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THE REACTION OF LEAD TETRAACETATE WITH UNSUBSTITUTED HYDRAZONES OF SOME AROMATIC KETONES AND ALDEHYDES*

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Abstract—N-Unsubstituted hydrazones of some aromatic ketones and aldehydes were found to react with lead tetraacetate giving the corresponding diazo compounds as primary reaction products, and the derived 1-monoacetoxy- and 1,1-diacetoxy-1-arylalkanes, as well as azines, as final products. The yields obtained depend on the stability of the diazo compound initially formed and on the experimental conditions employed (amount of lead tetraacetate, presence of acid or base). Mechanisms for the formation of products are discussed.

LEAD TETRAACETATE (hereafter referred to as LTA) has been reported to oxidize N-substituted ketohydrazones and other systems with the structural unit $>\dot{C}=N-NH-$ to stable or unstable α-acetoxyazo compounds (azoacetates) $R^1R^2C(OAc)N=NR^3$,[3-8] whereas N-substituted aldehyde hydrazones are converted either to heterocyclic compounds (when possible),[9, 10] or/and to N-acetyl hydrazide derivatives,[4, 10, 11] the latter products probably being formed via intermediate nitrilimines.[11]

Concerning the reaction of LTA with N-unsubstituted hydrazones, the only reported data, to our knowledge, are the conversion of hydrazones, such as $(F_3C)_2C=N-NH_2$, $(NC)_2C=N-NH_2$, etc, to the corresponding stable diazo compounds;[12] a brief statement about the possibility of oxidizing hydrazones to diacetoxyalkanes,[13] and two short communications dealing with the oxidation of some ketohydrazones,‡ particularly of the steroidal type,[14] which afford in this reaction as major products acetoxy-alkanes and alkenes.

As a part of our investigation of the action of lead tetraacetate on nitrogen-containing compounds,[2] we have now studied the reaction of this reagent with unsubstituted hydrazones of some aromatic ketones and aldehydes.§

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[‡] The communication by Barton *et al.*[14a] appeared during the preparation of the present paper for publication. The results of these authors, concerning the LTA oxidation of benzophenone hydrazone, are in general agreement with our own findings.

[§] Unsubstituted hydrazones are known to be relatively unstable compounds which can lose intermolecularly hydrazine to give the corresponding azines.[15] This is particularly true for hydrazones of simple aliphatic or alicyclic aldehydes and ketones, which are therefore rather difficult to prepare in a pure state.‡‖

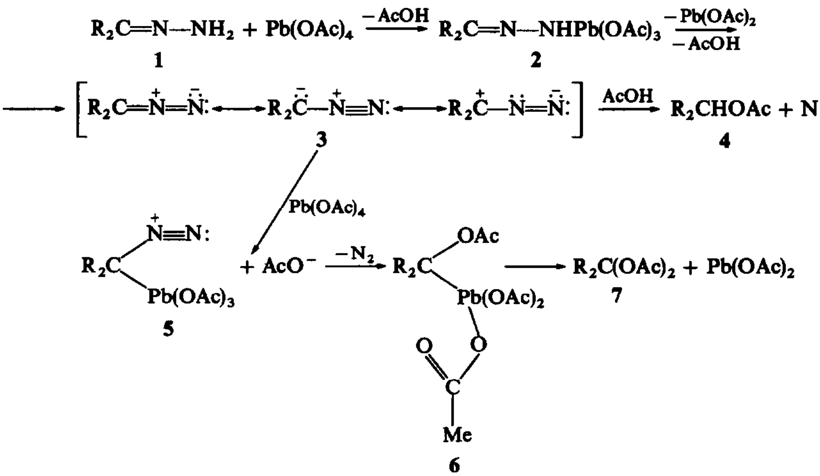
[‖] From the data reported on the preparation and properties of unsubstituted hydrazones,[16, 17] it was noticed that a parallel exists between the stability of hydrazones and their basicity which might be of some importance for a better understanding of their general behaviour.

When benzophenone hydrazone (I) was added to a benzene solution of LTA in a 1:2 molar ratio, a red-violet colouration was observed, which disappeared on further refluxing of the mixture. The neutral part of the reaction mixture afforded two compounds, which were identified as diacetoxydiphenylmethane (III, yield 25%) and monoacetoxydiphenylmethane (IV, yield 30%). When I was treated with LTA in a 1:1 molar ratio, the coloured intermediate was identified as diphenyldiazomethane (II) on the basis of its IR spectrum. Upon further addition of another LTA equivalent, the same reaction products III and IV were obtained. When I was oxidized with LTA in a 1:0·5 molar ratio, besides the acetoxylated products III and IV, unreacted I was isolated. In a repeated experiment, in which a reverse procedure was used (LTA was added to a benzene solution of I), the same reaction products (III and IV) were obtained. In none of these experiments could benzophenone azine be detected.

$$\underset{\text{I}}{Ph_2C{=}N{-}NH_2} \xrightarrow{Pb(OAc)_4} \underset{\text{II}}{Ph_2C{=}\overset{+}{N}{=}\overset{-}{\ddot{N}}:} \xrightarrow{Pb(OAc)_4} \underset{\text{III}}{Ph_2C(OAc)_2} + \underset{\text{IV}}{Ph_2CHOAc}$$

From the mechanism proposed for the LTA oxidation of amines,[2] the first step in the LTA-hydrazone reaction, as shown on Scheme 1, is the attack of LTA on the hydrazone **1**, leading to the formation of a hydrazone–lead–triacetate intermediate **2**, which, upon homolytic or heterolytic cleavage, gives rise to the diazoalkane **3**. It is more likely that heterolytic cleavage occurs, since free radical oxidation of I (with N-bromosuccinimide[18] or iodine[19]) is known to give the corresponding azine and does not involve the diazoalkane (II) as an intermediate.[20] Reaction of the diazoalkane **3** with acetic acid, liberated in the course of the LTA oxidation of the hydrazone **1** to diazoalkane **3**, would furnish the monoacetoxy compound **4**, whereas further attack of LTA on the diazoalkane **3**, possibly through intermediates of type **5** and **6** (or species with cationic character), would lead, with loss of nitrogen, to the diacetoxy compound **7**.*

SCHEME 1



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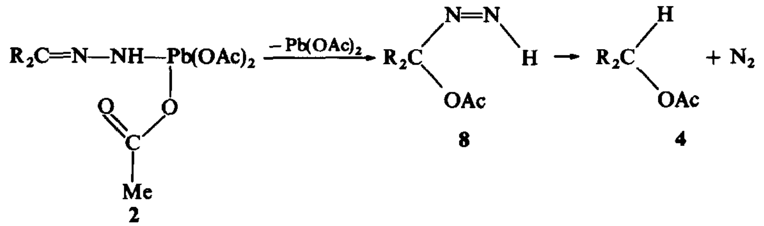
* The decomposition of diazoalkane 3 into nitrogen and carbene, which would react with acetic acid giving the monoacetoxy-alkane 4 and with LTA yielding the diacetoxy-alkane 7, does not seem probable, and attempts to trap the intermediate divalent carbon species were unsuccessful.

An alternative path for the formation of the monoacetate **4** may proceed via an intermediately formed azoacetate **8**, which loses nitrogen through a tetracentric transition state. However, this competing reaction course, if it occurs at all, must be of minor importance, since it does not involve the intermediacy of the diazoalkane **3**, whose existence was observed and confirmed in all experiments, and is not in accordance with the results of the oxidations described below.



In order to prove the proposed mechanism (Scheme 1; **1** → **4**, and **1** → **7**) we performed a series of LTA oxidations of benzophenone hydrazone (I) in methylene chloride, in the same solvent but in the presence of different amounts of pyridine, as well as in glacial acetic acid. The reaction mixtures were analysed by gas chromatography and the results obtained are summarized in Table 1. On the other hand, diphenyldiazomethane (II), prepared by oxidizing the hydrazone I with mercuric oxide, was also treated with LTA under various conditions, and the results of these experiments are given in Table 2.* In both cases the diacetoxydiphenylmethane (III) was identified in the form of its hydrolysis product benzophenone (V), since upon standing in (aqueous) acid III it is easily converted to V whereas the monoacetate IV remains unchanged. We also synthesized monoacetoxydiphenylmethane (IV) and treated it with one and two mole-equivalents of LTA in refluxing methylene chloride, in order to establish whether diacetoxydiphenylmethane (III) may (partly) arise from further LTA acetoxylation of the monoacetate IV. In this reaction the starting compound IV was recovered unchanged, thus confirming that the diacetoxyalkane III is most probably formed by direct action of LTA on the intermediate diazo compound II.

All data in Table 1 and Table 2 are consistent with steps **1** → **3**, **3** → **7** and **3** → **4** in Scheme 1. Therefore, contrary to the action of LTA on N-substituted ketohydrazones which leads to the initial formation of azoacetates,[3–5] our results indicate that with N-unsubstituted hydrazones of aromatic ketones and aldehydes (see below), the primary process consists in dehydrogenation. In oxidations carried out in the presence of pyridine, which acts as an acid scavenger, the yield of the monoacetate **4** (IV) decreases; a lower yield of **4** (IV) is also obtained in reactions with two molar equivalents of LTA, since the primarily formed diazoalkane **3** (see also II) can react further with LTA affording the diacetate **7** (i.e. III). In accordance with these results, the formation of the monoacetoxy compound **4** (i.e. IV) is favoured in pure glacial acetic acid. In the LTA oxidations of diphenyldiazomethane **3** (II), the diacetoxy compound **7** (III), i.e. the corresponding ketone (V), was always obtained as major product (Table 2); the formation of small amounts of monoacetate **4** (IV) may be ascribed to

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* The LTA oxidation of diazomethane and its diaryl substituted derivatives (of type **3**) to the corresponding diacetoxy compounds (of type **7**, has been reported previously in two cases.[13, 21]

Table 1. Reaction products obtained in the lead tetraacetate oxidation of benzophenone hydrazone (I) at room temperature

Oxidation system (moles per 1 mole of I)	Yields (in %)	
	$Ph_2C{=}O^a$ (V)	Ph_2CHOAc (IV)
LTA (1)—CH_2Cl_2	12	70
LTA (1)—CH_2Cl_2—UV	22·5	38·5
LTA (2)—CH_2Cl_2	44	45
LTA (2)—C_6H_6	32	48
LTA (1)—CH_2Cl_2—Pyridine (2)	24	40
LTA (1)—CH_2Cl_2—Pyridine (8)	diphenyldiazomethane (II)	
LTA (2)—CH_2Cl_2—Pyridine (2)	50	24
LTA (2)—CH_2Cl_2—Pyridine (8)	60	16
LTA (1)—AcOH	7	72
LTA (2)—AcOH	20	66

[a] Corresponds to the yield of diacetoxydiphenylmethane (III). The diacetate III was in most runs determined in the form of benzophenone (V), since it easily hydrolyses during the working upprocedure to ketone V and decomposes to the same ketone (V) upon gas chromatographic separation.

the action of acetic acid (generated by the decomposition of LTA in side reactions or by traces of moisture) on the diazoalkane **3** (II). When treated with two molar equivalents of acetic acid in methylene chloride, in the absence of LTA, diphenyldiazomethane (II, i.e. **3**) afforded quantitatively the monoacetate IV (**4**).

In the LTA oxidation of acetophenone hydrazone (VI) with a 1:1 molar ratio of reactants, in addition to the acetoxylated products X and XI, the nitrogen-containing compounds acetophenone azine (VIII) and N-acetylacetophenone hydrazone (IX) were also isolated. The primary formation of the corresponding diazoalkane VII was observed by the appearance of a red colouration, but the colour was unstable at room temperature and VII could not be proved spectroscopically.

The azine VIII, obtained in 22% yield, may be formed, in part, as the result of the dimerization of the diazoalkane VII (to product **9**) followed by loss of nitrogen,[22] but

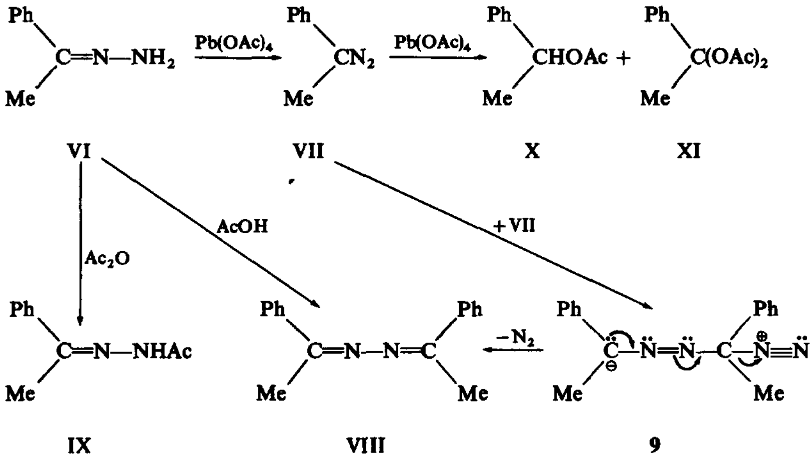
Table 2. Reaction products obtained in the lead tetraacetate oxidation of diphenyldiazomethane (II) at room temperature

Oxidation system (moles per 1 mole of II)	Yields (in %)	
	$Ph_2C{=}O^a$ (V)	Ph_2CHOAc (IV)
LTA (1)—CH_2Cl_2	64	11
LTA (1)—CH_2Cl_2—UV	64	11·5
LTA (2)—CH_2Cl_2	77	[b]
LTA (2)—CH_2Cl_2—Pyridine (8)	97	3

[a] See Remark *a*, Table 1.

[b] Not determined.

also—and probably to a greater extent—by isomerization of the starting hydrazone VI in the presence of (acetic) acid (liberated in the course of the reaction).[15, 16] The latter pathway is supported by the fact that in a repeated experiment (with a 1:1 molar ratio of reactants) in which the reverse procedure was used (slow addition of LTA to VI), thus decreasing the concentration of oxidizing agent in the course of the reaction and allowing prolonged contact of the substrate (VI) with the formed acetic acid, the yield of azine VIII increased to 53%. The N-acetylhydrazone IX possibly arises from acetylation of VI with acetic anhydride, which is known to be a by-product in various LTA oxidations.[2]



The formation of the diazoalkane 3, as the initial product, was proved by IR spectroscopy (ν_{max} 2020–2040 cm^{-1}) in the LTA oxidations of the hydrazones of *p*-nitroacetophenone and *p*-nitrobenzaldehyde (in benzene at room temperature with a 1:1 molar ratio of reactants). By addition of a few drops of triethylamine to the reaction mixture the yield of the corresponding diazoalkanes 3 was improved—in the case of *p*-nitrobenzaldehyde hydrazone it amounted to over 70%. This finding supports the assumption that the diazoalkane 3 arises by heterolytic decomposition of the initially formed hydrazone–lead triacetate intermediate 2. Other products obtained in these oxidations were azines and acetoxylated compounds. With two molar equivalents of LTA in refluxing benzene, *p*-nitroacetophenone hydrazone afforded the diacetoxy compound of type 7 in about 60% yield.

In the LTA oxidation of benzaldehyde hydrazone, performed with a 1:1 molar ratio of reactants, the main product was benzaldazine (over 55% yield), whereas by using two molar equivalents of LTA (per mole of hydrazone) a mixture of azine and benzaldehyde diacetate was obtained. In LTA oxidations of *o*-nitro- and *o*-hydroxybenzaldehyde hydrazones, the corresponding azines were isolated (in about 20% yield) together with resinous acetoxylated products. In these experiments, although a transitory change of colour upon mixing the reactants could be observed, the intermediate diazoalkanes (3) were too unstable to be proved by spectroscopic methods.

EXPERIMENTAL*

B.ps and m.ps are uncorrected. IR spectra: Perkin–Elmer Infracord, Models 137 and 337. NMR spectra: Varian A-60A spectrometer, solvent CCl_4 and $CDCl_3$. Gas chromatography: Perkin–Elmer instrument, Model 116-E, equipped with a thermistor detector; Carbowax was used for the separation of reaction products. TLC (according to Stahl): chromatoplates were developed with a mixture of cyclohexane and EtOAc, and spots were detected with I_2 vapour.

Hydrazones were prepared according to literature prodecures[16, 23] from hydrazine hydrate and the corresponding aldehydes and ketones.

Lead tetraacetate oxidation of benzophenone hydrazone (I). To a stirred soln of LTA (3·5 g, 0·008 mole) in 150 ml benzene, a benzene soln of I[16] (0·83 g, 0·004 mole) was added dropwise at room temp. The mixture turned violet-red and on refluxing the colour gradually faded. LTA disappeared after 2·5 hr. Anhyd ether was added and the mixture was worked up as described.[2] The neutral part[2] (0·4 g) was separated by column chromatography on silica gel; elution was performed with cyclohexane containing increasing amounts of EtOAc (up to 50%). The products obtained were III (0·2 g, 25%), m.p. 121°.[13] (Found: C, 72·0; H, 5·6. Calc. for $C_{17}H_{16}O_4$: C, 71·8; H, 5·6%), and IV (0·2 g, 30%), m.p. 40°.[24] (Found: C, 79·8; H, 6·2. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). Both compounds exhibited in their IR spectra maxima at 1730 and 1230 cm^{-1}, characteristic for the acetate group.

The presence of II in the crude reaction mixture was detected by IR spectroscopy (strong absorption at 2040 cm^{-1}).

The experiments summarized in Table 1 were carried out by adding the calculated amount of LTA, at room temp, to a methylene chloride soln of I (1·96 g, 0·01 mole) containing different amounts of dry pyridine, or to a soln of I in glacial AcOH. The reaction mixture was worked up as described,[2] except that the combined organic soln instead of being just washed with 3% HCl aq, was stirred with this aqueous acid for 10 hr, and the resulting neutral reaction products[2] were analysed by gas chromatography.

The LTA oxidations of II (Table 2), obtained by treating the hydrazone I with HgO,[13] were performed in the same way.

Lead tetraacetate oxidation of acetophenone hydrazone (VI). To a benzene soln of LTA (36·44 g, 0·08 mole), a soln of VI[19] (11·2 g, 0·08 mole) in the same solvent was added dropwise, at room temp, the consumption of LTA being completed upon addition (30 min). The neutral part[2] was first distilled (at 0·2 mm) and the crude fractions and residue obtained were separated by column chromatography on silica gel. Four out of five components were isolated. The azine VIII (0·4 g, 22%), m.p. and mixed m.p. 121°;[19] *1-acetoxy-1-phenylethane* (X), IR: 1724 (s) and 1235 (s) cm^{-1} for acetate, NMR: δ 1·68 (*s*, OAc) and δ 4·87 (CH). (Found: C, 73·6; H, 7·5. $C_{10}H_{12}O_2$ requires: C, 73·2; H, 7·3%); *1,1-diacetoxy-1-phenylethane* (XI). (Found: C, 64·4; H, 6·6. $C_{12}H_{14}O_4$ requires: C, 64·8; H, 6·4%); *N-acetylacetophenone hydrazone* (IX) was purified by sublimation, m.p. 132°, IR: 1660 cm^{-1} for amide, NMR: δ 1·95 (*s*, Me), δ 1·83 (*s*, Ac) and δ 7·4 (*s*, NH). (Found: C, 68·1; H, 7·0; N, 15·9. $C_{10}H_{12}ON_2$ requires: C, 68·2; H, 6·8; N, 15·9%); mol. wt. from saponification value, Found: 182; Requires: 176. Hydrolysis of IX afforded acetophenone (identified by TLC).

LTA (7·2 g, 0·015 mole) was added to a cooled soln of VI (2 g, 0·015 mole) in benzene. The yield of azine VIII, m.p. 120–121°,[19] was 53% (0·9 g). (Found: N, 12·1. Calc. for $C_{16}H_{16}N_2$: N, 11·8%).

Lead tetraacetate oxidation of p-*nitroacetophenone hydrazone*. This *hydrazone* was obtained in 90% yield by refluxing *p*-nitroacetophenone (2 g) with hydrazine hydrate (12 ml) in EtOH (20 ml) for 1 hr, m.p. 150°. (Found: N, 23·4. $C_8H_9N_3O_2$ requires: N, 23·4%). It was treated with LTA (1:1 molar ratio) in benzene at room temp, and the formation of the corresponding diazoalkane was followed by the IR absorption band at 2040 cm^{-1}. In the presence of 1–3 ml of Et_3N this band was strongly intensified, but the isolated product was not quite pure diazo compound, since it contained also some azine (proved by TLC).

From *p*-nitroacetophenone hydrazone (1 g, 0·005 mole), dissolved in a mixture of benzene (100 ml) and ether (20 ml), and LTA (4·8 g, 0·01 mole), an oil was obtained which solidified on standing. Recrystallization from ligroin afforded the *diacetate of* p-*nitroacetophenone*, m.p. 72°, IR: 1745 and 1250 cm^{-1}. (Found: C, 54·2; H, 5·0. $C_{12}H_{13}NO_6$ requires: C, 53·9; H, 4·9%).

Lead tetraacetate oxidation of benzaldehyde hydrazone and substituted benzaldehyde hydrazones. From benzaldehyde hydrazone (12 g, 0·01 mole), b.p. 132° at 9 mm,[25] and LTA (44·3 g, 0·1 mole) in 150 ml benzene, benzaldazine, m.p. and mixed m.p. 93°,[26] was obtained in 56% yield (11·7 g).

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o-Hydroxybenzaldehyde hydrazone[19] and *o*-nitrobenzaldehyde hydrazone[19] upon treatment with an equimolar amount of LTA in benzene afforded the corresponding azines, m.p. 212° [19] (Found: N, 11·4. Calc. for $C_{14}H_{12}N_2O_2$: N, 11·7%) and 105° [19] (Found: N, 19·1. Calc. for $C_{14}H_{10}N_4O_4$: N, 19·0%), respectively.

From *p*-nitrobenzaldehyde hydrazone[19] and different amounts of LTA in benzene, mixtures of diazo compound (IR: ν_{max} 2020 cm^{-1}), azine and acetoxylated products were obtained. In benzene alone and with a 1:1 molar ratio of reactants, the yield of diazo compound was low, but on addition of a few drops of Et_3N and by using more LTA (up to 2 equivs) the yield was increased up to 70–80%. (Found: N, 25·3. $C_7H_5N_3O_2$ requires: N, 25·8%).

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