Reactions of Lead Tetra-acetate. Part XVIII.[1] Oxidation of Aldehyde Hydrazones: A New Method for the Generation of Nitrilimines

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A number of aldehyde arylhydrazones have been oxidised with lead tetra-acetate. In many cases diacylhydrazines, RCO·NH·NAcAr, can be isolated in good yield. With benzaldehyde phenylhydrazone, provided that precautions are taken to avoid autoxidation, α-phenylazobenzyl acetate can be isolated in up to 27% yield. Evidence has been obtained that this compound is not the main precursor of the diacyl derivative PhCO·NH·NAcPh or of further oxidation products, but that these arise *via* the nitrilimine $\mathrm{PhC{\equiv}\overset{+}{N}{-}\overset{-}{N}Ph}$; this 1,3-dipolar compound has been trapped with acrylonitrile, to form 1,3-diphenylpyrazole-5-carbonitrile together with a small quantity of the isomeric 4-carbonitrile. Analogous nitrilimines have been similarly trapped during the oxidation of the *p*-nitrophenylhydrazones of benzaldehyde, propionaldehyde, benzoin, and benzil. Oxidations with lead tetrabenzoate, and with lead tetra-acetate in methanol, have also been carried out; they lead to azo-dibenzoates and azo-dimethyl ethers, respectively, and benzaldehyde phenylhydrazone also forms an azo-benzoate.

The acylhydrazones PhCH:N·NH·COR (R = Ph or $\mathrm{NPh_2}$) undergo oxidative cyclisation with lead tetra-acetate to give high yields of the corresponding oxadiazoles. Likewise, the phenyl- and *p*-nitrophenyl-hydrazones of *o*-nitrobenzaldehyde are cyclised to 3-arylazoanthranil 1-oxides. Nitrilimines, by implication, mediate in each case.

THE oxidation of aldehyde hydrazones with lead tetra-acetate was first studied by Bower and Doyle, who reported that certain compounds whose hydrazine grouping contains an appropriately sited heterocyclic ring can undergo oxidative cyclisation; for example, benzaldehyde 2-pyridylhydrazone gives 3-phenyl-*s*-triazolo[4,3-*a*]pyridine.[2] Further examples of such cyclisations have since been reported,[3-5] but oxidation of the 1-methyl-1*H*- or 2-methyl-2*H*-tetrazol-5-ylhydrazones of some aromatic aldehydes gives, in addition to cyclised products, considerable quantities of diacylhydrazines of the type (2).[4,5] Such diacyl compounds have also been obtained from three aldehyde hydrazones which cannot undergo cyclisation,[4,6] and we have recently shown, for the derivatives from aromatic aldehydes, that they can react further with the oxidant to give the azo-diacetates (3) and aroylazobenzenes (4) (R = aryl).[1]

$$\underset{(1)}{\mathrm{RCH{=}N{\cdot}NHAr}} \xrightarrow{\mathrm{Pb(OAc)_4}} \underset{(2)}{\mathrm{RCO{\cdot}NH{\cdot}N(COMe)Ar}} \xrightarrow{\mathrm{Pb(OAc)_4}} \underset{(3)}{\mathrm{RC(OAc)_2{\cdot}N{:}N{\cdot}Ar}} + \underset{(4)}{\mathrm{RCO{\cdot}N{:}N{\cdot}Ar}}$$

In contrast, simple ketone arylhydrazones are oxidised by lead tetra-acetate to azo-acetates, $\mathrm{R^1R^2C(OAc){\cdot}N{:}NAr}$.[7-9] Analogous compounds (5) from aldehyde arylhydrazones should be capable of undergoing a prototropic shift to give hydrazonyl acetates (6) which are known to undergo 1,4-acyl migration to give the diacylhydrazines (2);[10] this route to the compounds (2) has been implied in some previous discussions. We have studied the reactions of a number of aldehyde hydrazones with lead tetra-acetate and obtained evidence that the major pathway to the compounds (2) does not involve azo-acetates (5), and we have also examined the oxidations of some aldehyde hydrazones in which a substituent in the aldehyde grouping is suitably placed for taking part in an oxidative cyclisation.

$$\underset{(5)}{\mathrm{RCH(OAc){\cdot}N{:}N{\cdot}Ar}} \longrightarrow \underset{(6)}{\mathrm{RC(OAc){:}N{\cdot}NHAr}} \longrightarrow (2)$$

Formation of the Diacylhydrazines (2).—We established first that oxidation of a wide variety of aldehyde arylhydrazones with *ca.* 1 mol. of lead tetra-acetate in

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

[2] J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 1957, 727.

[3] A. Pollak and M. Tišler, *Tetrahedron*, 1966, **22**, 2073; B. Stanovnik and M. Tišler, *ibid.*, 1967, **23**, 387; H. Gehlen and F. Lemme, *Annalen*, 1967, **703**, 116; R. G. W. Spickett and S. H. B. Wright, *J. Chem. Soc.* (*C*), 1967, 498; K. T. Potts and C. Hirsch, *J. Org. Chem.*, 1968, **33**, 143.

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

[5] R. N. Butler and F. L. Scott, *J. Chem. Soc.* (*C*), 1968, 1711.

[6] B. T. Gillis and M. P. LaMontagne, *J. Org. Chem.*, 1968, **33**, 762.

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

[8] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.*, 1965, 3048.

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

[10] J. M. Burgess and M. Gibson, *J. Chem. Soc.*, 1964, 1500.

dichloromethane gives moderate to good yields of diacylhydrazines (Table); the yields of (2; Ar = p-$O_2N{\cdot}C_6H_4$, R = Ph or p-$O_2N{\cdot}C_6H_4$) are comparable to those obtained in acetic acid.[4] The p-nitrobenzaldehyde derivative required a higher temperature for oxidation than the others, and benzaldehyde *o*-nitro- and 2,4-dinitro-phenylhydrazone were essentially unreactive at the reflux temperature, the starting materials being recovered in high yield. Of the arylhydrazones in the Table, only the pyridine compound could in principle undergo oxidative cyclisation; by analogy with the behaviour of the *syn*-isomer of 2-benzoylpyridine phenylhydrazone with lead tetra-acetate,[11] the formation of an 8-azaindazolium salt might have been expected. The course of the reaction in this case may be dictated by the reactant's not having the appropriate stereochemistry for cyclisation.

Oxidation of aldehyde arylhydrazones (1) to *N*-acetyl-*N*′-acylarylhydrazines (2) with lead tetra-acetate in dichloromethane at room temperature (except where stated otherwise)

R	Ar	Yield (%)
Ph	p-$O_2N{\cdot}C_6H_4$	72
p-ClC_6H_4		64
p-$O_2N{\cdot}C_6H_4$		83[a]
p-MeC_6H_4		56
PhCH=CH		61[b]
Et		74
2-Pyridyl	Ph	53[c]

[a] Under reflux. [b] At 0°. [c] At −70°.

The possession of an N–H group in the hydrazone grouping was shown not to be a prerequisite for oxidation when we found that benzaldehyde diphenylhydrazone (7) gave the tetra-substituted hydrazine (8) in 72% yield, although this product is of necessity structurally different from those of type (2).

$$\underset{(7)}{\mathrm{PhCH{:}N{\cdot}NPh_2}} \xrightarrow{\mathrm{Pb(OAc)_4}} \underset{(8)}{\mathrm{PhCO{\cdot}N(COMe){\cdot}NPh_2}}$$

Oxidation of Benzaldehyde Phenylhydrazone.—When oxidised under the same conditions, at 0°, benzaldehyde phenylhydrazone gave a red oil, as had previously been found by Iffland and his co-workers.[7] Some high-melting solids were obtained from the oil which may have been dimeric and were not further investigated. It was shown that these products arose from autoxidation,[12,13] for they were not formed when reaction was carried out under nitrogen. All further oxidations of this hydrazone were therefore conducted in an atmosphere of nitrogen, and moreover, it was necessary to use an excess of lead tetra-acetate so as to destroy all the hydrazone, for otherwise aerial oxidation during the work-up increased the difficulty of separating the products.

Oxidation at room temperature in a mixture of dichloromethane and benzene containing a small proportion of acetic acid gave a mixture which was shown by t.l.c. to have four major components. Since one of these was benzoylazobenzene (15) which decomposes during chromatography,[1] the mixture was treated briefly with acidified methanol to convert the benzoylazobenzene into methyl benzoate [14] before the products were separated on an alumina column. The yield of methyl benzoate, estimated after hydrolysis to benzoic acid, demonstrated the formation of at least 34% of benzoylazobenzene. The second major product, isolated in 15% yield, was the azo-acetate (9), characterised by its u.v.,[7] i.r., and n.m.r. spectra, and by the appearance in the mass spectrum of both the parent ion and a fragment derived by loss of PhN_2. The azo-diacetate (14) and *N*′-benzoylphenylhydrazine were also isolated, each in 4% yield, and t.l.c. showed that the chromatographic fraction which yielded the latter compound also contained some *N*-acetyl-*N*′-benzoylphenylhydrazine (11). These two hydrazines are not necessarily direct oxidation products of the phenylhydrazone, since they are known to be readily oxidised by lead tetra-acetate at room temperature and the oxidant was present in excess. They are likely to have been formed, at least in part, from the azo-acetate during chromatography (see later).

When this experiment was repeated without acetic acid, the azo-acetate (9) was accompanied by non-volatile material which could not be removed by chromatography, and from which some of the benzylidenebenzohydrazidine (20) [15] could be isolated by crystallisation. It seems probable that under these conditions a small amount of lead dioxide, produced by adventitious water, brings about one-electron oxidations leading to dimeric products (in contrast to the two-electron processes which characterise the formation of the azo-acetate and related products; see later).

The azo-acetate (9) was isolated as a yellow oil of reasonable stability; for example, it was distilled at 125° under reduced pressure without significant decomposition, and after 2 months at room temperature its i.r. spectrum suggested that less than 5% had decomposed. Chromatography on alumina resulted in some conversion into a mixture of *N*′-benzoyl- and *N*-acetyl-*N*′-benzoyl-phenylhydrazine, but provided that the time of contact was kept to a minimum, this was not very significant. When a solution of the azo-acetate in acetic acid was set aside at room temperature, approximately 50% of the material was transformed (i.r. spectrum) in 72 hr., and chromatography of the residue after 11 days yielded 20% of unchanged material and 40% of *N*-acetyl-*N*′-benzoylphenylhydrazine.

The rate of disappearance of the azo-acetate, in solution in acetic acid at 66·5°, was followed by measurement of the optical density of the solution at 404 nm. A first-order plot was obtained for the first hour of the

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[11] R. Kuhn and W. Münzing, *Chem. Ber.*, 1952, **85**, 29.

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

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

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

[15] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, 1962, **27**, 4663.

reaction with $t_{\frac{1}{2}}$ *ca.* 5 hr.; the rate was unchanged when M-sodium acetate was added but became immeasurably fast when 0·0015M-sulphuric acid was included. Periodic scanning of the u.v. and visible spectra, under the first set of conditions, showed that an intermediate with $\lambda_{max.}$ *ca.* 337 nm. accumulated during the first 3 hr., remained at the same concentration for about 6 hr., and then decayed; some absorption by this intermediate at 404 nm. was probably responsible for the fact that the first-order plot for decomposition of the azo-acetate was not linear throughout the reaction. We attribute structure (10) to this intermediate, its decay by rearrangement leading to the product (11).

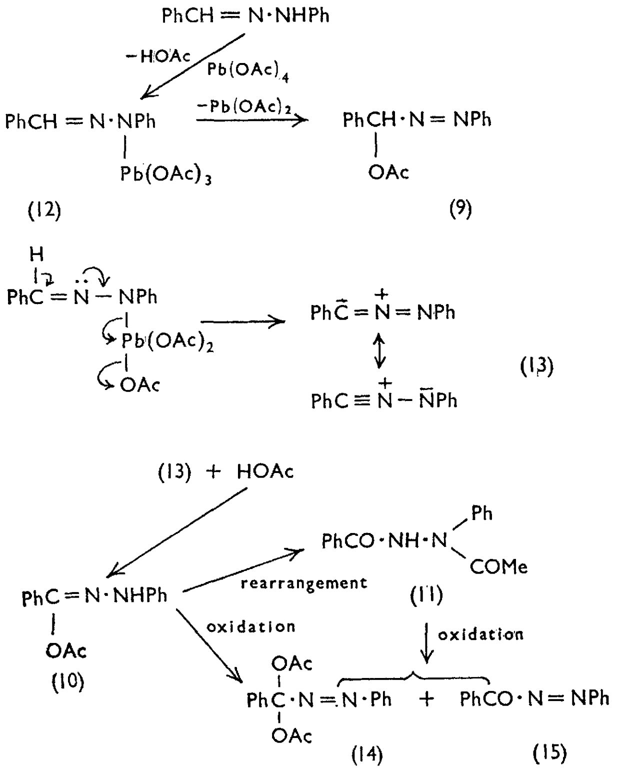
$$\underset{(9)}{\mathrm{PhCH(OAc){\cdot}N{:}N{\cdot}Ph}} \longrightarrow \underset{(10)}{\mathrm{PhC(OAc){:}N{\cdot}NHPh}} \longrightarrow \underset{(11)}{\mathrm{PhCONH{\cdot}NAcPh}}$$

The azo-acetate (9) was not affected by treatment with lead tetra-acetate in dichloromethane at room temperature for 1 hr., and when acetic acid was used as the solvent only 0·4 mol. of the oxidant had been consumed after 24 hr.

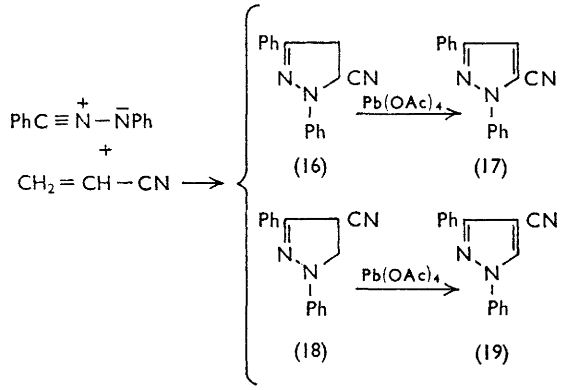
The relatively low rates both for the oxidation of the azo-acetate and for its tautomeric conversion into the hydrazonyl acetate (10), each under conditions under which benzaldehyde phenylhydrazone is oxidised rapidly to benzoylazobenzene and to the azo-diacetate (14) as well as to the azo-acetate, show that the first two oxidation products cannot be derived, at least to a significant extent, from the azo-acetate. We therefore considered the possibility that, as well as reacting to give the azo-acetate by way of the organolead intermediate (12) (*cf.* the oxidation of ketone arylhydrazones[9]), benzaldehyde phenylhydrazone might also give, by way of the same intermediate, the nitrilimine (13) and thence the hydrazonyl acetate (10) (*cf.* the formation of nitrile oxides from aldoximes and lead tetra-acetate[16]). This compound would then give the diacylhydrazine (11) by rearrangement, and the azo-diacetate (14) and benzoylazobenzene by further oxidation (see further below).

To test for this possibility, we carried out the oxidation of the hydrazone in acrylonitrile, which is known[17] to react with the nitrilimine (13) to form 1,3-diphenyl-2-pyrazoline-5-carbonitrile (16). It was found necessary to carry out the oxidation at a lower temperature (<0°) than usual, and with more dilute solutions, for otherwise a vigorous exothermic polymerisation occurred to give intractable material. However, with suitable control, the pyrazole (17) could be obtained in 64% yield, and 2% of the isomer (19) was also isolated.*

Reaction doubtless occurs by way of the corresponding pyrazolines (16) and (18); such compounds are known to be dehydrogenated by lead tetra-acetate under mild conditions.[18]



SCHEME 1



SCHEME 2

In order to determine whether the presence of a nucleophile would alter significantly the relative yields of the azo-acetate and of the products derived from the nitrilimine, further oxidations of benzaldehyde phenylhydrazone were carried out, in acetic acid containing M-sodium acetate, and in methanol. Oxidation under

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* The 4-cyano-isomer, which is apparently not obtained when the nitrilimine is generated by other methods,[17] was identified by its i.r., u.v., n.m.r., and high-resolution mass spectra, and by its conversion, by hydrolysis followed by decarboxylation, into 1,3-diphenylpyrazole. As expected, the acid did not decarboxylate as readily as the 5-carboxy-isomer; however, a suitable method was found which involved heating the acid with copper-bronze in *NN*-dimethylaniline at 200°.

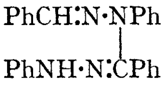
[16] G. Just and K. Dahl, *Tetrahedron*, 1968, **24**, 5251.

[17] R. Huisgen, M. Seidl, G. Wallbillich, and H. Knupfer, *Tetrahedron*, 1962, **17**, 3.

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

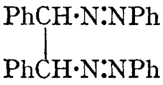
the former conditions gave higher yields of the azo-acetate (27%) and of the hydrazines which result from its decomposition during isolation (see above), and a lower yield of benzoylazobenzene (13% as benzoic acid); only a trace of the azo-diacetate (14) could be isolated, although this compound was shown to be stable under the reaction conditions.[*] On the other hand, the major product (62%) from oxidation in methanol was the azo-dimethyl ether (22), characterised by its u.v.,[†] n.m.r., and mass spectra. A small quantity of an unstable yellow oil was also obtained, whose properties suggested that it contained both the monomethoxy-isomers (24) and (26); the presence in the product mixture of the azo-acetate (9) was also indicated (t.l.c. and i.r. spectrum), but the pure material could not be isolated, probably owing to its decomposition during the slow chromatography needed to separate the methoxy-compounds.

When benzaldehyde phenylhydrazone was oxidised with lead tetrabenzoate in benzene containing benzoic acid, there was again evidence that two mechanistic pathways were being followed. The products included the azo-benzoate (25) (16%) (a reasonably stable low-melting yellow solid), the azo-dibenzoate (23) (35%), and benzoylazobenzene (7%); 13% of *NN'*-dibenzoylphenylhydrazine was also isolated, but this resulted from rearrangement of the azo-benzoate during chromatography.[‡]



$$\begin{array}{l}\text{PhCH:N·NPh}\\ \qquad |\\ \text{PhNH·N:CPh}\end{array}$$

(20)



$$\begin{array}{l}\text{PhCH·N:NPh}\\ \quad |\\ \text{PhCH·N:NPh}\end{array}$$

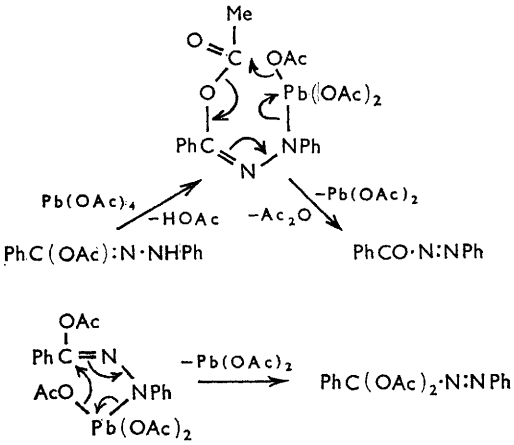
(21)

PhC(OR)$_2$·N:NPh
(22; R = Me)
(23; R = Bz)

PhCH(OR)·N:NPh
(24; R = Me)
(25; R = Bz)

PhC(OMe):N·NHPh
(26)

The products from consecutive oxidations, *i.e.*, benzoylazobenzene and the azo-derivatives (14), (22), and (23), might be formed from the hydrazonyl derivatives in either of two ways: by direct oxidation (*e.g.* Scheme 3) or by rearrangement to the diacylhydrazine and subsequent oxidation of the latter. The azo-dimethyl ether (22) evidently arises by direct oxidation because, firstly, methyl hydrazonates do not readily rearrange,[20] and, secondly, oxidation of diacylhydrazines in alcoholic solvents does not lead to azo-diethers.[1] In the other cases, however, there is evidence that both pathways are followed. Both the very much greater yield from the phenylhydrazone of the azo-dibenzoate (23) than of the azo-diacetate (14), and also the failure to isolate significant quantities of the azo-diacetate when the reaction is conducted in acetic acid, parallel the results obtained for lead tetra-acetate oxidation of the appropriate *NN'*-diacylhydrazines,[1] suggesting that the mechanistic pathway *via* these hydrazines is the major one. On the other hand, the yield of the azo-diacetate (14) from the phenylhydrazone, although small, is twice that obtainable, under identical conditions, from *N*-acetyl-*N'*-benzoylphenylhydrazine, showing that direct oxidation is also occurring to a small extent.



SCHEME 3

Oxidation of Benzaldehyde p-*Nitrophenylhydrazone*.—The formation of the azo-acetate (9) from benzaldehyde phenylhydrazone prompted us to re-examine the oxidation of the corresponding *p*-nitrophenylhydrazone but with an excess of oxidant and in the absence of air. However, neither the corresponding azo-acetate nor any related compound (the azo-methyl ether from reaction in methanol, or the azo-benzoate from reaction with lead tetrabenzoate) could be isolated. Oxidation in dichloromethane gave mainly 4-benzoylazonitrobenzene, from reaction of the first-formed product, *N*-acetyl-*N'*-benzoyl-*p*-nitrophenylhydrazine (see above), with the excess of oxidant,[1] and oxidation in methanol gave the azo-dimethyl ether (27) (47·5%), as well as 13% of the methyl hydrazonate (30). Oxidation with lead tetrabenzoate in dichloromethane gave *NN'*-dibenzoyl-*p*-nitrophenylhydrazine (43·5%), and the azo-dibenzoate (28) (12%).

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[*] Both this reaction and the oxidation of the phenylhydrazone with lead tetra-benzoate led to the isolation of very small quantities of 1,2-diphenyl-1,2-bisphenylazoethane (21). This compound, which is formed when benzaldehyde phenylhydrazone is oxidised with a number of reagents,[15] appeared to be quite uncontaminated by any other dimeric products, *e.g.*, benzil osazone or the benzylidenebenzohydrazidine (20). Its mode of formation remains obscure.

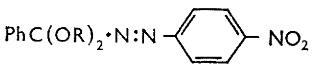
[†] This azo-dimethyl ether, and its *p*-nitrophenyl analogue (27), both show anomalous $n-\pi^*$ bands ($\lambda_{\text{max.}}$ 424 and 442 nm., respectively), as has previously been noted by Guthrie for azo-ethers derived from ketone arylhydrazones.[19]

[‡] That this hydrazine was indeed an artefact was shown by its failure to crystallise from ether–petroleum along with the azo-dibenzoate (see Experimental section). It was only isolated after a later chromatographic separation, the mixture for which was introduced in petroleum in which *NN'*-dibenzoylphenylhydrazine is insoluble.

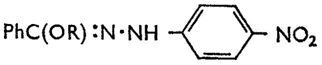
[19] J. Buckingham and R. D. Guthrie, *J. Chem. Soc.* (*C*), 1968, 1445.

[20] F. L. Scott and J. B. Aylward, *Tetrahedron Letters*, 1965, 841.

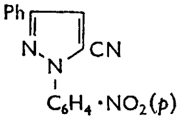
Evidence for the mediation of a nitrilimine in these reactions was again obtained from oxidation in acrylonitrile, both the pyrazole (32) * and the pyrazoline (33) being isolated. That this pyrazoline was not completely converted into the pyrazole under the reaction conditions, unlike the pyrazolines (16) and (18), is evidently because the *p*-nitro-substituent reduces the nucleophilicity of the heterocyclic nitrogen atom to which it is conjugated, and hence[18] the ease of reaction with lead tetra-acetate. However, it was found that treatment of the crude product with lead tetra-acetate in damp dichloromethane (*i.e.* the commercial solvent which had not been dried) gave the pyrazole (32) in 60% yield. It is probable that the oxidant in this case is lead dioxide, produced by hydrolysis, since the pyrazoline (33) was almost wholly recovered after treatment for 60 hr. with lead tetra-acetate in dichloromethane containing 6% of acetic acid. The pyrazole (32) was further characterised by hydrolysis to the corresponding acid (97%) and decarboxylation of the latter (77%) to give the known 1-*p*-nitrophenyl-3-phenylpyrazole.



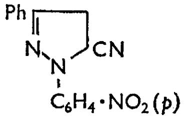
(27; R = Me)
(28; R = Bz)
(29; R = Ac)



(30; R = Me)
(31; R = Ac)



(32)



(33)

Although these experiments show that the primary oxidation product of benzaldehyde *p*-nitrophenylhydrazone is also a nitrilimine, two differences between the products formed from this hydrazone and from the corresponding phenylhydrazone are notable. First, the former did not give the azo-diacetate (29). This is probably because oxidation of the *p*-nitrophenylhydrazonyl acetate (31) is much slower than that of the phenyl analogue (10), so that rearrangement to the diacylhydrazine $PhCO{\cdot}NH{\cdot}N(Ac){\cdot}C_6H_4{\cdot}NO_2(p)$ occurs almost exclusively, oxidation of the latter then giving 4-benzoylazonitrobenzene.[1] Consistently with this, oxidation in methanol leads to the methyl hydrazonate (30) which does not rearrange[20] but which is, in part, directly oxidised to the azo-dimethyl ether (27). Secondly, as already mentioned, benzaldehyde *p*-nitrophenylhydrazone gave no azo-acetate. It is unlikely that this is because the *p*-nitro-substituted azo-acetate rearranges faster than the parent compound (9) since, as we have seen for the latter, the rearrangement is acid-catalysed and should be retarded by a nitro-substituent. However, the *p*-nitro-substituent should stabilise the nitrilimine,† and hence the transition state leading to it, and this factor could divert the reaction of an organolead intermediate of the type (12) towards formation of the nitrilimine rather than the azo-acetate (*cf.* Scheme 1). This effect can also underlie the formation of diacylhydrazines rather than azo-acetates from the other *p*-nitrophenylhydrazones in the Table; likewise, the nitrilimine from pyridine-2-carbaldehyde phenylhydrazone should be stabilised by the heterocyclic nitrogen atom. It should be noted, however, that the possession of a nitro-group can retard the rate of oxidation (*e.g.* *p*-nitrobenzaldehyde *p*-nitrophenylhydrazone is less readily oxidised than the benzaldehyde analogue ‡); thus, the rate-determining step is likely to be nucleophilic displacement by the hydrazone on

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* That the cyano-group is at the (expected) 5-position and not at the 4-position was established from the n.m.r. spectrum. The resonance for the pyrazole proton was at δ 7·38, *i.e.* slightly down-field of that of the corresponding proton in the 5-cyanophenyl analogue (17) (δ 7·26). The resonance for the pyrazole proton in the 4-cyano-isomer of (32) would be expected to occur at lower field than that (δ 8·35) of the corresponding proton in the 4-cyano-derivative (19).

† Although the effects of polar substituents in the olefinic component on the orientation of 1,3-dipolar additions have been extensively studied (*e.g.*, ref. 17), the effects of substituents on the stability of nitrilimines have received little attention. The rate of formation of diarylnitrilimines from 2,5-diaryltetrazoles is increased by electron-withdrawing substituents in the *N*-aryl ring and decreased by such substituents in the *C*-aryl ring, but it has been suggested that this is probably because there is an unsymmetrical activated complex of the type $ArC(\dot{:}N{\cdot}\bar{N}Ar){\cdot}N\dot{:}\overset{+}{N}$ (J. E. Baldwin and S. Y. Hong, *Chem. Comm.*, 1967, 1136); effects of this sort are not necessarily to be expected in the formation of the nitrilimine (13) and its derivatives by a concerted elimination of the type depicted in Scheme 1. Now, a diarylnitrilimine can be described as a hybrid of four canonical structures (a)—(d) (besides others derived from these by participation by one or more of the aromatic rings); the main contribution is made by the 'octet' structures (a) and (b), and owing to the

$$\begin{tikzcd}
\underset{(a)}{ArC{\equiv}\overset{+}{N}{-}\overset{-}{N}Ar} \arrow[r, leftrightarrow] & \underset{(b)}{Ar\overset{-}{C}{=}\overset{+}{N}{=}NAr} \arrow[d, leftrightarrow] \\
\underset{(d)}{Ar\overset{-}{C}{=}N{-}\overset{+}{N}Ar} \arrow[r, leftrightarrow] & \underset{(c)}{Ar\overset{+}{C}{=}N{-}\overset{-}{N}Ar}
\end{tikzcd}$$

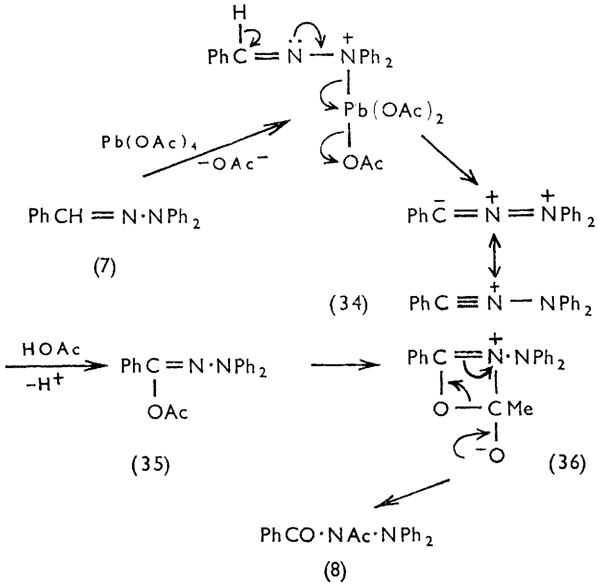
greater electronegativity of nitrogen than of carbon, particularly by (a). It follows that the two outer atoms of the C–N–N unit in the nitrilimine are associated with partial negative charges, so that it is reasonable to expect that stability should be conferred on the nitrilimine by electron-withdrawing groups in either aromatic ring.

‡ However, the even lower reactivity of benzaldehyde *o*-nitrophenylhydrazone can hardly be due to the polar effect of one nitro-group, and we infer that steric hindrance is responsible. This would be expected for attack at the NH group attached to the arylhydrazone ring (*cf.* ref. 9), but not if attack occurs at the aldehydic carbon atom, as has recently been suggested for reactions of this type.[21] Also consistent with attack at nitrogen, rather than at carbon, is the apparent absence of hindrance to the oxidation of hydrazones derived from *o*-nitrobenzaldehyde (see later).

[21] P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 4716.

lead tetra-acetate as in the oxidation of ketone arylhydrazones,[9] the ease of formation of the nitrilimine affecting only the distribution of the products.

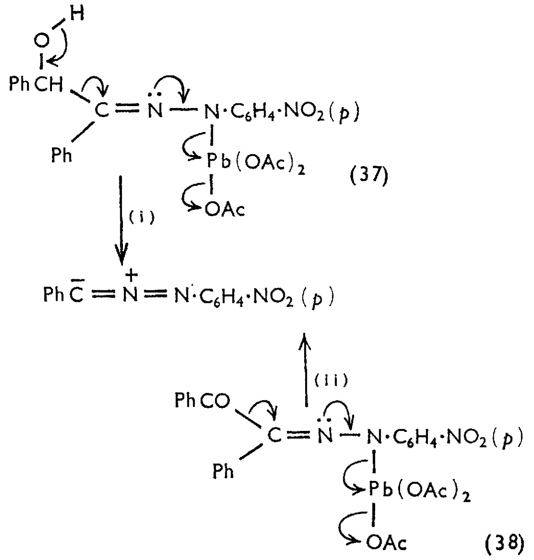
The formation of the tetra-substituted hydrazine (8) by oxidation of benzaldehyde diphenylhydrazone cannot involve a nitrilimine, but analogy suggests that the cation (34), generated similarly to a nitrilimine, may be an intermediate; reaction with acetate ion would give the hydrazonyl acetate (35) and thence, by a 1,3-shift, the product (8) (Scheme 4). A precedent for this migration is the ready rearrangement of the imidic derivatives, PhC(O·COAr):NAr′, for which an intermediate corresponding to (36) has been suggested.[22]



Scheme 4

Further Reactions of Hydrazones.—In order to see whether aliphatic nitrilimines could be generated by this method, the oxidation of propionaldehyde *p*-nitrophenylhydrazone was studied. Although, like the benzaldehyde analogue, it did not give an azo-acetate, oxidation in acrylonitrile and then in damp dichloromethane led to the pyrazole (32; Et for Ph); however, the yield (26%) was less than in the previous examples. This pyrazole was characterised by conversion (hydrolysis followed by decarboxylation) into 3-ethyl-1-*p*-nitrophenylpyrazole (85%).

We have already reported the formation of *N*-acetyl-*N*′-benzoyl-*p*-nitrophenylhydrazine in the lead tetra-acetate oxidation of the *p*-nitrophenylhydrazones of both benzoin and benzil,[23] and the identity of this product with that obtained from the benzaldehyde analogue suggested that the same nitrilimine intermediate might be implicated, being formed in these cases by fragmentation of the organolead derivatives (37) and (38) (Scheme 5). This was confirmed by our finding that oxidation of benzoin or benzil *p*-nitrophenylhydrazones in acrylonitrile gives the pyrazole (32). The yields (57 and 22% respectively) are consistent with the relative ease of formation of the nitrilimine to be expected in the two cases. Also consistent with our mechanistic arguments (above) is the oxidation of the phenylhydrazone of benzil to give the azo-acetate as the major product.[23]



(i) $-\mathrm{HOAc}$, $-\mathrm{Pb(OAc)_2}$, $-\mathrm{PhCHO}$

(ii) $-\mathrm{AcO^-}$, $-\mathrm{Pb(OAc)_2}$, $-\mathrm{PhCO^+}$

Scheme 5

Two types of aldehyde hydrazone which are potentially capable of oxidative cyclisation as an alternative to the formation of diacylhydrazines were also examined. First, the acylhydrazones (39) and (40) reacted with lead tetra-acetate at room temperature to give the corresponding oxadiazoles (42) and (43) in 87 and 76% yields, respectively; acetaldehyde acetylhydrazone gave nitrogen and some acetaldehyde but no oxadiazole.

Secondly, the *o*-nitrobenzaldehyde derivatives (44) and (45) gave, on oxidation, the corresponding 3-arylazoanthranil 1-oxides (47) and (48) in yields of 76 and 54%, respectively. This seems to be a more suitable method for the preparation of such compounds than that previously reported; the latter, which presumably also involves a nitrilimine intermediate, consists of treating a hydrazonyl bromide of the type (46) with base.[24] The hydrazonyl bromides are obtained by bromination of the corresponding hydrazones, but unless the aromatic ring in the hydrazone contains a strongly electron-withdrawing substituent, such as *p*-nitro, bromination of this ring cannot apparently be avoided,[10,20] so that it would not be possible to obtain, for example, the compound (47) in this way.

By analogy with the behaviour of benzaldehyde phenylhydrazone, we infer that these cyclisations also

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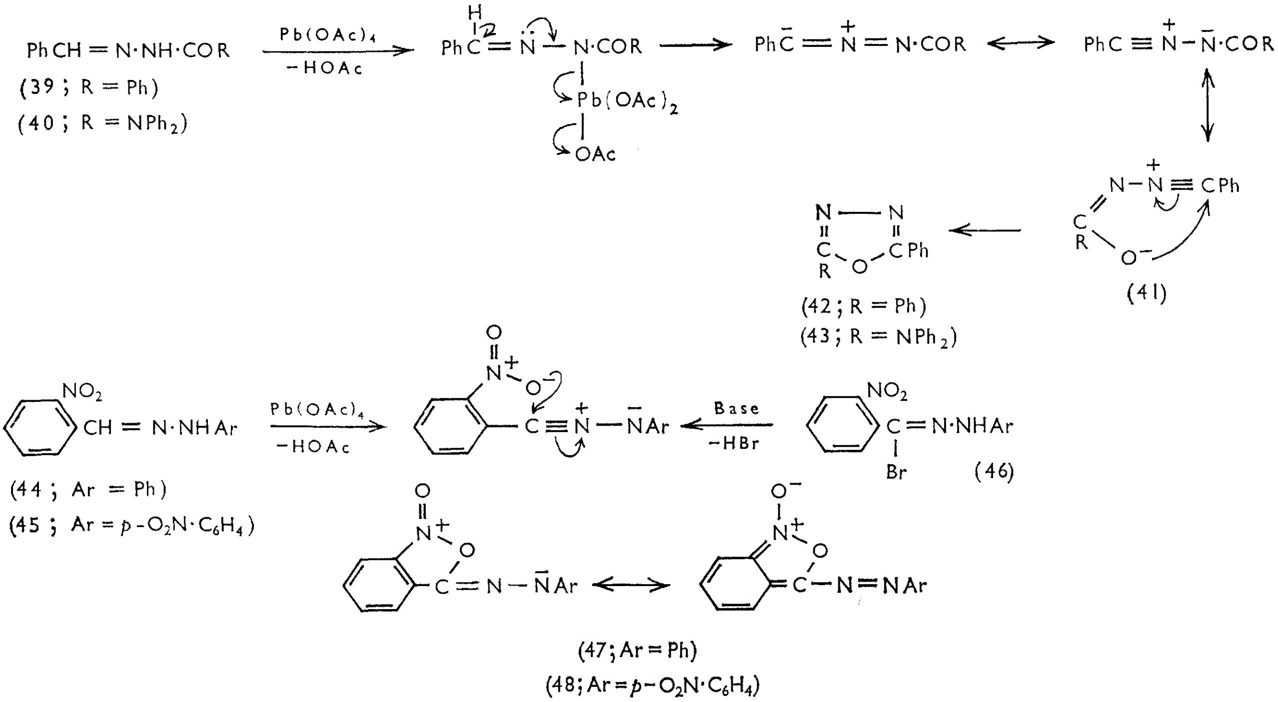
[22] D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 637.

[23] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc. (C)*, 1966, 1531.

[24] M. S. Gibson, *Tetrahedron*, 1962, **18**, 1377.



SCHEME 6

proceed *via* nitrilimines (Scheme 6), especially since in each case the formation of the nitrilimine should be facilitated, compared with that of (13), by the substituents [in two cases by the carbonyl group [*cf.* the contribution of the canonical structure (41)], and in the other two by the polar effect of the nitro-groups (*cf.* footnote earlier)].

EXPERIMENTAL

Except where stated, i.r. spectra were measured for Nujol mulls with a Perkin-Elmer 237 grating spectrophotometer, u.v. spectra for solutions in methanol with a Unicam SP 700C spectrophotometer, ^{1}H n.m.r. spectra for solutions in deuteriochloroform with a Varian A-60A spectrometer, and mass spectra with an A.E.I. MS 902 spectrometer. T.l.c. was performed on Stahl Kieselgel HF$_{254}$; the plates were developed in an iodine tank or sprayed with a 1 : 1 mixture of antimony trichloride and acetic acid. Except where stated, alumina for chromatography was the Woelm neutral product; Laporte alumina was type H, partially neutralised by the addition of 4% of 10% aqueous acetic acid.

Lead tetra-acetate (B.D.H., reagent grade) was recrystallised from acetic acid and dried *in vacuo* (KOH); in experiments including acetic acid in the solvent, this purification was omitted. Lead tetrabenzoate was as described previously.[1] Benzene was distilled from sodium, and dichloromethane from phosphorus pentoxide; *damp* dichloromethane was not so treated, and gave a brown colour with lead tetra-acetate. Petroleum had b.p. 60—80°. Acrylonitrile was dried over molecular sieve (B.D.H., type 4A) and distilled from phosphorus pentoxide. The aldehyde arylhydrazones were prepared by standard methods and had the properties previously reported. Benzaldehyde *NN*-diphenylhydrazone, prepared by heating a solution of benzaldehyde and *NN*-diphenylhydrazine under reflux, had m.p. 125° (lit.,[25] 122°). Benzaldehyde benzoylhydrazone and benzaldehyde *NN*-diphenylsemicarbazone, prepared similarly, had m.p. 210° (lit.,[26] 206°) and 177° (lit.,[27] 173—174°), respectively.

N-*Acetyl*-N′-*aroyl*-p-*nitrophenylhydrazines*.—A solution of *N*-(*p*-nitrophenyl)benzohydrazonyl bromide[20] (0·25 g.) and fused sodium acetate (0·3 g.) in glacial acetic acid (15 ml.) was heated under reflux for 4 hr. The cooled solution was poured into water, and the resulting precipitate was recrystallised from 95% ethanol to give *N*-acetyl-*N′*-benzoyl-*p*-nitrophenylhydrazine (0·10 g.), m.p. 186°. After concentration of the filtrates, a further quantity (0·04 g.) of this compound was obtained. Likewise *N*-(*p*-nitrophenyl)-*p*-nitrobenzohydrazonyl bromide gave 89% of *N*-acetyl-*N′*-*p*-nitrobenzoyl-*p*-nitrophenylhydrazine, and *N*-(*p*-nitrophenyl)-*p*-methylbenzohydrazonyl bromide gave 70% of N-*acetyl*-N′-p-*toluoyl*-p-*nitrophenylhydrazine*, m.p. 172° (from ethanol) (Found: C, 61·5; H, 4·9; N, 13·7. $C_{16}H_{15}N_3O_4$ requires C, 61·3; H, 4·8; N, 13·4%). The first two of these compounds have previously been shown to be identical with those obtained by acetylation of the corresponding *N*-aroyl-*N′*-(*p*-nitrophenyl)hydrazines.[4]

Oxidations.—Except where stated, products were worked up as follows: the reaction mixture was poured into water, and the ether extract was washed with water and with appropriate reagents (dilute hydrazine hydrate solution to reduce excess of lead tetra-acetate and sodium hydrogen carbonate solution to remove acids), dried (MgSO$_4$), and concentrated on a rotary evaporator at aspirator pressure. Reactions in the absence of oxygen were conducted in a closed apparatus which, after being charged with the reactants, was alternately evacuated until the solvents boiled and filled with dry nitrogen, these processes being repeated several times.

[25] E. Fischer, *Annalen*, 1878, **190**, 67.

[26] A. Pinner, *Ber.*, 1894, **27**, 984.

[27] W. Ried and H. Hillenbrand, *Annalen*, 1953, **581**, 44.

Reactions in air. Lead tetra-acetate (1·84 g.) in dichloromethane (20 ml.) was added during 20 min. to a well stirred suspension of benzaldehyde *p*-nitrophenylhydrazone (1 g.) in dichloromethane (50 ml.) at room temperature. After a further 15 min. the mixture was worked up and the oily product was crystallised from ethanol to give *N*-acetyl-*N*′-benzoyl-*p*-nitrophenylhydrazine (0·89 g.), m.p. 186°, identical (m.p., mixed m.p., and i.r. spectrum) with the authentic material. When treated similarly, *p*-tolualdehyde *p*-nitrophenylhydrazone, at room temperature, and *p*-nitrobenzaldehyde *p*-nitrophenylhydrazone, at 50°, gave the corresponding *N*-acetyl-*N*′-aroyl-*p*-nitrophenylhydrazines, identical (m.p., mixed m.p., and i.r. spectrum) with the authentic materials, in 56 and 83% yield, respectively. Likewise, *p*-chlorobenzaldehyde *p*-nitrophenylhydrazone, at room temperature, gave 64% of N-*acetyl*-N′-p-*chlorobenzoyl*-p-*nitrophenylhydrazine*, m.p. 162° (from ethanol) (carbonyl absorption at 1720 and 1670 cm.$^{-1}$ and N–H absorption at 3330 cm.$^{-1}$) (Found: C, 54·0; H, 3·6; Cl, 10·6; N, 12·7. $C_{15}H_{12}ClN_3O_4$ requires C, 54·0; H, 3·6; Cl, 10·6; N, 12·6%); cinnamaldehyde *p*-nitrophenylhydrazone, at 0°, gave 61% of N-*acetyl*-N′-*cinnamoyl*-p-*nitrophenylhydrazine*, m.p. 176° (from ethanol) (carbonyl absorption at 1680 and 1660 cm.$^{-1}$, NH absorption at 3320 cm.$^{-1}$, and CH=CH absorption at 1625 cm.$^{-1}$) (Found: C, 62·7; H, 4·7; N, 12·8. $C_{17}H_{15}N_3O_4$ requires C, 62·8; H, 4·6; N, 12·9%); pyridine-2-carbaldehyde phenylhydrazone, at −70°, gave 53% of N-*acetyl*-N′-(2-*picolinoyl*)-*phenylhydrazine*, m.p. 200—202° (from ethanol) (carbonyl absorption at 1680 and 1640 cm.$^{-1}$ and NH absorption at 3300 cm.$^{-1}$) (Found: C, 65·7; H, 5·3; N, 16·6. $C_{14}H_{13}N_3O_2$ requires C, 65·9; H, 5·1; N, 16·5%); and benzaldehyde *NN*-diphenylhydrazone, after 15 min. at −70° followed by a period during which the solution was allowed to warm to room temperature, gave 72% of N′-*acetyl*-N′-*benzoyldiphenylhydrazine*, m.p. 119° (from ethanol) (carbonyl absorption at 1700 and 1680 cm.$^{-1}$ and no N–H absorption) (Found: C, 76·4; H, 5·3; N, 8·6; $C_{21}H_{18}N_2O_2$ requires C, 76·3; H, 5·5; N, 8·5%).

Lead tetra-acetate (1·96 g.) in dichloromethane (20 ml.) was added to a stirred solution of benzaldehyde benzoylhydrazone (1 g.) in dichloromethane (50 ml.) at room temperature. After 10 min. the mixture was worked up and the residue was recrystallised from ethanol to give 2,5-diphenyl-1,3,4-oxadiazole (87%), m.p. 141° (lit.,[28] 139—140°); only an aromatic singlet, δ 7·35, in the ^1H n.m.r. spectrum (Found: C, 75·7; H, 4·6; N, 12·5. Calc. for $C_{14}H_{10}N_2O$: C, 75·7; H, 4·5; N, 12·6%). Likewise, benzaldehyde *NN*-diphenylsemicarbazone gave 2-*diphenylamino*-5-*phenyl*-1,3,4-*oxadiazole* (76%), m.p. 156° (from ethanol) (Found: C, 76·5; H, 4·9; N, 13·2. $C_{20}H_{15}N_3O$ requires C, 76·7; H, 4·8; N, 13·4%).

Lead tetra-acetate (1·84 g.) in dichloromethane (20 ml.) was added to a well stirred suspension of *o*-nitrobenzaldehyde *p*-nitrophenylhydrazone (1 g.) in dichloromethane (150 ml.) at 0°. The mixture was allowed to reach room temperature and was washed with water and dried ($MgSO_4$). The residue after distillation of the solvent was recrystallised from acetone to give 3-p-*nitrophenylazoanthranil* 1-*oxide* (54%), m.p. 159°; $\lambda_{max.}$ 271 and 401 nm., characteristic of azo-compounds[24] (Found: C, 54·5; H, 2·9; N, 19·7. $C_{13}H_8N_4O_4$ requires C, 54·9; H, 2·8; N, 19·7%). When oxidised similarly at −70°, *o*-nitrobenzaldehyde phenylhydrazone gave 3-*phenylazoanthranil* 1-*oxide* (76%), m.p. 149° (decomp.) (from acetone), $\lambda_{max.}$ 266 and 395 nm. (Found: C, 65·2; H, 4·0; N, 17·7. $C_{13}H_9N_3O_2$ requires C, 65·3; H, 3·8; N, 17·6%).

Reactions in absence of air. (a) *Oxidation of benzaldehyde phenylhydrazone.* (i) Lead tetra-acetate(5 g.; 0·5 mol.) in dichloromethane (150 ml.) was added during 40 min. to benzaldehyde phenylhydrazone (4·04 g.; 1 mol.) in dichloromethane (150 ml.). After a further 20 min. the mixture was worked up to give an orange oil which darkened in air. T.l.c. indicated that benzil osazone and the benzylidenebenzohydrazidine (20) were absent and that the major part of the oil was starting material, some of which (0·52 g.) crystallised on the addition of methanol. Owing to the rapid autoxidation of the unchanged phenylhydrazone, no pure product could be isolated.

(ii) Lead tetra-acetate (15 g.; 2 mol.) in a mixture of dichloromethane (200 ml.) and acetic acid (10 ml.) was added during 30 min. to a stirred solution of benzaldehyde phenylhydrazone (3 g.; 1 mol.) in benzene (200 ml.). After a further 10 min. the red solution was worked up to give an oil. T.l.c. showed that, in addition to small quantities of starting material and autoxidation products, four major constituents were present, of which three corresponded in R_F value[1] to benzoylazobenzene, α-acetoxy-α-phenylazobenzyl acetate, and *N*′-benzoylphenylhydrazine. (T.l.c. of a small portion of the mixture removed after the addition of only 1 mol. of oxidant showed the same constituents, there being more starting material and less benzoylazobenzene.) The oil was stirred for 15 min. in methanol (1 l.) containing a few drops of concentrated hydrochloric acid, during which time the red colour faded to yellow, and it was then poured into water (4 l.) and the benzene extracts were dried ($MgSO_4$) and concentrated. T.l.c. showed that benzoylazobenzene was absent, methyl benzoate had been formed, and the other components were unchanged. Chromatography on alumina (150 g., activity IV) gave, with petroleum–benzene (9 : 1, v/v), a pale yellow oil (774 mg.) which, after treatment with potassium hydroxide in aqueous methanol (24 hr.), yielded benzoic acid (590 mg.), equivalent to a yield of benzoylazobenzene of at least 34%. Petroleum–benzene (4 : 1) gave a yellow oil (621 mg.) which, after further chromatography on the same adsorbent (50 g.), yielded α-*phenylazobenzyl acetate* (545 mg., 15·3%), b.p. *ca.* 125°/0·05 mm.; $\lambda_{max.}$ (log ε) (dioxan) 275 (4·13) and 403 (2·32) nm.; $\nu_{max.}$ 1755 cm.$^{-1}$; δ *ca.* 7·5 (10H, m), 7·13 (1H, s), and 2·22 (3H, s), *m*/*e* 254 (*M*), 212 ($M - CH_2{\cdot}CO$), 195 ($M -$ OAc), 149 ($M - PhN_2$), 107 ($M - PhN_2 - CH_2{\cdot}CO$) (base peak), 77 ($Ph^+$), and 43 ($Me\overset{+}{CO}$) (Found: C, 70·2; H, 5·6; N, 11·3. $C_{15}H_{14}N_2O_2$ requires C, 70·85; H, 5·55; N, 11·0%). Petroleum–benzene (1 : 3) gave another yellow oil (250 mg.) which, after rechromatography, yielded α-acetoxy-α-phenylazobenzyl acetate (200 mg., 4·5%), identical (m.p., mixed m.p., t.l.c., and i.r. spectrum) with an authentic sample.[1] Finally, elution with benzene and with ether gave a gum (350 mg.) which crystallised from benzene to yield *N*′-benzoylphenylhydrazine (136 mg., 4·4%), identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample. T.l.c. of the mother liquors from this material indicated the presence of *N*-benzoyl-*NN*′-diphenylhydrazine and *N*′-benzoyl-*NN*-diphenylhydrazine (decomposition products of benzoylazobenzene[14]) and of a more polar compound which corresponded in R_F

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[28] R. Stolle, *J. prakt. Chem.*, **1904**, **70**, **393**.

value to *N*-acetyl-*N′*-benzoylphenylhydrazine. When this experiment was repeated on a larger scale and without the acetic acid, the resulting α-phenylazobenzyl acetate contained considerable quantities of non-volatile material which was not removed by chromatography on alumina. Addition of petroleum precipitated a crude mixture of dimers (8%) which, after several recrystallisations, gave N^2-benzylidene-N^1N^4-diphenylbenzohydrazidine, m.p. 200—202° (from ethanol–chloroform) (lit.,[15] 200·5—201°), $\lambda_{max.}$ ($CHCl_3$) 300 and 337 nm. (lit.,[15] 298 and 335 nm.), $\nu_{max.}$ 3320 cm.$^{-1}$ (NH) (lit.,[15] 3330 cm.$^{-1}$), and *m*/*e* 390 (*M*) and 195 (*M* − PhCH:N·NPh) (Found: C, 80·05; H, 5·8; N, 14·1. Calc. for $C_{26}H_{22}N_4$: C, 80·0; H, 5·7; N, 14·35%). The i.r. and u.v. spectra of this compound were very similar to, but not identical with, those of benzil osazone (*cf.* ref. 15). It was indistinguishable from the latter compound by t.l.c., but the mixed m.p. was 190—207°.

(iii) Benzaldehyde phenylhydrazone (5 g.) in dichloromethane (100 ml.) was added during 10 min. to a stirred solution of lead tetra-acetate (25 g.) and anhydrous sodium acetate (41 g.) in acetic acid (500 ml.). After a further 5 min., the mixture was worked up and the crude product was treated with methanolic hydrogen chloride as in the previous experiment. A similar series of chromatographies led to methyl benzoate (13·5% as benzoic acid), α-phenylazobenzyl acetate (1·61 g., 27%), α-acetoxy-α-phenylazobenzyl acetate (*ca.* 5 mg.), and a polar gum, which was rechromatographed on alumina (200 g.; Laporte). Elution with mixtures of benzene and chloroform gave, successively, mixed decomposition products of benzoylazobenzene (112 mg.) (see above), *N′*-benzoylphenylhydrazine (283 mg., 5·2%), and *N*-acetyl-*N′*-benzoylphenylhydrazine (680 mg., 10·5%), identical (m.p., mixed m.p., t.l.c., and i.r. spectrum) with an authentic sample. Addition of petroleum to the α-phenylazobenzyl acetate produced in this experiment precipitated a pale yellow solid (20 mg.) which, after recrystallisation from chloroform, gave 1,2-diphenyl-1,2-bisphenylazoethane, m.p. 174—176° (lit.,[15] 186—187°), $\lambda_{max.}$ ($CHCl_3$) 275 and 404 nm. (lit.,[15] 277 and 404 nm.), no C=N or NH i.r. absorption, *m*/*e* 390 (*M*), 285 (*M* − PhN_2), 105 (PhN_2^+), and 77 (Ph^+) (base peak) (Found: C, 79·4; H, 5·7; N, 14·2. Calc. for $C_{26}H_{22}N_4$: C, 80·0; H, 5·7; N, 14·35%). A chloroform solution of this material was treated with one drop of dilute methanolic hydrochloric acid; after 2 hr., the u.v. maxima had moved to 300 and 360 nm. (*cf.* ref. 15).

(iv) Benzaldehyde phenylhydrazone (2·06 g.) in dichloromethane (70 ml.) was added during 10 min. to lead tetra-acetate (30 g.) in methanol (800 ml.) at 0°. The mixture, which remained lemon yellow in colour, was stirred at room temperature for 1 hr., and then, after the addition of a further quantity of lead tetra-acetate (10 g.), for another 2 hr. It was poured into water and worked up to give a yellow oil (2·53 g.) which gradually darkened. T.l.c. (multiple elution with petroleum) showed the presence of three yellow compounds, one of which corresponded in R_F value to α-phenylazobenzyl acetate, the presence of which was also indicated by i.r. absorption at 1755 cm.$^{-1}$. A portion of this oil (735 mg.) was chromatographed on alumina (130 g.; activity III). Elution with petroleum gave initially a yellow oil (75 mg.) whose n.m.r. spectrum (in cyclohexane) [aromatic multiplet, singlet (3H) δ 3·22, and singlet (1H) δ 5·17] suggested that its major constituent was α-phenylazobenzyl methyl ether. The presence of substantial quantities of at least two other compounds was shown by the presence of other resonances in the methoxy-region (singlets at δ 3·43 and 3·57). The oil exhibited a typical azo u.v. spectrum [$\lambda_{max.}$ 442w and 317 nm.], and shoulders at 330 and 336 nm suggested that one of the other components might be of the hydrazone type. This oil darkened rapidly and could not be further purified. Further elution of the column with petroleum gave *α-methoxy-α-phenylazobenzyl methyl ether* (474 mg., 60·7%) as a yellow oil, b.p. *ca.* 140°/0·05 mm. (hot box), $\lambda_{max.}$ (dioxan) (log ε) 276 (3·98) and 424 (2·08) nm., $\nu_{max.}$ 1075, 1100, and 2850 cm.$^{-1}$, *m*/*e* 225 (*M* − OMe), 210 (*M* − OMe − Me), 151 (*M* − PhN_2) (base peak), 105 (PhN_2^+/$PhCO^+$), and 77 (Ph^+), δ *ca.* 7·8 (4H, m), *ca.* 7·4 (6H, m), and 3·45 (6H, s) (Found: C, 70·4; H, 6·1; N, 10·9. $C_{15}H_{16}N_2O_2$ requires C, 70·3; H, 6·3; N, 10·9%). Elution with ether gave a colourless gum which was not further investigated.

(v) Benzaldehyde phenylhydrazone (1·49 g.) in acrylonitrile (70 ml.) was added during 50 min. to a stirred suspension of lead tetra-acetate * (10 g.) in acrylonitrile (180 ml.) which was kept below 0°. The resulting thick suspension was stirred at room temperature for 30 min. and then diluted with ether (500 ml.). Lead compounds and polymeric material were filtered at the pump, and the combined filtrates were worked up in the usual way to give a brown solid (1·80 g.) which was chromatographed on alumina (150 g.; Laporte). Elution with petroleum–benzene (9 : 1) gave crude biphenyl (*ca.* 50 mg.) and the same solvents (4 : 1) gave 1,3-diphenylpyrazole-5-carbonitrile (1·185 g., 64%), m.p. 134—135° (from ethanol) (lit.,[17] 133—135°), CN absorption at 2240 cm.$^{-1}$, $\lambda_{max.}$ (log ε) 223 (4·38), 275 (4·01), and 291 (3·91) nm., $\lambda_{min.}$ (log ε) 216 (4·35), 270 (4·00), and 285 (3·97) nm., δ *ca.* 7·6 (10H, m) and 7·26 (1H, s) (Found: C, 78·5; H, 4·5; N, 17·3. Calc. for $C_{16}H_{11}N_3$: C, 78·3; H, 4·5; N, 17·1%). Further elution with petroleum–benzene (1 : 1) gave 1,3-*diphenylpyrazole-4-carbonitrile* (33 mg., 1·8%), m.p. 135—138° (from ethanol), CN absorption at 2235 cm.$^{-1}$, $\lambda_{max.}$ (log ε) 229sh (4·21) and 270 (4·32) nm., $\lambda_{min.}$ 240 nm. (log ε 4·02), δ 8·35 (1H, s) and *ca.* 7·5 (10H, m), *m*/*e* 245·095275 (Calc. for $C_{16}H_{11}N_3$: 245·095294) (Found: C, 78·2; H, 4·7; N, 16·9. $C_{16}H_{11}N_3$ requires C, 78·3; H, 4·5; N, 17·1%).

(vi) Benzaldehyde phenylhydrazone (2·45 g.) in benzene (200 ml.) was added during 1 hr. to lead tetrabenzoate (30 g.) and benzoic acid (50 g.) in benzene (700 ml.). The mixture was stirred for a further 30 min. then filtered, and the filtrate was worked up to give an orange oil, which crystallised upon the addition of ether to give α-benzoyloxy-α-phenylazobenzyl benzoate (1·73 g.), m.p. 183—185°, identical (m.p., mixed m.p., and i.r. spectrum) with authentic material.[1] The mother liquors were treated in methanol with a few drops of concentrated hydrochloric acid (as before) and worked up to give a petroleum-soluble yellow oil, which was chromatographed on alumina (200 g.; activity IV). Elution with petroleum–benzene (9 : 1) gave a pale yellow oil which, after treatment with potassium hydroxide in aqueous methanol, gave benzoic acid (106 mg.), equivalent to a yield of benzoylazobenzene of at least

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* This was the commercial material which had been filtered at the pump, washed with acetic acid, and dried with a filter paper. When the recrystallised and fully dried material was used, with more concentrated solutions at room temperature, a strongly exothermic reaction occurred during the addition and a white, intractable, solid polymer was formed.

7%. Elution with the same solvents (4 : 1) gave a yellow oil (650 mg.) which, upon the addition of petroleum, gave 1,2-diphenyl-1,2-bisphenylazoethane (10 mg.) (as before). The remaining oil crystallised only after a long time in the refrigerator, to give α-*phenylazobenzyl benzoate* (620 mg., 15·7%), m.p. 65—67° [from petroleum (b.p. 40—60°)], $\lambda_{max.}$ (dioxan) (log ε) 275 (4·09) and 405 (2·32) nm., $\nu_{max.}$ 1740 cm.$^{-1}$, *m*/*e* 316 (*M*), 211 (*M* — PhN_2), 105 (PhN_2^+/$PhCO^+$), and 77 (Ph^+) (base peak). In the n.m.r. spectrum, the signal due to the methine proton was hidden by the complex aromatic multiplet (Found: C, 76·1; H, 5·0; N, 9·1. $C_{20}H_{16}N_2O_2$ requires C, 75·9; H, 5·1; N, 8·9%). Elution with petroleum–benzene (2 : 1) gave a further quantity (196 mg.) of the dibenzoate (total yield 1·93 g., 35%), and elution with chloroform gave a colourless gum (600 mg.) which crystallised from benzene to give *NN*′-dibenzoylphenylhydrazine (509 mg., 12·9%), m.p. 178—179°, identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample.

(b) *Oxidation of benzaldehyde* p-*nitrophenylhydrazone*. (i) Benzaldehyde *p*-nitrophenylhydrazone (2·4 g.) in dichloromethane (200 ml.) was added during 1 hr. to lead tetra-acetate (10 g.) in dichloromethane (200 ml.). The usual work-up gave a dark red oily solid, whose i.r. spectrum showed that it was mainly 4-benzoylazonitrobenzene.[1] It was filtered through alumina (125 g., activity IV—V) in petroleum–benzene (1 : 1) and the filtrate was chromatographed on 100 g. of the same adsorbent, but α-acetoxy-α-*p*-nitrophenylazobenzyl acetate was not detected.

(ii) Benzaldehyde *p*-nitrophenylhydrazone (1·26 g.) in dichloromethane (120 ml.) was added during 15 min. to lead tetra-acetate (15 g.) in methanol (700 ml.) at 25°. The mixture darkened towards the end of the addition and, after a further 30 min., the test for lead tetra-acetate was negative. A further quantity (10 g.) of lead tetra-acetate was added and, after 30 min., the mixture, which had become bright yellow, was worked up and the resulting yellow oil was chromatographed on alumina (150 g., activity IV). Elution with petroleum–benzene (4 : 1) gave α-methoxy-α-*p*-nitrophenylazobenzyl methyl ether (750 mg., 47·5%) as orange-red plates, m.p. 99—101° (from petroleum), $\lambda_{max.}$ (dioxan) (log ε) 286 (4·24) and 442 (2·20) nm.; $\nu_{max.}$ 1100 cm.$^{-1}$, *m*/*e* 270 (*M* — OMe), 255 (*M* — OMe — Me), 151 (*M* — p-$O_2N{\cdot}C_6H_4{\cdot}N_2$) (base peak), and 105 ($PhCO^+$), δ 8·27 (A) and 7·83 (B) (4H, A_2B_2q, J_{AB} 9 Hz), *ca.* 7·4 (5H, m), and 3·45 (6H, s) (Found: C, 59·5; H, 5·0; N, 14·2. $C_{15}H_{15}N_3O_4$ requires C, 59·8; H, 5·0; N, 13·95%). Elution with petroleum–benzene (1 : 1) gave α-methoxybenzaldehyde *p*-nitrophenylhydrazone (192 mg., 13·5%), m.p. 169—171° (from acetone–petroleum), $\lambda_{max.}$ (dioxan) (log ε) 225 (4·09), 263sh (3·80), 291 (3·88), 321sh (3·66), and 398 (4·48) nm., $\lambda_{min.}$ (log ε) 271 (3·79) and 330 (3·61) nm., i.r. spectrum extremely similar to that of benzaldehyde *p*-nitrophenylhydrazone (NH absorption at 3340 cm.$^{-1}$, *m*/*e* 271 (*M*) and 239 (*M* — MeOH), δ 8·4br (1H, s, exchangeable), 8·14 (A) and 7·07 (B) (A_2B_2q, 4H, J_{AB} 9·5 Hz), *ca.* 7·5 (5H, m), and 3·83 (3H, s) (Found: C, 62·3; H, 4·8; N, 15·3. $C_{14}H_{13}N_3O_3$ requires C, 62·0; H, 4·8; N, 15·5%). Careful examination of the remaining eluates by preparative t.l.c. showed no trace of any materials exhibiting an azo-type u.v. spectrum.

(iii) Lead tetra-acetate (5·2 g.) in dichloromethane (120 ml.) was added during 20 min. to benzaldehyde *p*-nitrophenylhydrazone (1·32 g.) in acrylonitrile (100 ml.). Stirring was continued for a further 30 min., and then for 15 min. more after the addition of a further 1 g. of lead tetra-acetate. The mixture was worked up in the usual way and the product was chromatographed on alumina (300 g.; Laporte). Elution with petroleum–benzene (9 : 1) gave *p*-nitrobiphenyl (180 mg.), and the same solvents (1 : 1) gave 1-p-*nitrophenyl*-3-*phenylpyrazole*-5-*carbonitrile* (175 mg., 11%), m.p. 165—167° (from petroleum–benzene), CN absorption at 2230 cm.$^{-1}$, $\lambda_{max.}$ (log ε) 227·5 (4·34), 237 (4·34), 285sh (3·75), and 323 (4·25) nm., $\lambda_{min.}$ (log ε) 217 (4·29), 232 (4·33), and 279 (3·74) nm., δ 8·42 (A) and 8·06 (B) (A_2B_2q, 4H, J_{AB} 9 Hz), and 7·38 (s) superimposed on a multiplet (total 6H) (Found: C 66·2; H, 3·8; N, 19·4. $C_{16}H_{10}N_4O_2$ requires C, 66·2; H, 3·5; N, 19·3%). Elution with benzene gave an orange oil (590 mg.) which slowly deposited 1-p-*nitrophenyl*-3-*phenylpyrazoline*-5-*carbonitrile* (255 mg.), m.p. 206—208° (from acetone–petroleum), $\lambda_{max.}$ (log ε) 225 (4·23), 263sh (3·80), 308 (3·82), and 385 (4·46) nm., $\lambda_{min.}$ (log ε) 278·5 (3·59) and 329 (3·74) nm., δ [$(CD_3)_2SO$] 8·28 (A) and 7·42 (B) (4H, A_2B_2q, J_{AB} 9 Hz), *ca.* 7·7 (5H, m), and a second-order multiplet (3H) (analysed as AB_2 system, very similar to that in 2,6-lutidine [29]) δ 5·88 (A) and 3·95 (B) (J_{AB} 7 Hz) (Found: C, 65·9; H, 4·0; N, 19·0. $C_{16}H_{12}N_4O_2$ requires C, 65·75; H, 4·1; N, 19·2%). Chromatography of the mother liquors gave a further 48 mg. of this pyrazoline, together with benzil *p*-nitrophenylosazone (20 mg.) and a mixture (242 mg.) of these two and an unidentified yellow compound.

Lead tetra-acetate (300 mg.) was added to a solution of the above pyrazoline (110 mg.) in *damp* dichloromethane (80 ml.). The resulting brown suspension was kept overnight and worked up in the usual way, and the crude product was chromatographed on alumina (40 g.; Laporte). Elution with petroleum–benzene (3 : 1) gave 1-*p*-nitrophenyl-3-phenylpyrazole-5-carbonitrile (105 mg., 96%), identical (m.p., mixed m.p., and i.r. spectrum) with that already described. When the pyrazoline was treated with lead tetra-acetate in a mixture of dichloromethane and acetic acid it was recovered largely unchanged, even after 60 hr.

(iv) Benzaldehyde *p*-nitrophenylhydrazone (311 mg.) in acrylonitrile (40 ml.) was added during 45 min. to a stirred suspension of lead tetra-acetate (1·7 g.) in acrylonitrile (20 ml.). After a further 4 hr., the mixture was diluted with ether (200 ml.) and the filtrate was worked up in the usual way. A solution of the crude product in *damp* dichloromethane (15 ml.) was kept overnight with lead tetra-acetate (260 mg.). The resulting material was chromatographed on alumina (60 g.; Laporte), to give 1-*p*-nitrophenyl-3-phenylpyrazole-5-carbonitrile (225 mg., 60%).

(v) Lead tetrabenzoate (15 g.) in dichloromethane (200 ml.) containing benzoic acid (5 g.) was added during 1·5 hr. to a suspension of benzaldehyde *p*-nitrophenylhydrazone (3·92 g.) in dichloromethane (200 ml.). The hydrazone dissolved, and, after a further 20 min., the mixture was shaken with sodium hydrogen carbonate solution and the filtrate was worked up to give a red oil. Addition of ether precipitated *NN*′-dibenzoyl-*p*-nitrophenylhydrazine (2·3 g.), m.p. 167—169°, identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample. Extraction of the mother liquors with aqueous sodium hydroxide gave, after acidification, a further 260 mg. of this material (total 2·56

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[29] See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1965, vol. 1, p. 328.

g., 43·5%). The remaining material was diluted with benzene and filtered through alumina (150 g.; activity IV), and the filtrate was chromatographed on 110 g. of the same adsorbent. Elution with petroleum–benzene (4 : 1) gave, besides some *p*-nitrobiphenyl, α-benzoyloxy-α-*p*-nitrophenylazobenzyl benzoate (938 mg., 12%), m.p. 162—164° (from ether), identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample.[1] Elution with benzene gave small quantities (*ca.* 50 mg.) of benzil *p*-nitrophenylosazone and an unidentified yellow solid [$\lambda_{\text{max.}}$ 385 nm., $\nu_{\text{max.}}$ 3265 cm.$^{-1}$ (NH)].

(c) *Oxidation of propionaldehyde* p-*nitrophenylhydrazone*. (i) Lead tetra-acetate (2·3 g.) in dichloromethane (50 ml.) and acetic acid (5 ml.) was added during 30 min. to propionaldehyde *p*-nitrophenylhydrazone (1·05 g.) in dichloromethane (40 ml.). After a further 15 min., the mixture was poured into water and the organic layer was washed with water and with aqueous sodium hydrogen carbonate, and extracted with sodium hydroxide solution. The acidified alkaline extract was extracted continuously with ether for 16 hr. Concentration of the dried ($MgSO_4$) ether solution gave N-*acetyl*-N′-*propionyl*-p-*nitrophenylhydrazine* (1·015 g., 74%), m.p. 121—123° (from water containing a trace of acetic acid), $\nu_{\text{max.}}$ 1690 cm.$^{-1}$, δ 8·62br, (1H, s), 8·15 (A) and 7·55 (B) (4H, A_2B_2q, J_{AB} 9 Hz), 2·32 (2H, q, *J* 7·5 Hz), 2·17 (3H, s), and 1·18 (3H, t, *J* 7·5 Hz) (Found: C, 52·75; H, 5·0; N, 16·5. $C_{11}H_{13}N_3O_4$ requires C, 52·6; H, 5·2; N, 16·7%).

(ii) Propionaldehyde *p*-nitrophenylhydrazone (0·5 g.) in acrylonitrile (40 ml.) was added during 30 min. to lead tetra-acetate (3 g.) in acrylonitrile (160 ml.) at 0°. The mixture was stirred for 1 hr. at room temperature and worked up as described for benzaldehyde phenylhydrazone, and the crude product was treated overnight with lead tetra-acetate in *damp* dichloromethane. The resulting orange gum was chromatographed on alumina (50 g.; Laporte) to give, with light petroleum–benzene (1 : 1), a low-melting pink solid (200 mg.). This was rechromatographed on Woelm alumina (30 g.; activity II) to give, with petroleum–benzene (9 : 1), *p*-nitrobiphenyl (18 mg.) and then 1-p-*nitrophenyl*-3-*ethylpyrazole*-5-*carbonitrile* (164 mg., 26%), m.p. 69—70° (from petroleum); CN absorption at 2235 cm.$^{-1}$, $\lambda_{\text{max.}}$ (log ε) 226 (4·13), 247sh (3·65), and 303 (4·17) nm., $\lambda_{\text{min.}}$ 258 nm. (log ε 3·59), δ 8·38 (A) and 8·03 (B) (A_2B_2q, 4H, J_{AB} 9 Hz), 6·98 (1H, s), 2·80 (2H, q, *J* 7·5 Hz), and 1·33 (3H, t, *J* 7·5 Hz) (Found: C, 59·0; H, 3·75; N, 23·45. $C_{11}H_{10}N_4O_2$ requires C, 59·5; H, 4·2; N, 23·1%). In a similar experiment where more concentrated solutions were used and in which there was no cooling, the reaction mixture became warm, resulting in increased polymerisation and in a substantial reduction in the yield of the pyrazole.

(d) *Oxidation of benzoin and benzil* p-*nitrophenylhydrazones*. Benzoin *p*-nitrophenylhydrazone (460 mg.) in acrylonitrile (35 ml.) was added to lead tetra-acetate (1·8 g.) in acrylonitrile (25 ml.). The reaction was conducted and worked up as described for benzaldehyde *p*-nitrophenylhydrazone, giving 1-*p*-nitrophenyl-3-phenylpyrazole-5-carbonitrile (220 mg., 57·3%), identical (m.p., mixed m.p., and i.r. spectrum) with that described previously.

Oxidation of benzil mono-*p*-nitrophenylhydrazone (216 mg.) in a similar way gave the same pyrazole (40 mg., 22%).

(e) *Oxidation of* N-*acetyl*-N′-*benzoylphenylhydrazine*. Lead tetra-acetate (32 g.) was added to *N*-acetyl-*N*′-benzoylphenylhydrazine (1·60 g.) in a mixture of benzene (80 ml.), dichloromethane (80 ml.), and acetic acid (5 ml.). After 10 min. the mixture was poured into water, and the product, after work-up, was treated with hydrochloric acid in methanol, as in the oxidation of benzaldehyde phenylhydrazone. The resulting gum was chromatographed on alumina (150 g.; activity IV—V) to give, with petroleum–benzene (1 : 1), a pale yellow material (53 mg.). Recrystallisation from ether–petroleum gave α-acetoxy-α-phenylazobenzyl acetate (43 mg., 2·2%).

Stability of α-*Acetoxy*-α-*phenylazobenzyl Acetate to Sodium Acetate in Acetic Acid*.—A solution of α-acetoxy-α-phenylazobenzyl acetate (230 mg.) in acetic acid (50 ml.) containing anhydrous sodium acetate (4·1 g.) was set aside for 5 hr., and then partitioned between petroleum and water. The petroleum layer was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and concentrated to give crystalline starting material (226 mg.).

Reactions of α-*Phenylazobenzyl Acetate*.—(i) A solution of α-phenylazobenzyl acetate (4×10^{-3}M) in dioxan containing acetic acid (*ca.* 5%) was kept in the dark at 25° for several days. During this time, the absorption in the range 350—450 nm. did not change detectably.

(ii) Solutions of α-phenylazobenzyl acetate (4×10^{-3}M and 8×10^{-3}M) in acetic acid were kept at 66·5°. Samples were withdrawn at measured intervals, cooled, and examined by u.v. spectrophotometry. The experiment was repeated in the presence of (*a*) M-sodium acetate and (*b*) 0·0015M-sulphuric acid.

(iii) A solution of α-phenylazobenzyl acetate (141 mg.) in acetic acid (20 ml.) was kept at 25° in the dark for 11 days. It was poured into water and the ether extracts were washed with water and with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated to give a gum whose i.r. spectrum showed new carbonyl absorptions at 1670 and 1700 cm.$^{-1}$. (A small sample was removed from the reaction after 3 days and worked up in the same way. The intensities of the new carbonyl absorptions in the resulting material were about equal to that of the unchanged azo-acetate at 1755 cm.$^{-1}$). The gum was chromatographed on alumina (10 g.; Laporte). Elution with benzene gave unchanged α-phenylazobenzyl acetate (31 mg.) and, with benzene–chloroform (2 : 1), a colourless gum (89 mg.) which crystallised from a mixture of benzene, ether, and petroleum to give *N*-acetyl-*N*′-benzoylphenylhydrazine (55 mg.), identical (m.p., mixed m.p., and i.r. spectrum) with authentic material.[1]

(iv) A sample of α-phenylazobenzyl acetate (1·75 g.), from which polar materials had been chromatographically removed, was filtered through alumina (150 g.; activity IV). Unchanged material (1·61 g.) was eluted with petroleum–benzene (4 : 1); elution with benzene–ether (1 : 1) gave a white solid (121 mg.) which, after recrystallisation from benzene, gave *N*′-benzoylphenylhydrazine (95 mg.). T.l.c. of the mother liquors from this material indicated that *N*-acetyl-*N*′-benzoylphenylhydrazine was also present.

(v) A solution of α-phenylazobenzyl acetate (260 mg.) in dichloromethane (25 ml.) was treated with lead tetra-acetate (500 mg.). After 1 hr., the mixture was worked up to give an orange oil (262 mg.), the i.r. spectrum of which was identical in every way with that of the starting material.

A standardised solution (92 ml.) of lead tetra-acetate in acetic acid (*ca.* 0·024M) was added to α-phenylazobenzyl acetate (285 mg.). Portions (5 ml.) were removed at measured intervals and poured into aqueous potassium iodide, and the liberated iodine was titrated against 0·1N-sodium thiosulphate. The amounts (mol.) of oxidant consumed per mol. of azo-acetate after given times (in parentheses) were: 0·11 (1 min.), 0·12 (10 min.), 0·16 (1 hr.), 0·22 (3 hr.), 0·28 (6 hr.), and 0·42 (22 hr.).

Transformations of Pyrazolecarbonitriles.—(i) Following the procedure of Huisgen and his co-workers,[17] 1,3-diphenylpyrazole-5-carbonitrile (277 mg.) was heated under reflux for 2 hr. in a mixture (80 ml.) of equal volumes of acetic acid, water, and sulphuric acid, to give 1,3-diphenylpyrazole-5-carboxylic acid (250 mg.), m.p. 216—220° (decomp.) (from benzene–acetone) [lit.,[17] 225—227° (decomp.)]. This acid (114 mg.) was heated at 240° (oil bath) for 1 hr. and the product was filtered through alumina to give 1,3-diphenylpyrazole (88 mg., 93%), m.p. 83—85° (from petroleum) (lit.,[30] 84—85°), $\lambda_{max.}$ 278, 284sh, and 292sh nm. (Found: C, 82·0; H, 5·45; N, 13·0. Calc. for $C_{15}H_{12}N_2$: C, 81·8; H, 5·5; N, 12·7%).

(ii) 1,3-Diphenylpyrazole-4-carbonitrile (24 mg.) was treated like its isomer for 45 min. The ether extract of the diluted mixture was washed with water and extracted with aqueous sodium hydrogen carbonate. Acidification of this extract gave a crude white solid acid (16 mg.) which was not characterised. When this acid was heated at 240° as described for the 5-acid, much charring occurred and 1,3-diphenylpyrazole could only be isolated in minute amounts. A solution of the acid (9 mg.) in *NN*-dimethylaniline (0·2 ml.) was slowly heated to 200° with copper-bronze (5 mg.) and then allowed to reflux gently for 10 min. A solution of the crude product in ether (200 ml.) was washed successively with 0·1M-hydrochloric acid (2 × 50 ml.), water, and aqueous sodium hydrogen carbonate. Removal of the solvent from the dried ($MgSO_4$) solution left a residue (16 mg.) which was chromatographed on alumina (2 g.; activity III). Elution with petroleum gave 1,3-diphenylpyrazole (4·6 mg., 61%), m.p. 83—85° (from petroleum at −15°), identical (m.p., mixed m.p., t.l.c., and i.r. and u.v. spectra) with the product obtained in (i).

(iii) 1-*p*-Nitrophenyl-3-phenylpyrazole-5-carbonitrile (90 mg.) was treated as for the carbonitrile in (i). The ether extract of the diluted mixture was washed with water and extracted with aqueous sodium hydrogen carbonate. Acidification yielded 1-p-*nitrophenyl*-3-*phenylpyrazole*-5-*carboxylic acid* (71 mg., 75·5%), m.p. 246—248° (decomp.) (from acetone–benzene), $\lambda_{max.}$ (log ε) 228·5sh (4·37), 242sh (4·35), 284sh (3·85), and 322 (4·15) nm., $\lambda_{min.}$ 281 nm. (log ε 3·84) (Found: C, 62·3; H, 3·4; N, 13·7. $C_{16}H_{11}N_3O_4$ requires C, 62·1; H, 3·6; N, 13·6%). When the time of reflux was reduced to 45 min. the yield of this acid was was increased to 97%.

This acid (186 mg.) was heated at 250° (oil bath) for 1·5 hr. The resulting dark brown product was chromatographed on alumina (20 g.; activity I), to give, with benzene–ether (3 : 1), 1-*p*-nitrophenyl-3-phenylpyrazole (123 mg., 77%), m.p. 169—171° (from ethanol) (lit.,[31] 169—169·5°), $\lambda_{max.}$ (log ε) 228 (4·12), 250 (4·07), and 337 (4·38) nm., $\lambda_{min.}$ (log ε) 222 (4·11), 242 (4·06), and 281 (3·66) nm., δ (dioxan) 8·35 (A) and 7·98 (B) (4H, A_2B_2q, J_{AB} 9·5 Hz), *ca.* 7·7 (5H, m), and 7·35 (A) and 6·89 (B) (ABq, 2H, J_{AB} 2·5 Hz) (Found: C, 68·1; H, 4·2; N, 15·7. Calc. for $C_{15}H_{11}N_3O_2$: C, 67·9; H, 4·2; N, 15·8%).

(iv) 3-Ethyl-1-*p*-nitrophenylpyrazole-5-carbonitrile (139 mg.) was treated as for the carbonitrile in (i) for 1 hr. The ether extract of the diluted mixture was washed with water and extracted with aqueous sodium hydrogen carbonate. Acidification of this extract gave the crude carboxylic acid (142 mg.), which was heated at 200° (oil bath) for 30 min. The resulting brown solid was chromatographed on alumina (20 g.; Laporte) to give, with petroleum–benzene (3 : 1), 3-ethyl-1-*p*-nitrophenylpyrazole (106 mg., 85%), m.p. 120—121° (from ethanol) (lit.,[32] 121°), $\lambda_{max.}$ (log ε) 223 (3·95) and 323 (4·25) nm. [lit.,[32] 224 (3·89) and 323 (4·23 nm.)], δ 8·29 (A) and 7·82 (B) (4H, A_2B_2q, J_{AB} 9 Hz), 7·93 (A) and 6·37 (B) (ABq, 2H, J_{AB} 2·5 Hz), 2·75 (2H, q, J 7·5 Hz), and 1·30 (3H, t, J 7·5 Hz) (Found: C, 61·2; H, 5·35; N, 19·5. $C_{11}H_{11}N_3O_2$ requires C, 60·8; H, 5·1; N, 19·3%).

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