos, *J. Org. Chem.*, 1970, **35**, 1230.

[11] R. Jacquier, M.-L. Roumestant, and P. Viallefont, *Bull. Soc. chim. France*, 1967, 2634.

[12] N. N. Vorozhtsov and G. G. Yakobson, *Zhur. obshchei Khim.*, 1958, **28**, 40.

[13] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1962, p. 722.

(b) *Benzaldehyde 2,4-dinitrophenylhydrazone* (1f). A solution of the hydrazone in glacial acetic acid was treated as already described. Precipitated material was removed (filtrate A), washed with a few ml of cold ether and, when stirred in water (15 ml) to remove lead salts, yielded the starting hydrazone (210 mg, 21%). The filtrate (A) was carefully treated with cold water (250 ml) and the shrunken brown tarry solid which separated immediately (solid A) was removed. The resulting solution slowly (4 days) yielded white crystals of N-*acetyl*-N'-*benzoyl*-N-2,4-*dinitrophenylhydrazine* (3f) (filtrate B) (270 mg), m.p. 160—162° (from aqueous ethanol) (Found: C, 52·0; H, 3·4; N, 15·95. $C_{15}H_{12}N_4O_6$ requires C, 52·3; H, 3·5; N, 16·25%); $\nu_{max.}$ 3210 (NH), 1665 (conj. C:O), and 1710 cm^{-1} (non-conj. C:O), $\lambda_{max.}$ (MeOH) 237 (log ε 4·21), τ 7·75 (Ac) and 2·22 (2d, J 7 Hz, H_o of PhCO) [deshielding of H_o in compound

ether (5 × 150 ml) and the combined extracts were washed carefully with water and dilute aqueous sodium carbonate and evaporated. The residue, consisting of a red-yellow gum (B) (350 mg) and compound (5) (200 mg) [m.p. 191—193° (from aqueous ethanol) (lit.,[11] 193°) (Found: C, 50·2; H, 3·2; N, 29·0. Calc. for $C_8H_6N_4O_2$: C, 50·5; H, 3·15; N, 29·4%); $\nu_{max.}$ 1620 cm^{-1} C=N (no C:O absorptions); $\lambda_{max.}$ (MeOH) 288 (log ε 4·07) and 222 nm (3·79); τ (CDCl$_3$) 1·30 (5-H), 1·52 and 1·67 (A_2B_2), 1·84 (3-H), and 2·02 and 2·17 (A_2B_2)] was swirled in small quantities of cold ether to remove the gum. The solid (A) was dispersed on a column of neutral alumina which was eluted in turn with light petroleum (b.p. 40—60°), benzene, benzene–ether (4 : 1 followed by 1 : 1 and 1 : 4 v/v), ether, and chloroform. Various gums were encountered including a further quantity of (B) which was sweet smelling and showed a strong

TABLE 2

Analytical data

| Compound | Found (%) | | | Formula | Required (%) | | | τ Values [i] |
	C	H	N		C	H	N	H_A
Azo-acetates								
(2c) [a]	44·8	4·2	19·0	$C_{11}H_{12}N_4O_6$	44·6	4·1	18·9	3·72
(2d) [b]	49·1	5·45	16·5	$C_{14}H_{19}N_4O_6$ [h]	49·5	5·6	16·5	3·80
(2e) [b]	53·0	6·1	14·8	$C_{16}H_{22}N_4O_6$	52·45	6·0	15·3	3·68
(2f) [b]	50·65	4·8	17·3	$C_{10}H_{11}N_3O_4$	50·6	4·6	17·7	3·70
(2g) [b]	52·8	5·2	16·3	$C_{11}H_{13}N_3O_4$	52·5	5·2	16·7	3·90
NN'-Diacylhydrazines								NAc, H_o (ΔH_o)
(3c) [c]	44·55	4·3	19·1	$C_{11}H_{12}N_4O_6$	44·6	4·1	18·9	7·80, 1·78 (0·8) [j]
(3d) [d]	46·5	4·5	18·0	$C_{12}H_{14}N_4O_6$	46·45	4·5	18·05	7·74, 1·96 (0·5) [j]
(3e) [e]	52·8	6·2	15·3	$C_{16}H_{22}N_4O_6$	52·45	6·0	15·3	7·78, 1·98 (0·56) [j]
(3i) [f]	50·2	4·75	17·5	$C_{10}H_{11}N_3O_4$	50·6	4·6	17·7	7·75, 2·08—2·32 (0·64—0·8) [k,l]
(3j) [g]	52·3	5·3	16·5	$C_{11}H_{13}N_3O_3$	52·5	5·2	16·7	7·80, 2·06—2·33 (0·46—0·8) [j,l]
(3k) [e]	59·9	4·4	14·1	$C_{15}H_{13}N_3O_4$	60·2	4·35	14·05	7·72, 2·04

[a] From *slightly* warmed aqueous alcohol. [b] Oils purified by dissolving in ether or in pentane (at 30—40°) by Soxhlet extraction. [c] From aqueous alcohol. [d] From chloroform. [e] From ether–pentane (at 37°). [f] From ether. [g] From benzene. [h] Compound (2d) separated with 0·4 molecules of pentane of solvation. [i] N.m.r. spectra were measured with CDCl$_3$ as solvent except for compounds (3b and k) for which (CD$_3$)$_2$SO was the solvent. [j] Deshielding shift in H_o relative to that of the corresponding azo-acetate. [k] Deshielding shift in H_o on introduction of acetyl group into compound (7d). [l] Range indicates maximum and minimum shift limits. It was not possible to obtain exact shifts owing to overlapping of aromatic signals.

(7c) on insertion of the acetyl group, 0·80 p.p.m.]. The filtrate (B) was extracted with ether (3 × 150 ml) and the combined extracts were washed with water (4 × 200 ml) and evaporated. The residue consisted of compound (3f) (88 mg) and a brown-yellow gum (125 mg) which was removed by swirling in small quantities of cold ether.

Extensive and repeated work-up of the solid (A) yielded further small quantities of starting hydrazone and compound (3f) (total yield 370 mg, 40%) along with a sticky brown-yellow gum (110 mg). There appeared to be a trace of another compound also but this could not be isolated because of the nature of the mixture.

Compound (3f) was also prepared by briefly heating compound (7c) in 50% v/v acetic acid–acetyl chloride.

(ii) *Oxidation of 4-Nitrophenylhydrazones* (4).—The following are typical examples. (a) *Formaldehyde 4-nitrophenylhydrazone* (4a). A solution of the hydrazone in glacial acetic acid was treated as already described and after removal of the precipitated lead salts the mother liquor was carefully treated with water (250 ml). After removal of a sticky brown solid (A), the solution was extracted with

broad C=O band at 1740—1760 cm^{-1}. A further small quantity (9 mg; overall, 209 mg, 37%) of compound (5) was obtained from the benzene–ether (1 : 1) fraction along with another solid (1—3 mg, impure, m.p. 248—259°) from the chloroform fractions [$\nu_{max.}$ 3290 (NH) and 1720 and 1700 cm^{-1} (C:O doublet)]. It was not possible to obtain a pure sample of this minor product, which may possibly be N-acetyl-N'-formyl-N-4-nitrophenylhydrazine.

When formaldehyde 4-nitrophenylhydrazone was treated under the same conditions in the absence of lead tetraacetate, 84% was recovered unchanged and the above products were not encountered. The triazole (5) was also prepared by heating a mixture of 1,2,4-triazole, 4-fluoronitrobenzene, and dried potassium fluoride at 184—186° for 45 min, followed by separation of the isomers as previously described.[11] The sample obtained was identical (mixture m.p., i.r. and u.v. spectra) with that isolated from the LTA reaction.

(b) *Acetaldehyde 4-nitrophenylhydrazone* (4b). A solution of the hydrazone (1 g) in glacial acetic acid (45 ml) containing acetic anhydride (0·5 ml) was treated with LTA (2·99 g)

and stirred at ambient temperatures for 4 h. When the solution was worked up as described above, the combined ethereal extracts on evaporation yielded a yellow gum, which was removed in ether, along with NN'-*diacetyl*-N-4-*nitrophenylhydrazine* (3g) (920 mg, 70%), m.p. 185—187° (from aqueous ethanol) (Found: C, 50·5; H, 4·55; N, 17·9. $C_{10}H_{11}N_3O_4$ requires C, 50·6; H, 4·65; N, 17·7%); $v_{max.}$ 3260 (NH) and 1680—1695 cm^{-1}(broad C:O doublet); τ [$(CD_3)_2SO$] 7·87 and 7·99 (2 × NAc), and 1·70, 1·84, 2·23, and 2·40 (4H, A_2B_2, J_{AB} 10 Hz) [deshielding shift in H_o on introduction of acetyl group into compound (7b), 0·61 p.p.m.]. Compound (3g) was also prepared by stirring a mixture of p-nitrophenylhydrazine (1 g) in glacial acetic acid (35 ml) containing acetyl chloride (2 ml) at ambient temperature for 30 min. N-Acetyl-N'-p-nitrophenyl-hydrazine (7b) (55%) was removed and evaporation of the filtrate under a current of air yielded compound (3g) (30%), identical (mixture m.p. and i.r. spectra) with that obtained from the LTA reaction. Similar treatment of compound (7b) (m.p. 205°; lit.,[14b] 205°), using 1·5 ml of acetyl chloride, also yielded compound (3g) (15%), along with the unchanged monoacetyl derivative (78%).

(iii) *Oxidation of 2-Nitrophenylhydrazones* (6).—The oxidations of the hydrazones (6a—c) were carried out like those of the corresponding 2,4-dinitrophenylhydrazones, whose behaviour they closely paralleled. Azo-acetates

and diacylhydrazines were separated by the foregoing procedures. The products are described in Tables 1 and 2. Compound (3i) obtained from the oxidation of the hydrazone (6a) was also obtained by treating 2-nitrophenylhydrazine with 3 : 5 v/v acetyl chloride–acetic acid, followed by removing hydrazine hydrochloride which separated and evaporating the solution. The residue, when leached with ether, yielded compound (3i) in the ethereal solution. The sample obtained by this procedure was identical (mixture m.p. and i.r. spectra) with that obtained from the LTA oxidation of the hydrazone (6a).

The N-acyl-N'-arylhydrazines (7a) (m.p. 198—200°; lit.,[14a] 197—198°) (7c) (m.p. 211°; lit.,[14a] 206—207°), and (7d) (m.p. 142—144°; lit.,[14c] 140—141°) were generally prepared by treating the appropriate hydrazine with 1—2 mol. equiv. of the acid chloride at ambient temperature in acetic acid. The compounds gave satisfactory analyses.

[14] Z. Rappoport, ' Handbook of Tables for Organic Compound Identification,' The Chemical Rubber Co., Cleveland, 3rd edn., 1967, (*a*) p. 316; (*b*) p. 314; (*c*) p. 307.