Reactions of Lead Tetra-acetate. Part XVII.¹ Preparation and Properties of Azoacylals

By W. A. F. Gladstone,[†] Department of Chemistry, The University of Lancaster, Bailrigg, Lancaster

Lead tetra-acetate oxidation of N-benzoyl-NN'-diphenylhydrazine gives a mixture of cis- and trans-azobenzene. Similar oxidation of NN'-dibenzoylphenylhydrazine gives, according to the conditions, either benzoylazobenzene, or a-phenylazobenzylidene acetate benzoate, an example of the previously unknown azoacylals. A number of these compounds have been prepared, and their properties have been investigated. Mechanisms are proposed to account for these reactions.

THE oxidation of hydrazine derivatives by lead tetraacetate has been extensively studied. Substituted ketone hydrazones are converted into a-acetoxy-azocompounds, named ² ' azoacetates,' which may undergo further reactions to give a variety of products. Azines, and hydrazines derived from aldehydes, have also been oxidized; these reactions have been recently reviewed.³ Compounds containing the N·NH₂ grouping give rise to products which can be formally derived from the nitrene $N\cdot N;^4$ and NN'-disubstituted hydrazines are oxidized in very high yield to the corresponding azo-compounds.⁵⁻⁷ This last reaction has been used to prepare Diels-Alder adducts of unstable azo-compounds, the oxidation being carried out at low temperature in the presence of a suitable diene.⁷ In continuation of studies on the reactions of lead tetra-acetate with nitrogen-containing compounds, we report the oxidation of certain trisubstituted hydrazines, which might in principle give rise to azo-compounds while losing a suitable cationic grouping. Thus, oxidation of N-benzoyl-NN'-diphenylhydrazine (I) gave azobenzene (II) in almost quantitative yield. When the reaction was carried out in dichloromethane-acetic acid, the product was essentially trans,

but a reaction in dry benzene with lead tetra-acetate free from acetic acid gave over $20\%{0}$ of the cis-isomer, even though no precautions were taken to prevent equilibration of the two forms during isolation. This is consistent with reaction via pathways (a) and (b) (Scheme 1), the latter being significant only in the



absence of an external nucleophile. The type of intra-

molecular acetate transfer implicated in path (b) has recently been cited to explain other reactions of lead

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Present address: Department of Chemistry, Queen Mary College, Mile End Road, London E.1.

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tetra-acetate.^{8,9} Besides small quantities of two unidentified red solids, there was also obtained about 1%of o-acetoxyazobenzene (III) which was isolated, after hydrolysis, as the corresponding phenol. Since azobenzene is inert to lead tetra-acetate under the reaction conditions, the o-acetoxy-derivative presumably arises from the original hydrazine by a mechanism similar to that which occurs in the ortho-acetoxylation of phenols by lead tetra-acetate.¹⁰ The resulting N'-o-acetoxyphenyl-N-benzoyl-N-phenylhydrazine is then further oxidized to the corresponding azobenzene as in Scheme 1.

When NN'-diacylarylhydrazines were treated with lead tetra-acetate, however, a second reaction occurred. Oxidation of NN'-dibenzoylphenylhydrazine (IV) in dichloromethane-acetic acid gave a-phenylazobenzylidene acetate benzoate (XIII) (>40%), an example of the previously unknown azoacylals.* Microanalysis and molecular weight determination established the formula $C_{22}H_{18}N_2O_4$, consistent with the replacement of a hydrogen atom in the substrate by an acetate group. The ¹H n.m.r spectrum showed an acetate methyl (8 2.27, s) and fifteen aromatic protons, and the i.r. spectrum showed no NH absorption, but two strong bands in the carbonyl region, at 1730 and 1775 cm.⁻¹. The u.v. spectrum, which was similar to those of 'azoacetates,' as described by Iffiland,² ruled out the alternative structure AcO·NBz·NBzPh, which might have been formed by direct acetoxylation. Further evidence was provided by the mass spectrum:† although no parent ion was obtained, a major fragment had the composition

 $C_{16}H_{13}O_4$ consistent with the AcO·CPh·OBz ion resulting from loss of the phenylazo-group. Final support for the structure (XIII) was obtained through the preparaction of other compounds in this series.

Besides the azoacylal the reaction also yielded benzoic acid (59%) [‡] and a dark red oil which evolved nitrogen when chromatography on alumina was attempted. The latter evidently contained benzoylazobenzene (the product formed analogously to azobenzene), which is known to decompose on alumina, or in the presence of acid or base.⁵ Benzoic acid arises from the benzoyl moiety formed concomitantly with the benzoylazobenzene, and also through decomposition of the benzoylazobenzene, either in the reaction mixture or during the work-up.

Mechanistic considerations suggested that, by analogy with the formation of *cis*-azobenzene, the pathway leading to the azoacylal (XIII) might be favoured in an aprotic medium; this proved to be so. When the oxidation was carried out in dry benzene, the yield of

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(XIII) increased to 64%, while only 36% of benzoic acid was isolated. On the other hand, oxidation in acetic acid gave 97% of benzoic acid and only 8.5% of the azoacylal. Attempts to improve the yield still further were unsuccessful. The presence of calcium carbonate in the reaction mixture had no significant effect, and the reaction failed in petroleum, owing to the insolubility of both reactants. Attempts to prepare compounds of the type PhN:N·CPh(OR)·OBz by carrying out the oxidation in the presence of alcohols, as we have done for ketone arylhydrazones,8 were also unsuccessful, and resulted only in greatly decreased yields of (XIII). Oxidation in benzene-dichloromethane containing n-propanol (5%)gave only 39.5% of the azoacylal, and a reaction in absolute ethanol proceeded with evolution of nitrogen and led only to ethyl benzoate (116%).

The reaction proved to be generally applicable to NN'-diacylarylhydrazines, and lead tetrabenzoate could also be used as the oxidant. The azoacylals listed in Scheme 2 were prepared by the addition of the solid tetravalent lead salt to a stirred solution of the hydrazine in dry benzene at 25°. When the hydrazine was only sparingly soluble at this temperature, it was dissolved in boiling benzene, and the solution was cooled and stirred to produce a finely divided slurry. Hydrazines totally insoluble in benzene were dissolved in dichloromethane, and the resulting solution was then added to the oxidant in benzene.

Unlike the original example, most of the azoacylals could not be isolated directly by crystallisation, and had to be separated from the accompanying acylazobenzene by other means. Although chromatography on alumina (type H) resulted in complete decomposition of both products, azoacylals could be recovered unchanged from neutral alumina (Woelm) of activity III or less: this material, however, rapidly decomposed the acylazobenzenes. Since prolonged contact of an azoacylal with even this adsorbent was undesirable, a solution of the crude product in benzene was filtered through a short column of adsorbent, so that the azoacylal was rapidly eluted, together with small quantities of biphenyls, benzenes, and azobenzenes. The substituted hydrazines resulting from decomposition of the acylazobenzene,§ however, remained on the column. A second and more careful chromatography of the eluted material then removed the last impurities. Azoacylals could also be purified, although less efficiently, by chromatography on silica gel.

^{*} Iffland ² has reported the isolation, from the lead tetraacetate oxidation of benzaldehyde phenylhydrazone, of a red oil tentatively identified as α -phenylazobenzylidene diacetate. Its properties, however, are quite different to those of that compound as described here.

[†] The mass spectra of these compounds will be the subject of a future publication.

[‡] All yields of benzoic acid and alkyl benzoates are based on the loss, from the hydrazine of one benzoyl group. A second molecule may be formed through decomposition of the resulting acylazobenzene.

[§] The major products of the catalytic decomposition of benzoylazobenzene in the presence of benzene have been shown to be N-benzoyl-NN'-diphenylhydrazine, N'-benzoyl-NN-diphenylhydrazine, biphenyl, and azobenzene.⁵ In our case, 4-benzoylazonitrobenzene led similarly to p-nitrobiphenyl, nitrobenzene, and traces of p-nitroazobenzene, besides hydrazine-type products which were not investigated.

⁸ M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone, J. Chem. Soc. (C), 1967, 735. ⁹ J. A. Marshall and G. L. Bundy, Chem. Comm., 1966, 500;

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¹⁰ E. Hecker and R. Lattrell, Annalen, 1963, 662, 48; see also

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Application of the above methods led to the azoacylals (XIII)-(XXV) mostly in yields of 50-70% (see Table 1). Oxidations involving the hydrazines (VI), (VIII), and (XII), however, in which the nitrogen bearing the aryl group is substituted by an acetyl group, gave only very low yields of azoacylals (1.5-9%), and from one experiment 58% of 4-benzoylazonitrobenzene isolated. Since α -p-nitrophenylazobenzylidene was acetate benzoate (XVIII), which was isolated in only 1.5% yield from the lead tetrabenzoate oxidation of N-acetyl-N'-benzoyl-p-nitrophenylhydrazine, could be obtained in 80% yield from the corresponding NN'dibenzoyl-p-nitrophenylhydrazine, the fact that these vields are low is not due to instability of the products, but must be connected with the mechanism of the reaction.

A mechanism accounting for the formation of azoacylals is depicted in Scheme 3. Electrophilic attack of lead tetra-acetate on the hydrazine and subsequent loss of acetic acid leads to an intermediate, which may be regarded either as a covalent structure existing in two conformations (c) and (d), or as a mixture of ion pairs (c') and (d'), in which the two acyl groups lie *cis* and *trans* to one another respectively. Intramolecular acetate transfer leads in case (c) to the azoacylal and in case (d) to the acylazobenzene, whereas external nucleophilic attack on the acyl group \mathbb{R}^1 leads in both cases to the acylazobenzene,* thus accounting for the lower yields of azoacylals in nucleophilic solvents. The idea

* No distinction has been made between the *cis*- and *trans*forms of the acylazobenzene, since equilibration of these *via* the dipolar structure (e) (Scheme 3), or its conjugate acid, might be expected to be relatively rapid.



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that the peculiar effect of the N-1 acetyl groupdiverting the reaction into the path (d)-might be electronic in origin, *i.e.* in some way connected with the instability of MeCO⁺ relative to ArCO⁺, can be rejected; lead tetra-acetate oxidation of the N'-benzoyl-p-nitrophenylhydrazines (IX), (VII), and (X), substituted on N-1 by p-nitrobenzoyl, benzoyl, and p-anisoyl respectively, gives yields of azoacylals (66, 80, and 36%, respectively) which imply that the susceptibility of the R¹CO carbonyl group to nucleophilic attack must be a factor in determining the relative yields of the two products. The obvious failure of the N-1 acetyl

(XII), steric effects are less important and a slightly higher yield of the azo-diacetate (XXV) results.

Properties of Azoacylals.—The physical properties of azoacylals are summarised in Table 1. Most of those prepared are stable yellow crystalline solids, very soluble in chloroform and in benzene, but insoluble in petroleum and in methanol. Although the phenylazo-derivatives crystallise readily from methanol or from mixtures of petroleum with benzene or ether, the p-nitrophenylazoanalogues are much less accommodating, and even when pure crystallise only with great difficulty (see Experimental section). The compounds (XV), (XXIII), and

TABLE 1

Properties of azoacylals

| | Viold | | ν _n | ax. | | | Chemical shifts ⁹ | Foi | ınd (| %) | | Re | eqd. (° | %) |
|---------|-----------|--------------------------------------|---|---|-----------------------------|----------------------|-------------------------------------|--------------|---------------------|-------------|---|--------------|---------------------|-------------|
| | (%) | M.p. ^b | MeCO. | ArCO. e | λmax [nm | $(\log \varepsilon)$ | group (δ) | C | H | N | Formula | C | | N |
| (XIII) | 66 | 126—127° | 1775 | 1730 | 276 (4.13) 281sh (4.12) | 401 (2.50) | $2 \cdot 27 h$ (3H) | 70.8 | $5 \cdot 2$ | 7.5 | $C_{22}H_{18}N_2O_4$ | 70.6 | 4.85 | 7.5 |
| (XIV) | 61 | 185 | | $\begin{array}{c} 1740 \\ 1755 \end{array}$ | 276 (4.16) 281sh (4.15) | 401 (2.52) | | 74.1 | 4.4 | $6 \cdot 3$ | $\mathrm{C_{27}H_{20}N_2O_4}$ | 74.3 | 4·6 | $6{\cdot}4$ |
| (XV) | 57 | B.p. ca. 150°/0·05 mm | 1770 | 1740 đ | 274 | 403 | 2·15 (3H) 2·22 (3H) | 65.6 | $5 \cdot 1$ | 8.6 | $C_{17}H_{16}N_2O_4$ | 65 ∙4 | $5 \cdot 2$ | 9.0 |
| (XVI) | 70 | 82-84 | | $\frac{1735}{1750}$ | 275 (4.13) 282sh (4.09) | $403 \ (2 \cdot 35)$ | $2{\cdot}32{}^i(3\mathrm{H})$ | 70.65 | $4 \cdot 5$ | 7.7 | $\mathrm{C}_{22}\mathrm{H}_{18}\mathrm{N}_{2}\mathrm{O}_{4}$ | 70.6 | 4.85 | $7 \cdot 5$ |
| (XVII) | 3 | 99100 | 1765 | 2100 | 280 (4.13) | 401 (2.48) | 2.25~(6H) | 64.3 | $5 \cdot 2$ | 9·1 | $C_{17}H_{16}N_2O_4$ | 65.4 | $5 \cdot 2$ | 9.0 |
| (XVIII) | 80 a | 97—99 | 1775 | 1745 | 279sh (4·31) 283 (4·31) | 410 (2.68) | $2{\cdot}28{}^j(3\mathrm{H})$ | $62 \cdot 6$ | 4 ∙0 | 10.0 | $C_{22}H_{17}N_3O_6$ | 63·0 | 4.1 | 10.0 |
| (XIX) | 54 | 163 | | $\begin{array}{c} 1735\\ 1750 \end{array}$ | 278 (4.29) 283 (4.29) | 410 (2·70) | | 67.3 | $3 \cdot 8$ | 8.8 | ${\rm C_{27}H_{19}N_{3}O_{6}}$ | 67.4 | 4 ∙0 | 8.7 |
| (XX) | 5 | 133 - 134 | 1770 | | 283(4.23) | 409(2.67) | 2.28 (6H) | 57.25 | $4 \cdot 5$ | 12.1 | C ₁₇ H ₁₅ N ₂ O ₆ | 57.1 | $4 \cdot 2$ | 11.8 |
| (XXI) | 66 | 135137 | $\begin{array}{c} 1760 \\ 1780 \end{array}$ | $\begin{array}{c}1740\\1750\end{array}$ | 270 (4·40) | 405 (2·66) | 2-31 (3H) | 57.6 | 3.6 | 12.45 | $C_{22}H_{16}N_4O_8$ | 56.9 | 3.5 | 12.1 |
| (XXII) | 36.5 | 137—139 | 1780 | 1730 | 267 (4·46) 273sh (4·45) | 410 (2.68) | 2·29 (3H) 3·87 ^k (3H) | 61.3 | $4 \cdot 2$ | 9·1 | $\mathrm{C}_{23}\mathrm{H}_{19}\mathrm{N}_{3}\mathrm{O}_{7}$ | 61.5 | $4 \cdot 3$ | 9.35 |
| (XXIII) | 72 | B.p. <i>ca</i> . 170°/0·05 mm. | 1765 | 1740 ° | 277 282sh | 410 | $2 \cdot 21^{l}$ (6H) | 56.6 | 4.4 | 12.0 | $C_{17}H_{15}N_3O_6$ | 57.1 | $4 \cdot 2$ | 11.8 |
| (XXIV) | 62 | 100-102 | | 1745 | 277 (4.30) 281 sh (4.29) | 410 (2·58) | $2 \cdot 33 i (3H)$ | $63 \cdot 4$ | 4 · 4 | 10.15 | ${\rm C_{22}H_{17}N_{3}O_{6}}$ | 63∙ 0 | 4·1 | 10.0 |
| (XXV) | 9 | B.p. ca. 120°/0·05 mm, | 1770 • | | 279 | 401sh | 2·02 ⁱ (3H) 2·18 (6H) | 49 ·7 | 4 ∙7 | 14.0 | $C_{12}H_{13}N_3O_6$ | 4 8·8 | 4 · 4 | 14.2 |

^a Also prepared (1.5%) from N-acetyl-N'-benzoyl-p-nitrophenylhydrazine; ^b corrected; ^c in Nujol; ^d neat liquid; ^c in chloroform; f in p-dioxan; e in deuteriochloroform; phenylazo-compounds also showed multiplets in the aromatic region; t tertiary methyl; j p-nitrophenylazo-compounds also showed A₂B₂ quartets, $\delta ca. 8.3$ (A) and ca. 7.87 (B), J 9 Hz; * OMe; i in pyridine solution two singlets split by 6 Hz.

analogue (VIII) to fit into this scheme suggests that in this case electronic effects are of secondary importance.

On the other hand, the 'acetyl effect' can be rationalised on steric grounds. In the crowded transition state, the favoured conformation is that in which the bulky lead triacetate group lies *trans* to the largest group on N-1. When R¹ is any the two groups on N-1 are of approximately equal size, and there is very little energy difference between the two conformations. On the other hand, when R^1 is methyl, the conformation (d) is favoured and reaction proceeds mainly to the acylazobenzene. Thus oxidation of the hydrazine (VIII) gives only 5% of the azo-diacetate (XX). When the oxidant is lead tetrabenzoate, the effect is even more marked and the yield of (XVIII) is only 1.5%, whereas in the case of the less crowded NN'-diacetyl analogue

(XXV) are yellow oils which can be distilled in vacuo without decomposition at temperatures up to 170°. Azoacylals show two u.v. absorption bands, a relatively weak one at wavelengths just over 400 nm. and a much stronger one at ca. 280 nm. In the carbonyl region of the i.r. spectrum acetates absorb from 1760 to 1780 cm.⁻¹ and benzoates at rather lower frequency, from 1730 to 1750 cm.⁻¹: the bands are frequently narrow doublets. The ¹H n.m.r. spectra of azoacylals having an acetate group or groups show singlets between δ 2.18 and 2.31, but the resonances due to tertiary methyl groups occur over a wider range, from $\delta 2.02$ to 2.33.

Besides being stable to heat, to silica gel, and to neutral alumina, azoacylals are also resistant to dilute acids and bases. At room temperature a-phenylazobenzylidene acetate benzoate (XIII) was unaffected after

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treatment for 3 days with either 0.1M-hydrochloric acid in aqueous acetone, or 0.06M-sodium carbonate in aqueous methanol. Treatment with Lewis acids, however, converts azoacylals into acylazobenzenes. When a benzene solution of the compound (XVIII) was stirred with a few drops of boron trifluoride-ether complex, the mixed acetic benzoic anhydride was eliminated and 4-benzoylazonitrobenzene could be isolated in 62% yield. Treatment of compound (XIII), either similarly, or with anhydrous aluminium trichloride in benzene, led to similar products, but the azo-dibenzoate (XXIV) gave benzoic acid (1.62 mol.) as the only isolable product. More vigorous treatment with Lewis acids led only to tarry products, and in no case was there evidence for the formation of an indazole derivative, as might have been expected by analogy with azoacetates.¹¹

Unlike azoacetates, which are converted into azoethers,⁸ azoacylals are unaffected by mild treatment with alcohols. Both the phenyl and p-nitrophenyl derivatives (XIII) and (XVIII) were recovered unchanged from propan-2-ol solution either after 4 months in the dark, or after 4 days under reflux. On the other hand, prolonged treatment in the dark with boiling n-butanol decomposes azoacylals to give, besides benzoic acid and n-butyl benzoate,* a mixture of substituted hydrazines resulting from reduction by the n-butanol: the detailed results are set out in Table 2. The formation of these reduction products is not unexpected: we have already noted the ready conversion of azoacetates into arylhydrazones by a number of reagents, including some alcohols,¹² and the cyclic azo-compound 4-phenyl-1,2,4-triazoline-3,5-dione is reported to oxidize alcohols at room temperature.13

| | | TABLE 2 | | |
|--|------------------------|-----------------------------|---|--|
| | Re | actions in n-butanol | | |
| Starting material OAc | n-Butanol (ml.) 200 | Time of reflux (hr.) 330 | Products isolated (%) BzOH Bu ⁿ OBz | (91·4) (50) |
| $\begin{array}{c} PhN=N-C-Ph (3.44 \text{ g.}) \\ \\ OBz \end{array}$ | | | Ph•NH–NHBz PhN(Ac)•NHBz PhN(Bz)•NHBz | $(23 \cdot 5) \\ (5 \cdot 5) \\ (1 \cdot 5)$ |
| OAc | 50 | 194 | $PhN(Ac) \cdot NHBz$ | (5) |
| PhN=N- \dot{C} -Ph (226 mg.) | | | | |
| OBz PhN=N-C-Ph (847 mg.) | 70 | 264 | BzOH PhN(Bz)•NHBz PhNH•NHBz | (117) (16·7) (Trace) |
| OBz | | | | |
| OBz $p-NO_2 \cdot C_6H_4 \cdot N=N \cdot C - Ph (1 g.)$ | 90 | 230 | Starting material p-NO ₂ ·C ₆ H ₄ ·N(Bz)·NHBz | (40) (24) |
| ÓBz | | | | |
| PhN=N-Bz (280 mg.) | 40 | 12 | PhNH•NHBz | (30) |
| p-NO ₂ ·C ₆ H ₄ ·N=NBz (509 mg.) | 50 | 24 | <i>p</i> -NO₂•C ₆ H₄NH•NHBz | (32) |
| PhN(Bz)·NHBz (290 mg.) | 60 | 94 | Starting material | (100) |
| PhN(Ac)·NHBz (109 mg.) | 30 | 96 | Starting material PhNH•NHBz | (>95) (Trace) |

Azoacylals are also smoothly decomposed by aqueous methanolic potassium hydroxide, according to reactions (1) and (2). Thus, the mixed acetate benzoate (XIII)

$$\begin{array}{c} \begin{array}{c} O \cdot COR^{1} \\ \downarrow \\ ArN:N \cdot CR^{3} \end{array} \xrightarrow{2OH^{-}} ArN:N \cdot COR^{3} + R^{1}CO_{2}^{-} \\ \downarrow \\ O \cdot COR^{2} \end{array} \xrightarrow{OH^{-}} ArH + N_{2} + R^{3}CO_{2}^{-} \end{array} (1)$$

and the corresponding dibenzoate (XIV) gave rise to 1.93 and 2.99 mol. of benzoic acid respectively.

* Decomposition products of the benzoylazoarene are also formed, and, when appropriate, both acetic acid and n-butyl acetate. None of these compounds was estimated.

¹¹ W. A. F. Gladstone and R. O. C. Norman, J. Chem. Soc., 1965, 3048, 5177; J. Chem. Soc. (C), 1966, 1527.
¹² W. A. F. Gladstone, M. J. Harrison, and R. O. C. Norman,

J. Chem. Soc. (C), 1966, 1781.

Oxidations with diethyl azodicarboxylate have also been reported.14 Although hydrogen atom abstraction has been suggested to account for these reactions,¹⁴ a hydride ion transfer mechanism is also possible, particularly since the reduction of azoacetates is catalysed by Lewis acids.12

Of the three possible hydrazines which can result from an unsymmetrical azoacylal, the diacyl derivatives are clearly formed (as shown in Scheme 4) by attack of hydrogen at N-1, loss of an acyloxy-group, and subsequent rearrangement of the resulting hydrazidic ester. There is ample precedent for the rearrangement: for example treatment of hydrazidic bromides with sodium acetate in acetic acid, or with sodium benzoate in

Comm., 1966, 744. ¹⁴ F. Yoneda, K. Suzuki, and Y. Nitta, J. Amer. Chem. Soc., 1966, **88**, 2328; E. C. Taylor and F. Yoneda, Chem. Comm., 1967, 199.

¹³ R. C. Cookson, I. D. R. Stevens, and C. T. Watts, Chem.

acetonitrile, leads to NN'-diacylarylhydrazines.¹⁵ The formation of the monoacyl derivative could, however, occur in any of three ways: (i) by solvolysis of a previously formed diacylhydrazine; (ii) by solvolysis of an intermediate hydrazidic ester; and (iii) by conversion of the azoacylal into an acylazobenzene, either thermally or by solvolysis, and subsequent reduction of the latter. Mechanism (i) can be rejected since both *N*-acetyl-*N'*benzoyl- and *NN'*-dibenzoylphenylhydrazine are essentially unchanged by boiling n-butanol, and mechanism (ii) because *N'*-benzoylphenylhydrazine, which is the major product from the mixed acetate benzoate (XIII), is only formed in trace quantities from either the corresponding diacetate (XVIII) or the dibenzoate (XIV),

washed with water and with suitable reagents (dilute hydrazine acetate solution to reduce excess of oxidant, sodium hydrogen carbonate solution to remove acids), dried ($MgSO_4$), and concentrated at aspirator pressure.

Acyl derivatives of Phenyl- and p-Nitrophenyl-hydrazine.— These were prepared in pyridine according to the general scheme:

$$\begin{array}{l} \operatorname{ArNH}^{\circ}\mathrm{NH}_{2} \xrightarrow{\mathrm{R}^{\circ}\mathrm{COCl}} & \operatorname{ArNH}^{\circ}\mathrm{NH}^{\circ}\mathrm{COR}^{1} \\ \end{array} \\ \begin{array}{l} \operatorname{ArNH}^{\circ}\mathrm{NH}^{\circ}\mathrm{COR}^{1} \xrightarrow{\mathrm{R}^{\circ}\mathrm{COCl}} & \operatorname{ArN}(\mathrm{COR}^{2})^{\circ}\mathrm{NH}^{\circ}\mathrm{COR}^{1} \end{array}$$

The acid chloride was added at 0° and the mixture was set aside overnight at room temperature. Under these conditions N'-benzoyl-*p*-nitrophenylhydrazine reacted only slightly with *p*-anisoyl chloride; the reaction was completed



although the same hydrazidic intermediates must necessarily be involved. Moreover, consistent with the operation of mechanism (iii), both benzoylazobenzene and 4-benzoylazonitrobenzene are reduced to the corresponding hydrazines in over 30% yield.

EXPERIMENTAL

General Methods .- Except where stated, i.r. spectra were measured for Nujol mulls with a Perkin-Elmer 237 grating spectrophotometer, u.v. spectra for solutions in p-dioxan with a Unicam SP 700C spectrophotometer, and ¹H n.m.r. spectra for solutions in deuteriochloroform with a Varian A-60A spectrometer. Except where stated, alumina for chromatography was the Woelm neutral product; Laporte alumina was type H, partially neutralised by the addition of 10% aqueous acetic acid (4%). T.l.c. was performed on Stahl Kieselgel HF_{251} ; the plates were developed in an iodine tank, or sprayed with antimony trichloride-acetic acid (1:1). Lead tetra-acetate (B.D.H.) was washed with petroleum immediately before use. Lead tetrabenzoate was prepared by the method of Hey, Stirling, and Williams,¹⁶ and recrystallised from dichloromethane. Benzene was dried over sodium and distilled just before use; dichloromethane was dried over molecular sieve (B.D.H. type 4A). Petroleum had b.p. 60-80°.

Reaction mixtures were stirred magnetically, and except where a more detailed description is given, the following work-up procedure was used. The reaction mixture was poured into water, and the combined ether extracts were by heating on a steam-bath for 2 hr. The products, isolated after extraction into alkali, had the properties previously reported, except for NN'-dibenzoyl-p-nitrophenylhydrazine, which had m.p. 167—169° (from ethanol) (lit.,¹⁷ 154°), ν_{max} . 1660 and 1695 cm.⁻¹ (Found: C, 66·8; H, 3·9; N, 11·8. Calc. for C₂₀H₁₅N₃O₄: C, 66·5; H, 4·2; N, 11·6%).

N-Acetyl-N'-benzoylphenylhydrazine crystallised slowly and with great difficulty from a mixture of benzene, ether, and petroleum; it had m.p. 117—119°, $\nu_{max.}$ 1670 and 1695 cm.⁻¹ (Found: C, 71.0; H, 5.7; N, 11.3. C₁₅H₁₄N₂O₂ requires C, 70.85; H, 5.55; N, 11.0%).

NN'-Diacetyl-p-nitrophenylhydrazine had m.p. 183—186° (from ethanol), v_{max} . 1685 and 1695 cm.⁻¹ (Found: C, 50.6; H, 4.4; N, 17.6; C₁₀H₁₁N₃O₄ requires C, 50.6; H, 4.7; N, 17.7%). NN'N'-Triacetyl-p-nitrophenylhydrazine was isolated as a by-product, m.p. 176—178° (from ethanol), v_{max} . 1720 and 1745 cm.⁻¹, $\delta 8.28$ (A) and 7.49 (B) (A₂B₂q, 4H, J_{AB} 9 Hz), 2.45 (6H, s), and 2.18 (3H, s) (Found: C, 51.5; H, 4.75; N, 14.8. C₁₂H₁₃N₃O₅ requires C, 51.6; H, 4.7; N, 15.0%).

N-Acetyl-N'-benzoyl-p-nitrophenylhydrazine had m.p. 159 —161° (from benzene-methanol), v_{max} . 1670 and 1680 cm.⁻¹ (Found: C, 60·15; H, 4·1; N, 13·9. $C_{15}H_{13}N_3O_4$ requires C, 60·2; H, 4·4; N, 14·0%).

¹⁶ D. H. Hey, C. J. M. Stirling, and G. H. Williams, J. Chem. Soc., 1954, 2747.
¹⁷ G. Lockemann, T. Lobenstein, and W. Neumann, Ber.,

¹⁷ G. Lockemann, T. Lobenstein, and W. Neumann, *Ber.*, 1942, **75**, 1911.

¹⁵ F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 1925, **127**, 975, 1687; J. M. Burgess and M. S. Gibson, *ibid.*, 1964, 1500; 1965, 2999; R. N. Butler and F. L. Scott, *J. Chem. Soc.* (C), 1967, 239.

N-p-Anisoyl-N'-benzoyl-p-nitrophenylhydrazine had m.p. 191—194° (from ethanol), v_{max} . 1665 and 1700 cm.⁻¹ (Found: C, 64·4; H, 4·35; N, 11·0. C₂₁H₁₇N₃O₅ requires C, 64·45; H, 4·4; N, 10·7%).

Reaction of N-Benzoyl-NN'-diphenylhydrazine with Lea.' Tetra-acetate.---N-Benzoyl-NN'-diphenylhydrazine (2.074 g.) in benzene (100 ml.) was added, under nitrogen, during 30 min. to a stirred mixture of lead tetra-acetate (5 g.), benzene (200 ml.), and calcium carbonate (2 g.) which had previously been heated under reflux for 10 min. and allowed to cool. Stirring was continued for 15 min., and after the addition of water (50 ml.) containing two drops of hydrazine hydrate, for a further 3 hr. The residue, after work up, was chromatographed on alumina (Laporte; 120 g.). Elution with petroleum gave trans-azobenzene (1.005 g., 77%), m.p. 66.5-67°, identical (m.p., mixed m.p., t.l.c., and i.r. spectrum) with an authentic sample. Further elution with petroleum-benzene (4:1) gave an oily red solid (9 mg.) which was rechromatographed on alumina (activity I; 5 g.) to give, besides some azobenzene, two unidentified red solids (4 mg. and 1 mg. respectively). Elution with petroleum-benzene (1:1) gave cis-azobenzene (280 mg., 21%), m.p. 65-67° (from petroleum) (mixed m.p. with the trans-form 40-50°). The i.r. and u.v. spectra of this material were identical to those published.^{18,19} This compound (31 mg.), when left overnight in a mixture of methanol (10 ml.) and water (2 ml.) containing a drop of concentrated hydrochloric acid, gave the trans-form (29 mg.). Further elution of the column with benzene and with ether gave a red oil (29 mg.) $\nu_{max.}$ 1765 cm. $^{-1}$ (C=O). It was treated with boiling aqueous methanolic potassium hydroxide (2 hr.). The phenolic material was separated and chromatographed on alumina (activity III; 10 g.) to give, with benzene-ether (1:1), o-hydroxyazobenzene (13 mg.), m.p. 152-154° (from benzene), identical (m.p., mixed m.p. and i.r. spectrum) with an authentic sample.

When the reaction was carried out in dichloromethaneacetic acid (4:1), and the products were chromatographed as before, *cis*- and *trans*-azobenzene were obtained in yields of 6.3 and 89.8% respectively.

Reaction of NN'-Dibenzoylphenylhydrazine with Lead Tetra-acetate.---(a) Finely powdered NN'-dibenzoylphenylhydrazine (15 g.) was added to a stirred solution of lead tetra-acetate (25 g.) in dichloromethane (250 ml.) and acetic acid (25 ml.). The mixture was stirred until all the solids dissolved (30 min.) and for a further 2 hr. It was then washed with water and stirred with saturated sodium hydrogen carbonate for 3 hr. (Acidification of the carbonate layer gave benzoic acid (3.4 g., 59%). The organic layer was washed with 0.5N-sodium hydroxide solution (acidification of the washings gave a small quantity of starting material), dried (MgSO₄), and concentrated. The resulting deep red oil was dissolved in a mixture of ether and petroleum; the solution slowly deposited bright yellow crystals of α -phenylazobenzylidene acetate benzoate (XIII) (Table 1) (7.4 g., $42\%),~m.p.~126{---}127^\circ$ (from petroleum-benzene) [M (Mekrolab osmometer) 386], m/e (A.E.I., MS 902) 269.08152 (Calc for C₁₆H₁₃O₄: 269.08138). The mother liquors evolved nitrogen when chromatography on alumina was attempted and were not further investigated.

(b) A solution of NN'-dibenzoylphenylhydrazine (10 g.) in boiling benzene (900 ml.) was allowed to cool to 35° , with

¹⁸ R. J. W. Le Fèvre, M. F. O'Dwyer, and R. L. Werner, Austral. J. Chem., 1953, 6, 341. vigorous stirring. To the resulting fine slurry was added lead tetra-acetate (20 g.), in portions, during 2 hr. The mixture was stirred, first overnight, and then for 8 hr. with water (100 ml.) containing a few drops of hydrazine hydrate. The organic layer was extracted with sodium hydrogen carbonate solution and with sodium hydroxide solution [acidification gave, respectively, benzoic acid (1.40 g., 36%), and starting material (*ca.* 200 mg.)], dried (MgSO₄), and concentrated to give the azoacylal (6.81 g.) as before. Chromatography of the mother liquors on alumina (activity III; 150 g.) gave more (0.78 g.) of (XIII) (total yield 7.59 g., 64%).

(c) When reaction (b) was repeated in the presence of calcium carbonate (6 g.), an exactly similar work-up led to (XIII) (66%).

(d) A suspension of NN'-dibenzoylphenylhydrazine (5 g.) in acetic acid (150 ml.) containing acetic anhydride (5 ml.) and lead tetra-acetate (9 g.) was stirred overnight at room temperature, diluted with water, and concentrated at 25°. The residue was worked up to yield benzoic acid (1.5 g., 97%), starting material (1 g.), and a red oil (2.2 g.), which gave the azoacylal (0.4 g., 8.5%) as before.

(e) An attempt to carry out the reaction in petroleum gave poor results, owing to the insolubility of both reactants. After 3 hr. under reflux, 42% of the starting material was recovered and the azoacylal (XIII) was obtained in only 13% yield.

(f) A suspension of NN'-dibenzoylphenylhydrazine (6 g.) in dichloromethane (200 ml.) was added during 10 min. to a stirred solution of lead tetra-acetate (17 g.) in benzene (220 ml.) and n-propanol (8 g.). The mixture was stirred for 1 hr. and filtered, and the filtrate was worked up to give a dark red oil, which on addition of ether deposited the azoacylal (XIII) (2.2 g.). The mother liquor was concentrated, and the residue, in benzene, was filtered through alumina (activity IV; 65 g.). The filtrate was chromatographed on a similar column. Elution with petroleum gave a pale orange oil (mainly n-propyl benzoate) and with petroleum-benzene (4:1) more (0.6 g.) of (XIII) (total yield 2.8 g., 39.5%). The product (XIII) from this experiment was identical (m.p., mixed m.p., and i.r. spectrum) with that obtained before. A careful examination of the chromatography fractions by t.l.c. revealed no trace of α -phenylazo- α -n-propoxybenzyl benzoate.

(g) When NN'-dibenzoylphenylhydrazine was treated with lead tetra-acetate in absolute ethanol, the resulting deep red solution evolved nitrogen and turned yellowbrown. Ethyl benzoate (116%) was the only product isolated.

 α -Phenylazobenzylidene Dibenzoate (XIV).—A stirred solution of NN'-dibenzoylphenylhydrazine (3 g.) in boiling benzene (400 ml.) was cooled to 45°, and lead tetrabenzoate (7·3 g.) was added. The mixture was stirred overnight and then for 6 hr. with water (5 ml.). Lead compounds were filtered off, and the filtrate was worked up to give an orange gum which crystallised from ether-petroleum to give the *dibenzoate* (XIV) (2·53 g., 61%), m.p. 185—187° (decomp.) (from petroleum-benzene).

1-Phenylazoethylidene Acetate Benzoate (XV).—Lead tetraacetate (3 g.) was added to N'-acetyl-N-benzoylphenylhydrazine (1.432 g.) in benzene (150 ml.). The mixture was stirred for 30 min., then worked up, and the resulting red oil was chromatographed on alumina (activity IV; 70 g.).

¹⁹ G. Zimmermann, Lue-yung Chow, and Un-jin-Paik, J. Amer. Chem. Soc., 1958, **80**, 3529.

Elution with petroleum-benzene (9:1) gave initially some biphenyl and then a yellow oil which, after a second chromatography, gave the *azoacylal* (1.01 g., 57%) as a yellow oil, b.p. *ca*. 150°/0.05 mm.

1-Phenylazoethylidene Dibenzoate (XVI).—When the same hydrazine (0.95 g.) was treated in the same way with lead tetrabenzoate (3 g.), the yellow oil resulting after chromatography crystallised from ether at -50° to give the dibenzoate (966 mg., 69%), m.p. 82—84° (from petroleum).

 α -Phenylazobenzylidene Diacetate (XVII).—N-Acetyl-N'benzoylphenylhydrazine (1·1 g.) was treated with lead tetra-acetate (2·5 g.), as in the preparation of (XV). A benzene solution of the resulting dark red oil was filtered through alumina (activity IV; 100 g.), and the concentrated filtrate (471 mg.) was chromatographed on 60 g. of the same adsorbent. Elution with benzene-petroleum (7:3) gave a yellow gurn (68 mg.), which gave the diacetate (55 mg., $3\cdot2\%$) as long yellow needles, m.p. 99—100° (from petroleum).

α-p-Nitrophenylazobenzylidene Acetate Benzoate (XVIII). -(a) A stirred solution of NN'-dibenzoyl-p-nitrophenylhydrazine (3.61 g.) in boiling benzene (900 ml.) was cooled to 30° and treated during 15 min. with lead tetra-acetate (6.5 g.). The mixture was stirred for 5 hr. and worked up to give benzoic acid (190 mg., 15.6%), a trace of starting material, and a red oil which could not be crystallised. The i.r. and t.l.c. properties of the oil indicated that it was essentially the azoacylal (XVIII). It was chromatographed on silica gel (B.D.H. lab. reagent; 250 g.), initially with petroleum-benzene (4:1) and finally with pure benzene as eluant. Twenty fractions were collected, one of which was finally induced to crystallise when a concentrated solution in ether was treated with small chips of solid carbon dioxide, and scratched vigorously with a glass rod. By use of these crystals as seeds, the other fractions were crystallised. This method was essential in effecting crystallisation of all the p-nitrophenylazo-derivatives described later. The total yield of azoacylal (XVIII) was 2.59 g. (62%), m.p. 97-99° (from ether-petroleum). When the crude product from a subsequent experiment was dissolved in ether-petroleum, compound (XVIII) was obtained in 80% yield by seeding.

(b) A suspension of N-acetyl-N'-benzoyl-p-nitrophenylhydrazine (3 g.) in benzene (400 ml.) and dichloromethane (50 ml.) was treated with lead tetrabenzoate (7.5 g.) at 40° . Most of the substrate dissolved, and after 30 min. the red filtrate was concentrated to 100 ml. and filtered through alumina (activity IV; 100 g.). The concentrated filtrate was chromatographed on a further 80 g. of the same adsorbent, with petroleum-benzene (4:1) as eluant. T.l.c. of the eluate suggested the presence of compound (XVIII). The appropriate fractions were again chromatographed on the same adsorbent (120 g.). Elution with petroleumbenzene (9:1) gave some nitrobenzene and 4-nitrobiphenyl, while the same solvents (4:1) gave the product (XVIII) as a yellow oil (84 mg.) which crystallised when seeded. Recrystallisation from ether-petroleum gave pure material (61 mg., 1.5%), identical (m.p., mixed m.p., t.l.c., and i.r. spectrum) with the material obtained in (a).

 α -p-Nitrophenylazobenzylidene Dibenzoate (XIX).—NN'-Dibenzoyl-p-nitrophenylhydrazine (1.81 g.) in benzene (250 ml.) was treated with lead tetrabenzoate (3.65 g.), at 45°. After work-up, filtration of a benzene solution of the crude product through alumina (activity IV—V), followed by chromatography on 100 g. of the same adsorbent gave a yellow oil (1.53 g.). A solution of this in ether was treated with solid carbon dioxide [as described for compound (XVIII)] to give *dibenzoate* (XIX) (1·30 g., 54%), m.p. 163-165° (from petroleum-benzene).

α-p-Nitrophenylazobenzylidene Diacetate (XX).—N-Acetyl-N'-benzoyl-p-nitrophenylhydrazine (1.828 g.) in dichloromethane (220 ml.) was added during 30 min. to a stirred mixture of lead tetra-acetate (5 g.), calcium carbonate (2 g.), and benzene (300 ml.), which had previously been heated under reflux for 10 min. and allowed to cool. The filtrate was worked up to give a dark red solid, which was recrystallised from petroleum (b.p. 80—100°)–isopropyl acetate to give 4-benzoylazonitrobenzene (904 mg., 58%) as copper-coloured leaflets, m.p. 98—100°, λ_{max} 237 (log ε 4·12), 285 (4·31), and 459 (2·19) nm., ν_{max} 1710 cm.⁻¹ (Found: C, 61·2; H, 3·6; N, 16·3. C₁₃H₉N₃O₃ requires C, 61·2; H, 3·55; N, 16·5%) *

A benzene solution of the mother liquor was filtered through alumina (activity IV—V; 100 g.) and the concentrated filtrate was chromatographed on the same adsorbent (50 g.) to give, on elution with petroleum-benzene (1:2), the *diacetate* (XX) (107 mg., 5%), m.p. 133—134° (from ether-petroleum).

Other Azoacylals.—Treatment of N'-benzoyl-N-p-nitrophenylhydrazine with lead tetra-acetate, as in the preparation (a) of compound (XVIII), gave, after work-up and purification, α -p-nitrophenylazobenzylidene acetate p-nitrobenzoate (XXI) (66%), m.p. 135—137° (from petroleumbenzene).

Similarly, treatment of *N-p*-anisoyl-*N'*-benzoyl-*p*-nitrophenylhydrazine with lead tetra-acetate led to α -p-nitrophenylazobenzylidene acetate p-anisate (XXII) (36.5%), m.p. 137—139° (from petroleum-benzene), also obtained (31%) by the method used for the preparation of compound (XX).

Treatment of N'-acetyl-N-benzoyl-p-nitrophenylhydrazine as in the preparation of compound (XX) gave 1-pnitrophenylazoethylidene acetate benzoate (XXIII) (72%), b.p. ca. $170^{\circ}/0.05$ mm. (hot box).

Treatment of the same hydrazine with lead tetrabenzoate, as in the preparation of compound (XIX), gave, after chromatography, 1-p-nitrophenylazoethylidene dibenzoate (XXIV) (62%), m.p. 100—102° (from petroleum-ether).

Treatment of NN'-diacetyl-*p*-nitrophenylhydrazine as in the preparation of compound (XX) led, after multiple chromatography, to 1-*p*-nitrophenylazoethylidene diacetate (XXV) (9%), b.p. ca. 120°/0.05 mm.

Reactions of Azoacylals.—(a) Stability. A solution of α -phenylazobenzylidene acetate benzoate (396 mg.) in petroleum-benzene (1:1) was filtered through alumina (activity III; 25 g.). Concentration of the filtrate gave a gum which, on addition of methanol (5 ml.), gave crystalline starting material (371 mg.).

A solution of the same compound (850 mg.) in acetone (75 ml.) was treated with 0.4M-hydrochloric acid (30 ml.). After 3 days, water (50 ml.) was added; starting material (700 mg.) then slowly crystallised.

The same compound (XIII) was again recovered after 3 days in a mixture of methanol (100 ml.), water (50 ml.), and sodium carbonate (1 g.).

Solutions of the compound (XIII) and of its p-nitrophenyl analogue (XVIII) in propan-2-ol were kept in the dark for 4 months: the materials were then recovered unchanged.

 $[\]ast$ Identical material was obtained (81%) when N'-benzoyl-p-nitrophenylhydrazine was treated with lead tetra-acetate in dichloromethane.

When a solution of compound (XIII) in propan-2-ol was heated under reflux for 96 hr., 84% of the material crystallised on cooling. T.l.c. of the concentrated mother liquors showed only traces of decomposition products. A similar result was obtained when the compound (XVIII) was treated in the same way.

(b) Reactions with Lewis acids. α -p-Nitrophenylazobenzylidene acetate benzoate (1.9 g.) in benzene (150 ml.) was stirred with several drops of boron trifluoride-ether complex for 2 min. Aqueous sodium hydrogen carbonate was then added, and stirring was continued for 3 hr. The benzene layer was dried (MgSO₄) and filtered through silica gel (B.D.H. lab. reagent; 50 g.). Concentration of the filtrate left an oily solid which crystallised from ethyl acetate-petroleum to give 4-benzoylazonitrobenzene (713 mg., 62%), m.p. 98-100°, identical with the sample prepared before.

Similar treatment of α -phenylazobenzylidene acetate benzoate gave a dark red petroleum-soluble oil, the i.r. spectrum of which was identical with that of a sample of benzoylazobenzene prepared by the lead tetra-acetate oxidation of N'-benzoylphenylhydrazine.⁵ Treatment of α -phenylazobenzylidene acetate benzoate with anhydrous aluminium trichloride in benzene led to the same product, while the action of larger quantities of Lewis acids gave only intractable tars.

Treatment of 1-*p*-nitrophenylazoethylidene dibenzoate with boron trifluoride–ether complex in benzene led to an

almost colourless solution; benzoic acid (1.62 mol.) was the only product isolated.

(c) *Hydrolysis*. α -Phenylazobenzylidene acetate benzoate (755 mg.) in benzene (10 ml.) was added to potassium hydroxide (5.6 g.) in water (25 ml.) and methanol (75 ml.). After 48 hr. the mixture was separated into neutral, sodium hydrogen carbonate soluble, and sodium hydroxide soluble fractions in the usual way. Acidification of the carbonate solution gave benzoic acid (474 mg., 1.93 mol.); the small quantities of material present in the other fractions were not further investigated.

A suspension of α -phenylazobenzylidene dibenzoate (800 mg.) in potassium hydroxide (5.6 g.) in water (25 ml.) and methanol (75 ml.) was stirred for 3 days. The solid slowly dissolved, forming a pale brown solution. The same work-up as in the previous experiment gave benzoic acid (735 mg., 2.99 mol.).

(d) Reactions with *n*-Butanol.—Solutions of the compounds in n-butanol were heated under reflux in the dark, normally until the yellow colour faded and the reaction appeared to be complete. After concentration *in vacuo*, acidic material was removed by extraction with aqueous sodium hydrogen carbonate, and the remaining products were separated by chromatography on Laporte alumina. n-Butyl benzoate was estimated by hydrolysis to benzoic acid.

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