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THE REACTION OF LEAD TETRAACETATE WITH PRIMARY AND SECONDARY AMINES CONTAINING AN α-METHYLENE GROUP[1,2]

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Abstract—Primary alkyl- and arylalkyl-amines containing a methylene group in the α-position were dehydrogenated by means of lead tetraacetate to give the corresponding cyanides in yields ranging up to 60%. By-products of this reaction are N-alkylacetamides, N-alkylamides of the corresponding alkanoic acids and other acetoxylated derivatives.

In the oxidation of dibenzylamine with lead tetraacetate N-benzylidenebenzylamine (Schiff base), benzaldehyde, benzylamine and benzonitrile are formed. The possible reaction pathways leading to the observed products are discussed.

ALTHOUGH the reaction of lead tetraacetate with various compounds containing OH groups, unsaturated systems and C—H and C—C bonds has been extensively studied,[4] its action on amino compounds has received relatively little attention.

The 1,2-glycol splitting action of lead tetraacetate has also been applied[4,5] to α-hydroxyamines ($RCHNH_2{\cdot}CHOHR$), α-amino acids and α-diamines ($RCHNH_2{\cdot}CHNH_2R$), the initial step consisting in the cleavage of the C—C bond with the formation of unstable imines ($RCH{:}NH$), which are further dehydrogenated to the corresponding nitriles ($RC\!\vdots\!N$) with excess lead tetraacetate.[6,7] If one hydrogen atom of the amine function is substituted by a tosyl group[5,6] or carbethoxy group,[8] the oxidation affords substituted imines, $RCH{:}NR_1$ (R_1 = Ts or COOEt), whereas substitution of hydrogen by an acetyl or benzoyl group inhibits the action of lead tetraacetate.[5,6,9,10]

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[1] Part 2 of the series "The reaction of lead tetraacetate with nitrogen-containing compounds"; Part XI in the series "Reactions with lead tetraacetate".

[2] For Part 1 see M. Lj. Mihailović, A. Stojiljković and V. Andrejević, *Tetrahedron Letters* No. 8, 461 (1965).

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[4] R. Criegee, Oxidations with Lead Tetraacetate, in *Oxidations in Organic Chemistry* (edited by K. Wiberg) Part A; pp. 277–366. Academic Press, New York (1965), and Refs. therein.

[5] R. Criegee, *Angew. Chem.* **53**, 321 (1940), and Refs. therein.

[6] J. Bollinger, Thesis, University of Marburg, Germany (1937).[4,5]

[7] H. J. Roth and A. Brandau, *Arch. Pharm.* **293**, 27 (1960).

[8] P. Karrer and J. Meyer, *Helv. Chim. Acta* **20**, 407 (1937).

[9] F. Knoop, F. Ditt, W. Hecksteden, J. Maier, W. Merz and R. Härle, *Hoppe-Seyler's Z. Physiol. Chem.* **239**, 30 (1936).

[10] O. Süs and S. Rosenberg [*Liebig's Ann.* **564**, 137 (1949)], however, reported that N-acyl- and N-benzoyl-α-amino acids ($RCONHCH_2COOH$) are attacked by lead tetraacetate in AcOH at 100° to give decarboxylated α-acetoxy derivatives ($RCONHCH_2OAc$).

In some cases the oxidative C—C cleavage of N-primary- and N-secondary-1,2-amino alcohols has been carried out in order to differentiate diastereoisomeric alcohols on the basis of their reaction rates.[11] The lead tetraacetate oxidation of N-tertiary-1,2-hydroxyamines ($R_2N{\cdot}CH_2CHOHR$) is different in that it occurs with C—N cleavage to give secondary amines (R_2NH) and the corresponding carbonyl compounds.[7,12]

Primary aromatic amines react easily with lead tetraacetate giving the corresponding azo compounds (substituted anilines)[13,14] and/or quinones, amino- and N-acetylamino-quinones, quinoneimines and quinol acetates (*p*-anisidine, *p*-phenetidine, α- and β-naphthylamine, mesidine).[13,15] *o*-Phenylenediamines are readily oxidized by lead tetraacetate at room temperature with C—C cleavage and formation of the corresponding *cis,cis*-muconitriles.[16] Tertiary aryldialkylamines were found to be oxidatively dealkylated by lead tetraacetate giving, in the presence of acetic anhydride, the acetyl derivative of the secondary arylalkylamines and aliphatic aldehydes.[17]

In the present paper we report the oxidation of a series of aliphatic primary amines (from n-butylamine to n-octylamine), benzylamine, dibenzylamine and N-benzylidenebenzylamine (Schiff base).

RESULTS AND DISCUSSION

Primary amines

Lead tetraacetate oxidations of primary amines were carried out in boiling benzene with a 1:1 and 1:2 molar ratio of amine to lead tetraacetate. After completion of the oxidation, the reaction products were separated into neutral, acid and basic parts and each part was investigated separately.

The major reaction products were in the neutral parts and consisted of cyanides corresponding to the starting amines. Cyanides were identified on the basis of their physical constants, IR spectra (CN bands 2260–2220 cm^{-1}) and by hydrolysis to the parent acids. When the reactants were used in a 1:1 molar ratio, the reaction was complete in less than 1 hr and the yields of nitriles ranged from 20 to 36% (Table 1); when the amount of the oxidizing agent was increased to 2 molar equivalents, the time required for complete consumption of lead tetraacetate was considerably prolonged, and the yields of cyanides were almost doubled (Table 1).

Other neutral products of the oxidation of primary amines were partially resinified and high-boiling nitrogen compounds (see below). In case of benzylamine, the resulting benzonitrile was accompanied by a small amount of benzaldehyde (2–4%); no aldehyde could be detected in the reaction with aliphatic amines.

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[11] Th. Posternak, *Helv. Chim. Acta* **33**, 1597 (1950); G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.* **73**, 5164 (1951); M. Pesez, *Bull. Soc. Chim. Fr.* 520 (1954); M. Pesez, J. Mathieu and A. Allais, *Anal. Chim. Acta.* **20**, 291 (1959).

[12] N. J. Leonard and M. Rebenstorf. *J. Amer. Chem. Soc.* **67**, 49 (1945); H. J. Roth, *Arch. Pharm.* **294**, 427 (1961).

[13] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.* 4003 (1954); see also H. J. Richter and R. L. Dressler, *J. Org. Chem.* **27**, 4066 (1962).

[14] E. Baer and A. L. Tosoni, *J. Amer. Chem. Soc.* **78**, 2857 (1956).

[15] F. Wessely, L. Holzer and H. Vilcsek, *Monatsh.* **84**, 655 (1953).

[16] K. Nakagawa and H. Onoue, *Chem. Comm.* 396 (1965). For the lead tetraacetate oxidations of N-sulphonyl and other N-substituted derivatives of aromatic diamino compounds to quinone mono- and diimides see R. Adams and R. R. Way, *J. Amer. Chem. Soc.* **76**, 2763 (1954); R. Adams, R. R. Holmes and J. W. Way, *Ibid.* **75**, 5901 (1953), and previous publications.[4]

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

In basic parts some amine was always recovered unchanged (about 20% with aliphatic amines and 43% with benzylamine when a 1 : 1 molar ratio was used and considerably less when the ratio was 1 : 2). Products of oxidative coupling (hydrazines) or intramolecular cyclization (pyrrolidines or piperidines) have not been detected.

TABLE 1. YIELDS OF CYANIDES (%) OBTAINED IN THE LEAD TETRAACETATE OXIDATION OF PRIMARY AMINES

Amine	Molar ratio 1 : 1*	Molar ratio 1 : 2*
n-Butylamine	20	39
n-Hexylamine	30	41
n-Heptylamine	32	62
n-Octylamine	32	60
Benzylamine	37	59

* Amine to lead tetraacetate.

The acid parts contained, in addition to acetic acid, traces of alkanoic acids corresponding to the starting amines, which were probably formed by hydrolysis of the nitriles in the course of the reaction or during the working up procedure.

As in the oxidation of 1,2-diamines, 1,2-aminoalcohols and 1,2-amino acids,[4–8] the conversion of an alkyl- or arylalkylamine (I) to the corresponding cyanide (III) by means of lead tetraacetate might be regarded as a two-step dehydrogenation process (1) involving the intermediate formation of an unstable aldimine (II).

$$\underset{\text{I}}{RCH_2{-}NH_2} \xrightarrow[(-2H)]{Pb(OAc)_4} \underset{\text{II}}{RCH{=}NH} \xrightarrow[(-2H)]{Pb(OAc)_4} \underset{\text{III}}{RC{\equiv}N} \qquad (1)$$

The intermediate formation of aldimine is supported by the isolation of benzaldehyde (in case of the benzylamine oxidation), which probably arises from hydrolysis of the primarily produced benzaldimine. Presumably such intermediates are formed in all lead tetraacetate oxidations if amines having an α-methylene group, but in case of aliphatic amines the resulting unsubstituted aldimines are known to be very unstable and to polymerize rapidly to high boiling material;[18] probably this is the reason why aldimines (II) or their hydrolysis products (i.e. aldehydes) are not detected upon oxidation of aliphatic amines. Moreover, the yield of nitrile decreases and that of resins increases with decreasing molecular weight of the oxidized amine, this fact being consistent with the decreasing stability of the corresponding aldimine. The proposed reaction course (1) is further substantiated by the identification of the by-products isolated in the oxidation of n-hexylamine and by the results obtained in the reaction of dibenzylamine with lead tetraacetate (see below).

Since the oxidation of benzylamine with 2 and 3 molar equivalents of lead tetraacetate proceeds also photolytically (UV irradiation with a high pressure mercury lamp) at room temperature giving benzonitrile in considerably improved yield (83%), it appears that, in the two-step dehydrogenation of amines (2 and 3) in non-polar solvent, the decomposition of the intermediate amino-lead-triacetate (IV) and imino-lead-triacetate (VI)[19] to the corresponding aldimine (II) and nitrile (III), respectively,

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[18] L. Henry, *C. R. Acad. Sci. Paris* **120**, 837 (1895).

[19] The postulated reversible aminolysis of lead tetraacetate (*a*) in the dehydrogenation processes (2) and (3), leading to the intermediate salts IV and VI, respectively, is closely similar to the equilibrium controlled alcoholysis of lead tetraacetate.[4]

proceeds by homolytic cleavage of bonds, either directly (*b*) or possibly via formation (*c*) of radical pairs containing nitrogen radicals (V and VII, respectively).[20]

$$\begin{tikzcd}
\underset{\mathrm{I}}{\mathrm{RCH_2{\cdot}NH_2 + Pb(OAc)_4}} \arrow[r, shift left, "(a)"] & \underset{\mathrm{IV}}{\mathrm{RCH_2{\cdot}NH{\cdot}Pb(OAc)_3 + AcOH}} \arrow[l, shift left] \arrow[d, "(b)"] \arrow[dl, "(c)"'] \\
\underset{\mathrm{V}}{\mathrm{[RCH_2{\cdot}\dot{N}H + \dot{P}b(OAc)_3]}} \arrow[r, "(d)"] & \underset{\mathrm{II}}{\mathrm{RCH{:}NH + Pb(OAc)_2 + AcOH}}
\end{tikzcd} \qquad (2)$$

$$\begin{tikzcd}
\underset{\mathrm{II}}{\mathrm{RCH{:}NH + Pb(OAc)_4}} \arrow[r, shift left, "(a)"] & \underset{\mathrm{VI}}{\mathrm{RCH{:}N{\cdot}Pb(OAc)_3 + AcOH}} \arrow[l, shift left] \arrow[d, "(b)"] \arrow[dl, "(c)"'] \\
\underset{\mathrm{VII}}{\mathrm{[RCH{:}\dot{N} + \dot{P}b(OAc)_3]}} \arrow[r, "(d)"] & \underset{\mathrm{III}}{\mathrm{RC{:}N + Pb(OAc)_2 + AcOH}}
\end{tikzcd} \qquad (3)$$

To avoid the inhibiting and retarding effect which acetic acid, generated from lead tetraacetate in the course of the reaction, might have on the dehydrogenation processes (2) and (3) (see below), the oxidations of primary amines were repeated in the presence of pyridine or calcium carbonate, using different ratios of base to lead tetraacetate. However, neither of these bases noticeably affects the yield of nitriles, but pyridine in large excess accelerates the reaction considerably, which, under these conditions, proceeds even at room temperature. Pyridine as solvent might change the mechanism of the dehydrogenation (*b*) in reactions (2) and (3) from radical to polar, by assisting the removal of the proton from the α-carbon atom in the amino-lead-triacetate (IV) and imino-lead-triacetate (VI), respectively, and thus cause heterolytic decomposition of these intermediates, or else it might only promote reactions (2) and (3), without actually changing the nature of the dehydrogenation mechanism, by capturing the acetic acid formed in the equilibrium controlled aminolysis steps (*a*).

As mentioned above, the neutral parts contained, in addition to cyanide and resins, high-boiling nitrogen compounds which were investigated in detail in the case of n-hexylamine. When the oxidation was performed with a 1 : 1 molar ratio of reactants, after the distillation of the cyanide fraction, a high-boiling fraction was obtained which was purified by column chromatography; the resulting compound, on the basis of its elemental analysis, IR spectrum (amide bands at 1653, 1550 and 1290 $\mathrm{cm^{-1}}$) and hydrolysis products (n-hexylamine and acetic acid), was identified as N-hexylacetamide (n-$\mathrm{C_6H_{13}NHCOCH_3}$), this structure being confirmed by comparison with an authentic specimen, prepared by synthesis. N-Hexylacetamide (VIII) is probably formed by acetylation of the starting amine (or the corresponding amino-lead-triacetate IV) with acetic anhydride, which is produced from lead tetraacetate in the course of the reaction (4),[21] and/or by direct nucleophilic attack of the amino-nitrogen

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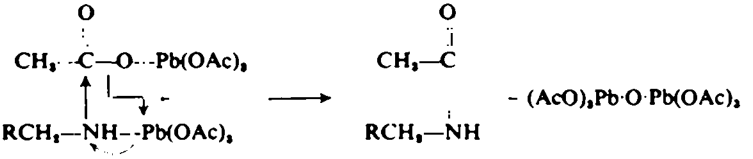
[20] H. Lemaire and A. Rassat, *Tetrahedron Letters* No. 33, 2245 (1964), have detected (by ESR) nitrogen-radical formation in the oxidation of diphenylamine with lead tetraacetate.

[21] The formation of acetic anhydride was established in the lead tetraacetate oxidation of aliphatic alcohols.[22]

[22] M. Lj. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović and Lj. Lorenc, *Tetrahedron* **21**, 1395 (1965).

in the aminolysis product IV on one of the carboxylic carbon atoms of lead tetraacetate (5).[23,25]

$$2Pb(OAc)_4 \rightleftharpoons \underset{IX}{(AcO)_3Pb{\cdot}O{\cdot}Pb(OAc)_3} + Ac_2O \quad (4)$$


(5)

IV VIII IX

On the other hand, when two molar equivalents of lead tetraacetate were used, the second fraction of the neutral part contained, in addition to N-hexylacetamide, three products which were separated by chromatography on silica gel. According to elemental analyses, physical and chemical properties, IR spectra and R_f values, two of these products were identified as benzyl acetate and N-hexylcaproamide ($n\text{-}C_6H_{13}NH{\cdot}COC_5H_{11}\text{-}n$), while the third product appears to be an acetoxylated nitrogen compound (Table 2).

TABLE 2. NEUTRAL PRODUCTS (%) OBTAINED IN THE LEAD TETRAACETATE OXIDATION OF n-HEXYLAMINE

Reaction product	Molar ratio 1:1*	Molar ratio 1:2*
n-Pentyl cyanide	30	41
N-Hexylacetamide	4	12
N-Hexylcaproamide	—	5
Benzyl acetate	—	traces
Acetoxylated N-hexylidene-hexylamine	—	traces

* Amine to lead tetraacetate.

The way in which small amounts of benzyl acetate are formed in almost all oxidations with lead tetraacetate in benzene, was described previously.[22] The acetoxylated nitrogen compound, obtained only in traces, might have the structure of a C-acetoxy-N-hexylidenehexylamine and could be formed by addition of starting hexylamine to the intermediary hexaldimine, followed by loss of ammonia from the

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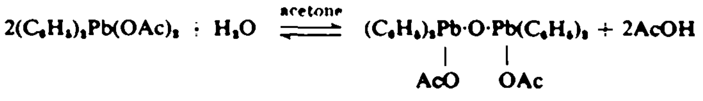
[23] This acylation reaction (5) is similar to the scheme proposed by Heusler[24] for the acetylation of alcohols with lead tetraacetate.

[24] K. Heusler, Personal communication; see also M. Lj. Mihailović, R. I. Mamuzić, Lj. Žigić-Mamuzić, J. Bošnjak and Ž. Čeković, *Tetrahedron* **23**, 215 (1967).

[25] As can be seen, both reactions (4) and (5) follow the same course. A close analogy to the lead oxane structure IX is found in the formation of the organo dilead-oxane X from diphenyl-lead-diacetate and small amounts of water (6).[26]

(6)



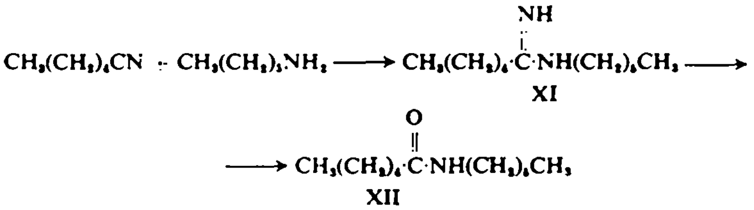
$$2(C_6H_5)_2Pb(OAc)_2 + H_2O \xrightleftharpoons{\text{acetone}} \underset{AcO\qquad OAc}{(C_6H_5)_2Pb{\cdot}O{\cdot}Pb(C_6H_5)_2} + 2AcOH$$

X

[26] E. M. Panov, N. N. Zemlyanskii and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR* **143**, 603 (1962).

so-produced unstable 1,1-diaminoalkane and acetoxylation of the resulting N-hexylidenehexylamine.[27]

The constitution of N-hexylcaproamide (XII) has been confirmed by hydrolysis to n-hexylamine and caproic acid, and by comparison with a synthetic product prepared from caproic acid chloride and n-hexylamine. Its formation most probably takes place in the following way: pentyl cyanide, resulting from the oxidation of hexylamine, undergoes (7) addition of the parent amine present in the reaction mixture to give the intermediate aldamidine (XI), which is hydrolysed, in the course of the oxidation or during the working up procedure, to the corresponding amide (XII).[28] In order to prove the proposed route for N-hexylcaproamide formation (7), pentyl cyanide was treated with a benzene solution of n-hexylamine under conditions approximating those of the oxidation procedure (but in the absence of lead tetraacetate); the neutral part contained, in addition to unreacted cyanide, small amounts of the expected N-hexylcaproamide (XII).



$$\mathrm{CH_3(CH_2)_4CN + CH_3(CH_2)_5NH_2 \longrightarrow \underset{XI}{CH_3(CH_2)_4{\cdot}\overset{NH}{\overset{\|}{C}}{\cdot}NH(CH_2)_5CH_3} \longrightarrow \underset{XII}{CH_3(CH_2)_4{\cdot}\overset{O}{\overset{\|}{C}}{\cdot}NH(CH_2)_5CH_3}} \qquad (7)$$

The presence of similar by-products in the lead tetraacetate oxidations of other primary amines has been confirmed by IR spectral data.

Finally, it was of interest to investigate the oxidation of primary amines with lead tetraacetate in the presence of acetic acid. However, when n-hexylamine acetate was oxidized with 1 or 2 molar equivalents of the reagent, the reaction was retarded, and the yield of pentyl cyanide was decreased whereas the yields of by-products were augmented (Table 3).

TABLE 3. NEUTRAL PRODUCTS (%) OBTAINED IN THE LEAD TETRAACETATE OXIDATION OF n-HEXYLAMINE ACETATE

Reaction product	Molar ratio 1:1*	Molar ratio 1:2*
n-Pentyl cyanide	20	34
N-Hexylacetamide	15	12
N-Hexylcapronamide	—	10·5

* Amine to lead tetraacetate.

From data presented above one can draw the conclusion that the dehydrogenation of primary amines containing an α-methylene group by means of lead tetraacetate might be of preparative value, since the corresponding nitriles are easily isolated and are obtained in satisfactory yields.

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[27] Such imine–primary amine exchange reactions are known to occur and have been used for obtaining N-alkyl imines. See, for example, R. W. Layer, *Chem. Revs.* **63**, 489 (1963).

[28] A. Bernthsen, *Liebig's Ann.* **192**, 1 (1878); H. J. Backer and W. L. Wanmaker, *Rec. Trav. Chim. Pays-Bas* **70**, 638 (1951).

Secondary arylalkyl amines

The lead tetraacetate oxidations of dibenzylamine were carried out in the same way as those of primary amines. When the reactants were used in a 1:1 molar ratio, the reaction was complete in 30 min ; by increasing the amount of the oxidizing agent to 2 molar equivalents, the required reaction time was prolonged to 2 hr. The reaction products are listed in Table 4.

TABLE 4. PRODUCTS (%) OBTAINED IN THE LEAD TETRAACETATE OXIDATION OF DIBENZYLAMINE IN REFLUXING BENZENE

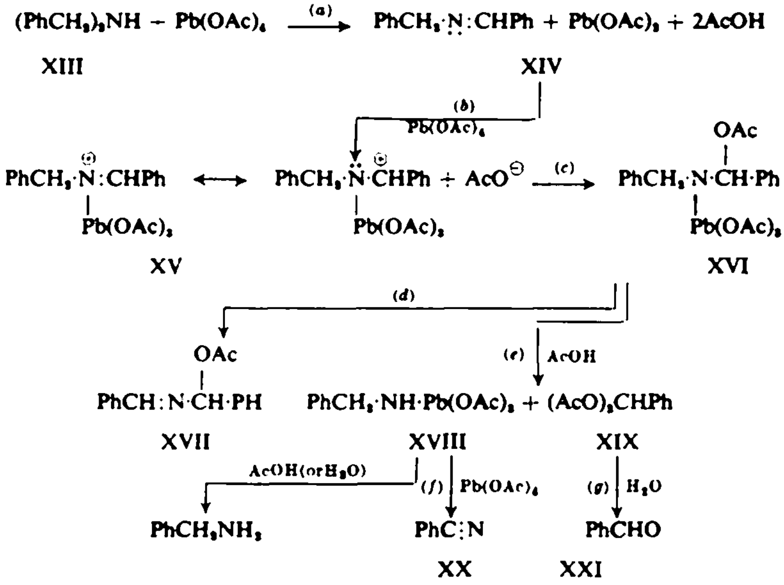
Reaction product	Molar ratio 1:1*	Molar ratio 1:2*
Benzaldehyde	30	60
Benzonitrile	13	24
N-benzylidene-α-acetoxybenzylamine	—	14
Benzylamine	32	—
N-Benzylidenebenzylamine	27	6

* Amine to lead tetraacetate.

The presence of benzaldehyde and benzonitrile in the neutral part was established from IR spectra (CHO band 1700 cm^{-1}; CN band 2130 cm^{-1}), and their yields by means of gas chromatography and quantitative determination of benzaldehyde. When the oxidation was performed with a 1:2 molar ratio of amine to lead tetraacetate, the neutral part contained a third component, which could not be distilled without decomposition. According to its IR spectrum, which exhibits strong absorption maxima for —C=N— (1649 cm^{-1}) and acetoxy groups (1739 and 1235 cm^{-1}), and on the basis of analytical data (elemental analysis and saponification value) and hydrolysis products (benzaldehyde, ammonia, acetic acid), this compound was assigned the structure of N-benzylidene-α-acetoxybenzylamine ($C_6H_5CH(OAc){\cdot}N{:}CHC_6H_5$).

In the oxidation with a 1:1 molar ratio of reactants, the basic part contained two products, one of which was benzylamine and the other N-benzylidenebenzylamine (Schiff base). The structure of the latter compound was established from its analysis, IR spectrum and rapid, near quantitative acid hydrolysis to benzaldehyde and benzylamine, as well as by comparison with a synthetic sample and conversion into the known crystalline tribromide. When the oxidation of dibenzylamine was carried out with 2 molar equivalents of lead tetraacetate, no benzylamine was detected, the sole basic reaction product being N-benzylidenebenzylamine.

A possible route (8) leading to the observed reaction products (Table 4) (without entering into the detailed mechanism of each step) involves the dehydrogenation (*a*) of dibenzylamine (XIII) to N-benzylidenebenzylamine (XIV) [in the way postulated for the dehydrogenation of primary amines to aldimines (2)], as the first oxidation step, followed by reaction of Schiff base (XIV) with lead tetraacetate (*b*) to give the triacetoxy-lead immonium-carbonium ion (XV),[7,12b] which, in turn adds an acetate anion to the positive α-carbon atom (*c*). The resulting product XVI can then either undergo dehydrogenation (*d*) to N-benzylidene-α-acetoxybenzylamine (XVII), or, by attack of acetic acid (*e*) (or water) generated during the reaction, afford benzylamino-lead-triacetate (XVIII), which is further dehydrogenated (*f*) by lead tetraacetate [according to reactions (2) and (3)] to benzonitrile (XX), and α,α-diacetoxytoluene (XIX) (or directly benzaldehyde), which is hydrolysed (*g*) (during the reaction or the working up procedure) to benzaldehyde (XXI).[28]



(8)

The rather high yield of N-benzylidenebenzylamine (27%) obtained in the 1:1 molar ratio oxidation of dibenzylamine, as compared to the amount (6%) isolated in the 1:2 molar ratio oxidation (Table 4), suggests that the Schiff base (XIV) is the primary reaction product. For that reason it was of interest to investigate the action of lead tetraacetate on N-benzylidenebenzylamine (XIV) itself. With a 1:1 molar ratio of reactants (2 hr), benzaldehyde (20%), benzonitrile (47%), N-benzylidene-α-acetoxybenzylamine (XVII), the starting Schiff base (XIV) (13%) and a small amount of benzoic acid were obtained, but no benzylamine was detected, these results being similar to those observed in the 1:2 molar ratio oxidation of dibenzylamine (Table 4). Moreover, by heating N-benzylidenebenzylamine (1 mole) with lead diacetate (1 mole) and acetic acid (2 moles) in benzene, i.e. under reaction conditions approximating those of the lead tetraacetate oxidation procedure, 70% of the Schiff base (XIV) was acetolysed in ½ hr, whereas attempts to synthesize N-benzylidenebenzylamine (XIV) from benzaldehyde and benzylamine, under similar conditions, failed. These observations represent further evidence that in the lead tetraacetate oxidation of dibenzylamine benzaldehyde and benzylamine arise from the primarily formed N-benzylidenebenzylamine (8), rather than by direct C—N fragmentation of the starting amine (XIII), with subsequent condensation to the Schiff base (XIV).[29]

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[29] Another, less probable pathway, which might be envisaged for explaining the formation of products (Table 4), would consist in the initial cleavage of one C—N bond in dibenzylamine (XIII) to give benzylamino-lead-triacetate (XVIII) and α,α-diacetoxytoluene (XIX), possibly through XVI (generated by direct acetoxylation of dibenzylamine XIII); XVIII would then undergo either dehydrogenation to benzonitrile (XX) or else condensation with XIX to N-benzylidenebenzylamine (XIV), this Schiff base being further acetoxylated.

EXPERIMENTAL[20]

M.ps and b.ps are uncorrected. IR spectra (Perkin–Elmer Infracord, Model 137, as films or in CCl_4). Gas chromatography (Perkin–Elmer instrument, Model 116-E, equipped with thermistor detectors). TLC (according to Stahl; chromatoplates were developed with a mixture of cyclohexane and AcOEt (50:50) or phenol and water (80:80), spots being detected with I_2 vapour).

The preparation, drying and purity determination of $Pb(OAc)_4$ was described previously.[18,21] Starting amines were commercial products which were thoroughly dried and fractionated before use. Thiophene-free benzene, dried over Na, was used as solvent for the oxidations.

General oxidation procedure. The starting amine (0·1 mole) and the required amount of $Pb(OAc)_4$ (0·1 or 0·2 moles) in benzene (100–200 ml) were refluxed with stirring, until the oxidizing agent was completely consumed. After cooling to room temp, ether (100 ml) was added, the separated $Pb(OAc)_2$ removed by filtration and washed several times with ether; it was then dissolved in water and the aq soln was extracted with ether. The ethereal extracts and washings were added to the benzene–ether filtrate. The combined organic soln was washed successively with 3% HClaq, 5% $NaHCO_3$aq and H_2O, thus giving the *neutral part*. The HCl washings and the original aq soln containing $Pb(OAc)_2$ were combined, made strongly basic with NaOHaq and continuously extracted with ether; this ethereal extract represents the *basic part*. The *acid part* was obtained from the $NaHCO_3$ washings, upon acidification with HClaq and extraction with ether.

The resulting nitriles, fatty acids and recovered amines were identified on the basis of their physical constants (b.ps, refractive indices, IR spectra, gas chromatographic retention times) and by conversion to derivs.[22] Hydrolysis of nitriles to the corresponding carboxylic acids was effected by refluxing with a 5–8-fold excess of 60% H_2SO_4 for 3 hr.

The amount of $Pb(OAc)_4$ used in different runs (values in g and moles given below) are based on a product of 100% purity.

Primary amines

n-*Hexylamine*

Oxidation in benzene alone. (a) The reaction of n-hexylamine (10·1 g; 0·1 mole) with $Pb(OAc)_4$ (44·3 g; 0·1 mole) in benzene was complete after 30 min. In the acid part only AcOH was detected. From the basic part unreacted n-hexylamine was isolated in about 20% yield. Distillation of the neutral part gave two fractions; fraction I, b.p. 58° at 17 mm, was identified as pentyl cyanide (2·9 g, 30%), and fraction II, b.p. 120–125° at 3 mm, upon chromatography on SiO_2 (using as eluent different ratios of cyclohexane–AcOEt), afforded as major product N-hexylacetamide (0·6 g, 4%), which was identical with a synthetic product.[23] (Found: C, 67·7; H, 12·0; N, 9·9. Calc. for $C_8H_{17}NO$: C, 67·1; H, 12·0; N, 9·8%).

(b) The same reaction was repeated by using 2 molar equivs of $Pb(OAc)_4$ (88·7 g; 0·2 moles) per mole of n-hexylamine (10·1 g; 0·1 mole) in 200 ml benzene. The consumption of the oxidizing agent was complete after refluxing for 16 hr. In the acid part, in addition to AcOH, traces of caproic acid were detected. In the basic part only unreacted starting amine was present in small amounts. Distillation of the neutral part afforded 2 fractions; the first fraction, b.p. 58°/17 mm. consisted again of pentyl cyanide (3·95 g, 41%); the second fraction, b.p. 122–127°/3 mm, was chromatographed on SiO_2 and on elution with cyclohexane–AcOEt in different ratios gave N-*hexylcaproamide* (1·05 g, 5%). (Found: C, 71·7; H, 11·7; N, 6·8, $C_{12}H_{25}NO$ requires: C, 72·3; H, 12·6; N, 7·0%), which was identical with a synthetic product (see below), and N-hexylacetamide (1·7 g, 12%) identical with the amide isolated in oxidation (*a*) and with an authentic specimen.[23] In addition, the second fraction

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[20] We thank Mrs. R. Tasovac and Miss R. Dimitrijević, from the Microanalytical Laboratory of our Department, for the elemental microanalyses.

[21] M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, Lj. Lorenc and R. I. Mamuzić, *Tetrahedron* **21**, 2799 (1965).

[22] R. L. Shriner, R. C. Fuson and D. Y. Curtin, *The Systematic Identification of Organic Compounds* (5th Ed) J. Wiley, New York (1964); A. I. Vogel, *Practical Organic Chemistry* (3rd Ed) Longmans Green, London (1961).

[23] H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, *J. Amer. Chem. Soc.* **80**, 4588 (1958). See also L. G. Donaruma and M. L. Huber, *J. Org. Chem.* **21**, 965 (1956); B. Prajsnar and C. Troszkiewics, *Roczniki Chem.* **36**, 853 (1962).

contained traces of benzyl acetate and an acetoxylated nitrogen comp, which, according to its IR spectrum, might be a C-acetoxy-N-hexylidenehexylamine. The resinous residue of the distillation (2·8 g) was not investigated.

Oxidation in the presence of pyridine. The oxidation of n-hexylamine (10·1 g; 0·1 mole) with 0·1 mole (44·3 g) $Pb(OAc)_4$ in 100 ml benzene, in the presence of anhyd pyridine (32 g; 0·4 moles) was complete after refluxing for 30 min, and afforded 29% (2·8 g) pentyl cyanide and 2·5% (0·5 g) N-hexylcaproamide.

Oxidation in the presence of AcOH. (a) n-Hexylamine (10·1 g; 0·1 mole) was first treated with an equiv amount of glacial AcOH (0·1 mole) and then oxidized in refluxing benzene (100 ml) with 0·1 mole (44·3 g) $Pb(OAc)_4$, the reaction being complete after 1 hr. Distillation of the neutral part afforded 20% (2·0 g) pentyl cyanide and 15% (2·15 g) N-hexylacetamide; residue (not investigated) 3·75 g.

(b) The same amount of n-hexylamine acetate (0·1 mole) was oxidized with 0·2 moles (88·7 g) $Pb(OAc)_4$ in 200 ml benzene. Since even after 23 hr of refluxing the tetravalent lead reagent was not completely consumed, the reaction was stopped and unreacted $Pb(OAc)_4$ was decomposed with KI and $Na_2S_2O_3$.[34] Distillation of the neutral part gave 34% (3·34 g) pentyl cyanide, 10·5% (2·1 g) N-hexylcaproamide and 12% (1·75 g) N-hexylacetamide (residue 2·65 g).

Hydrolysis of N-*hexylacetamide and* N-*hexylcaproamide*. These products, obtained in various above described oxidations of n-hexylamine, were refluxed with 40% NaOHaq for 5 hr, and the reaction mixtures were worked up as usual. N-Hexylacetamide afforded n-hexylamine and AcOH, while N-hexylcaproamide gave n-hexylamine and caproic acid.

Preparation of N-*hexylcaproamide*. To an ice-cooled mixture of n-hexylamine (5·6 g) and 10% NaOHaq (30 ml), caproic acid chloride (7·6 g) was added dropwise, with constant stirring. After standing for 30 min at room temp, the reaction mixture was extracted with ether, the ethereal layer dried (Na_2SO_4) and distilled, to give 7·4 g (66%) of N-*hexylcaproamide*, b.p. 176–178°/12 mm.[35] (Found: C, 72·4; H, 12·7; N, 6·9. $C_{12}H_{25}NO$ requires: C, 72·3; H, 12·6; N, 7·0%.)

N-*Hexylcaproamide from* n-*pentyl cyanide and* n-*hexylamine*. Equivalent amounts of the reactants were refluxed in anhyd benzene for 16 hr (conditions approximating those of the oxidation reaction). The reaction mixture was washed successively with 3% HClaq, 5% $NaHCO_3$aq and H_2O. Distillation of the neutral soln afforded unreacted n-pentyl cyanide and a small residue whose IR spectrum was identical with that of N-hexylcaproamide obtained synthetically (see above) or from the $Pb(OAc)_4$ oxidation of n-hexylamine. When the same reaction was effected in the presence of an equiv amount of AcOH, chromatography on SiO_2 of the distillation residue afforded, in addition to small amounts of N-hexylcaproamide, also some N-hexylacetamide. (Found: C, 66·9; H, 12·0; N, 9·9. Calc. for $C_8H_{17}NO$: C, 67·1; H, 12·0; N, 9·8%.)

n-*Butylamine*

Oxidation in benzene. (a) The reaction of n-butylamine (10 g, 0·137 moles) with 1 equiv of $Pb(OAc)_4$ (60·7 g; 0·137 moles) in 100 ml refluxing benzene was complete after 40 min. Fractional distillation of the neutral part afforded 20% (1·9 g) of n-propyl cyanide, b.p. 94–98°/760 mm (residue 1·9 g).

(b) By oxidizing n-butylamine (10 g; 0·137 moles) with 2 equiv of $Pb(OAc)_4$ (121·5 g; 0·274 moles) in 200 ml benzene, the reaction was not over even after 43 hr of refluxing. Excess of the reagent was decomposed with KI and $Na_2S_2O_3$[34] and the reaction mixture worked up as usual. The total yield of n-propyl cyanide in the neutral part according to gas chromatography, amounted to 39% (3·72 g).

n-*Heptylamine*

Oxidation in benzene alone. (a) The oxidation of n-heptylamine (11·5 g; 0·1 mole) with 1 equiv of $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml refluxing benzene (reaction time 40 min) afforded, from the neutral part 32% (3·6 g) n-hexyl cyanide, b.p. 69–71°/15 mm (residue 1 g), and from the basic part 19·5% (2·25 g) unreacted starting amine.

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[34] M. Lj. Mihailović, Ž. Čeković and D. Jeremić, *Tetrahedron* **21**, 2813 (1965).

[35] B.p. 108–111°/0·07 mm was reported by R. F. Moore, *Polymer* **4**, 493 (1963).

(b) When n-heptylamine (11·5 g; 0·1 mole) was oxidized with 2 equiv of $Pb(OAc)_4$ (88·7 g; 0·2 moles) in 200 ml benzene, the reaction was complete after refluxing for 16 hr and distillation of the neutral part furnished n-hexyl cyanide in 62% yield (6·9 g) (residue 4·15 g).

Oxidation in the presence of $CaCO_3$. By oxidizing n-heptylamine (11·5 g; 0·1 mole) with 1 equiv $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml benzene, in the presence of anhyd $CaCO_3$ (12 g; 0·1 mole + 20% excess), dried *in vacuo* over P_2O_5 (reaction time 50 min), n-hexyl cyanide was obtained in 31% yield (3·45 g) (residue 1·1 g).

Oxidation in the presence of pyridine. (a) The yield of cyanide (31·5%; 3·5 g) was the same when the reaction of n-heptylamine (11·5 g; 0·1 mole) with $Pb(OAc)_4$ (44·3 g; 0·1 mole) was carried out in 100 ml benzene, in the presence of anhyd pyridine (15·8 g; 0·2 moles), the oxidation being complete after refluxing for 40 min.

(b) n-Heptylamine (8·5 g; 0·07 moles) was oxidized with 2 equiv of $Pb(OAc)_4$ (62·1 g; 0·14 moles) in 100 ml benzene and 100 ml dry pyridine at 60°, the reaction being complete after 30 min. Fractionation of the neutral part (6·27 g) afforded 65% (5·05 g) of n-hexyl cyanide, b.p. 75–76°/18 mm.

(c) The reaction with the same amounts of reactants was repeated in 50 ml benzene and 150 ml dry pyridine at room temp, whereby $Pb(OAc)_4$ was completely consumed after 12 hr. Distillation of the neutral part gave n-hexyl cyanide, b.p. 78–79°/19 mm, in 55% yield (4·27 g).

n-*Octylamine*

Oxidation in benzene alone. (a) From n-octylamine (12·9 g; 0·1 mole) and 1 equiv $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml benzene, after refluxing for 40 min, n-heptyl cyanide, b.p. 68°/13 mm, was obtained in 31·6% yield (3·95 g) (residue 1 g).

(b) The same reaction was repeated with 0·1 mole (12·9 g) n-octylamine and 2 equiv of $Pb(OAc)_4$ (88·7 g; 0·2 moles) in 200 ml refluxing benzene, the reaction being complete after 16 hrs. Distillation of the neutral part afforded n-heptyl cyanide in 60% yield (7·5 g) (residue 5·3 g).

Benzylamine

Thermal oxidation in benzene. (a) The reaction between benzylamine (10·7 g; 0·1 mole) and 1 equiv $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml benzene was complete after refluxing for 50 min. From the basic part 43% (4·64 g) unreacted benzylamine was isolated. Distillation of the neutral part gave a fraction (b.p. 68–71°/14 mm) which was subjected to gas chromatographic separation and identified as a mixture of benzonitrile (3·77 g; 36·6%) and benzaldehyde (0·22 g; 2%).

The same oxidation, but in the presence of dry pyridine (19 g; 0·2 moles + 20% excess), gave from the neutral part a fraction (4 g) containing 34% benzonitrile and 4% benzaldehyde (according to gas chromatography). When $CaCO_3$ (12 g; 0·1 mole + 20% excess), dried *in vacuo* over P_2O_5, was used as base instead of pyridine, the same oxidation afforded 41% benzonitrile and 4% benzaldehyde.

(b) The oxidation of benzylamine (10·7 g; 0·1 mole) with 2 equiv $Pb(OAc)_4$ (88·7 g; 0·2 moles) in refluxing benzene (200 ml) was complete after 12 hr. The fraction (6·5 g), b.p. 68–71°/14 mm, obtained by fractional distillation of the neutral part, was separated by gas chromatography to give 59% benzonitrile and 4% benzaldehyde. From the basic part unreacted benzylamine was isolated in 9% yield.

Photolytic oxidation in benzene. (a) A mixture of benzylamine (1·07 g; 0·01 mole) and $Pb(OAc)_4$ (8·9 g; 0·02 moles) in 200 ml benzene (+ 2 ml dry pyridine) was irradiated with stirring in a Pyrex vessel with a Hanau high pressure mercury lamp in a central water-cooled Pyrex jacket at 18° during 11 hr, after which time the reaction mixture gave a negative test for lead(IV) salts. Gas chromatographic separation of the neutral part (0·9 g) afforded 0·80 g (83%) of benzonitrile and 0·01 g (1%) of benzaldehyde.

(b) The same reaction with 1·07 g (0·01 mole) benzylamine and 3 equiv $Pb(OAc)_4$ (13·3 g; 0·03 moles) was interrupted after 16 hr. Decomposition of unreacted $Pb(OAc)_4$ with KI and $Na_2S_2O_3$[24] and usual working up of the reaction mixture afforded, upon chromatographic separation, 0·8 g (83%) of benzonitrile and 0·04 g (4%) of benzaldehyde.

Secondary arylalkyl amine

Dibenzylamine

Oxidation. (a) The reaction between dibenzylamine (19·7 g; 0·1 mole) and 1 equiv of $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml refluxing benzene was complete in 30 min. Fractional distillation of the neutral part gave a fraction (5 g), b.p. 64–67°/13 mm, which was identified as a mixture of benzaldehyde and benzonitrile, by comparison of IR spectra and retention times with those of ref. samples. Gas chromatographic separation and quantitative determination of benzaldehyde in the form of its 2,4-dinitrophenylhydrazone (m.p. 237°),[36] showed that benzaldehyde was formed in 30% yield (3·15 g) and benzonitrile in 13% yield (1·35 g). Upon distillation of the basic part two products were obtained, unreacted dibenzylamine, b.p. 80°/18 mm, in 32% yield (3·45 g) and N-benzylidenebenzylamine, b.p. 168°/14 mm, in 26·6% yield (3·45 g) (Found: N, 7·4. Calc. for $C_{14}H_{13}N$: N, 7·2%). N-Benzylidenebenzylamine was identical with a synthetic product, b.p. 167–168°/14 mm, obtained in 67% yield (13·1 g) from benzaldehyde (10·6 g; 0·1 mole) and benzylamine (10·7 g; 0·1 mole) in ethereal soln in the cold,[37] and when treated with Br_2 water in chf soln gave a crystalline tribromide (m.p. 148°)[38] which did not depress the m.p. of the tribromide obtained from the synthetic compd.

(b) By oxidizing dibenzylamine (19·7 g; 0·1 mole) with 2 equiv $Pb(OAc)_4$ (88·7 g; 0·2 moles) in 200 ml refluxing benzene, the reaction was complete in 2 hr. Distillation of the neutral part folllowed by gas chromatography of the fractions furnished benzonitrile (2·5 g; 24%), benzaldehyde (6·44 g; 69%) and, as residue, N-*benzylidene-α-acetoxybenzylamine* (XVII) (3·5 g; 14%); IR: 1739 and 1235 cm^{-1} (acetate), 1649 cm^{-1} ($-C=N-$); mol. wt. (determined from saponification value[33]): found 269, calc. 253 (Found: N, 5·2. $C_{16}H_{15}NO_2$ requires: N, 5·5%); by acid hydrolysis it is readily converted to benzaldehyde, ammonia and AcOH. From the basic part only N-benzylidenebenzylamine was isolated (1·2 g; 6%).

(c) Oxidation (b) was repeated, but without working up the reaction mixture with HCl and $NaHCO_3$. Direct distillation of the filtered benzene–ether soln (see *General procedure*) and gas chromatography of the fraction, b.p. 70–72°/13 mm, showed that benzaldehyde was present in about 11% yield [compared to the 60% yield in oxidation (b)], indicating that only part of the aldehyde was formed during the oxidation reaction itself, while the major part was liberated from derivatives of benzaldehyde (e.g. α,α-diacetoxytoluene XIX) in the course of the normal working up procedure.

Hydrolysis of N-*benzylidenebenzylamine.* The Schiff base (5·0 g; 0·025 moles), glacial AcOH (3·0 g; 0·05 moles) and anhyd $Pb(OAc)_2$ (8·0 g; 0·025 moles) were refluxed in anhyd benzene (100 ml) for 30 min (conditions approximating those of the oxidation reaction). Working up of the reaction mixture in the usual way afforded benzaldehyde, benzylamine and unchanged N-benzylidenebenzylamine in 30% yield (1·5 g).

Benzylamine and benzaldehyde, under the same reaction conditions, did not give detectable amounts of N-benzylidenebenzylamine.

Oxidation of N-*benzylidenebenzylamine*

The reaction of this Schiff base (19·5 g; 0·1 mole) with $Pb(OAc)_4$ (44·3 g; 0·1 mole) in 100 ml refluxing benzene was complete in 4·5 hr. The neutral products were identified as benzonitrile (4·9 g; 47·5%) and benzaldehyde (2·13 g; 20%), and the IR spectrum of the distillation residue (4·5 g) indicated the presence of N-benzylidene-α-acetoxybenzylamine. From the acid part PhCOOH was isolated in small amount (0·1 g), while the basic part afforded unchanged N-benzylidenebenzylamine in 13% yield (2·54 g).

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[37] A. T. Mason and G. R. Winter, *J. Chem. Soc.* **65**, 191 (1894).

[38] H. Franzen, H. Wegrzyn and M. Kritschewsky, *J. prakt. Chem.* **95** (2), 389 (1917).