182. *The Reaction of Lead Tetra-acetate with the Toluene-*p*- and Benzene-sulphonylhydrazone of Benzaldehyde.*

By Asharam Bhati.

Lead tetra-acetate reacts with benzaldehyde toluene-*p*- and benzene-sulphonylhydrazone to give the corresponding monoacetoxylated compounds (I) and (III). The reaction effects substitution at the benzylic carbon atom rather than at the nitrogen atom directly linked to the sulphonyl group. Lithium aluminium hydride reduction of the benzaldehyde and salicylaldehyde toluene-*p*-sulphonylhydrazone gives di-*p*-tolyl disulphoxide.

This reaction was studied in 1956 as a preliminary to an investigation of the lead tetra-acetate oxidation of the toluene-*p*-sulphonylhydrazones of some phenolic aldehydes. Quantitative estimations showed that the toluene-*p*-sulphonylhydrazone of benzaldehyde consumed, in glacial acetic acid medium, one mole of lead tetra-acetate during the first 10 min. No further reaction occurred in the next 12 hr. The reaction product was a crystalline compound, which from its reactions and spectral properties was found to be α-(toluene-*p*-sulphonylhydrazono)benzyl acetate (I). Thus (I) gave, on reduction with lithium aluminium hydride, *N*-toluene-*p*-sulphonyl-*N'*-benzoylhydrazine (II) and, on being heated with aqueous sodium hydrogen carbonate, benzaldehyde and toluene-*p*-sulphinic acid. In the infrared compound (I) showed bands at 3292 (NH), 1715 and 1264 (OAc), 1670 (C:N), 1164 and 1326 (SO_2·N) cm.$^{-1}$. That the 3292 cm.$^{-1}$ band was due to the NH stretching absorption was confirmed by deuterium exchange. In the spectrum of the deuterated compound (I) this band shifted to 2435 cm.$^{-1}$. In the ultraviolet spectrum (I) showed $\lambda_{max.}$ at 234 and 276 mμ (log ε, 4·40 and 3·50, respectively).

p-Me·C_6H_4·SO_2·NH·N:CPh·OAc (I)

p-Me·C_6H_4·SO_2·NH·HH·COPh (II)

Ph·SO_2·NH·N:CPh·OAc (III)

The benzenesulphonylhydrazone of benzaldehyde reacted similarly with lead tetra-acetate to yield α-(benzenesulphonylhydrazono)benzyl acetate (III), which is also a crystalline compound. The infrared and ultraviolet absorption characteristics (*vide* Experimental section) of compound (III) are similar to those of compound (I).

The mode of formation of compounds (I) and (III) is probably similar to that recently proposed [1] for the formation of the so-called " azo-acetates," AcO·CR^1R^2·N:N·Ph, from the phenylhydrazones of ketones and lead tetra-acetate.

During the present work it was also found that lithium aluminium hydride reduction of the toluene-*p*-sulphonylhydrazones of benzaldehyde and salicylaldehyde, under somewhat forcing conditions, leads to di-*p*-tolyl disulphoxide. This result evidently has some bearing on the mechanism of the recently reported [2] method of reducing ketones and aldehydes, *via* their toluene-*p*-sulphonylhydrazones, to the corresponding methylene compounds by $LiAlH_4$ or $NaBH_4$.

Experimental

Melting points are uncorrected, and were determined on a Kofler hot-stage apparatus. Ultraviolet spectra refer to 95% ethanol solution, and were determined on a Unicam S.P. 500 spectrophotometer. The infrared spectra were kindly determined by Dr. G. Eglington and his associates on Nujol mulls, and the elemental analyses carried out by Mr. J. M. L. Cameron and his staff. The sulphonylhydrazones were prepared by refluxing equivalent quantities of the components in ethanol for 10 min. The toluene-*p*-sulphonylhydrazone of benzaldehyde crystallized from ethanol

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

[2] L. Caglioti and P. Grasseli, *Chem. and Ind.*, 1964, 153.

in long shiny needles, m. p. 127—128°; $\nu_{max.}$ 3220 (NH), 1663 (C:N), 1166 and 1324 (SO_2·N) cm.$^{-1}$; $\lambda_{max.}$ 272 mμ (log ε, 4·28).

The benzenesulphonylhydrazone of benzaldehyde crystallized from benzene in small shiny needles, m. p. 110—112°; $\nu_{max.}$ 3212 (NH) and 1673 (C:N) cm.$^{-1}$, 1167 and 1327 (SO_2·N) cm.$^{-1}$; $\lambda_{max.}$ 274 mμ (log ε, 4·3) [lit.,[3] $\lambda_{max.}$ (EtOH) 275 mμ (log ε, 4·3)].

The toluene-*p*-sulphonylhydrazone of salicylaldehyde crystallized from ethanol in yellowish white prisms, m. p. 149—151°; $\nu_{max.}$ 3160 (NH or OH), 1615 (C:N), 1180 and 1330 (SO_2·N) cm.$^{-1}$; $\lambda_{max.}$ 275 (log ε, 4·15) (Found: C, 58·2; H, 5·1; N, 9·7; S, 10·8. $C_{14}H_{14}N_2O_3S$ requires C, 57·9; H, 4·9; N, 9·7; S, 11·0%).

The infrared spectra of the above-mentioned sulphonylhydrazones are complex. Only the bands due to the relevant groups NH, C:N, and SO_2·N are given here. The intensity of the NH band was medium and that of the C:N band was weak. The same remarks apply to the infrared spectra of their acetoxy-derivatives. There is however a great enhancement in the intensities of these bands in the acetoxy-compounds. Further, there is a shift in the frequencies of the NH band (see below). The SO_2·N bands were strong in all compounds.

*The Reaction of Lead Tetra-acetate with the Toluene-*p*-sulphonylhydrazone of Benzaldehyde* (*Experiment A*).—(*a*) *Quantitative estimation.* A known weight (*ca.* 20 mg.) of the sulphonylhydrazone was shaken at room temperature with 20 ml. of 0·05M-solution of lead tetra-acetate in A.R. glacial acetic acid. At regular intervals 1 ml. of the reaction mixture was withdrawn and treated with 10 ml. of an aqueous buffer solution (containing 20 g. of potassium iodide and 200 g. of sodium acetate trihydrate per litre), and the liberated iodine titrated with 0·02N-sodium thiosulphate. A blank experiment, using the same lead tetra-acetate solution, was run at the same time. In this way it was found that one mole of the toluene-*p*-sulphonylhydrazone of benzaldehyde consumed 0·9499 mole of $Pb(OAc)_4$ in the first 10 min.

(*b*) A suspension of the toluene-*p*-sulphonylhydrazone (1·46 g.) and 95·6% lead tetra-acetate (3·81 g.) in A.R. glacial acetic acid (50 ml.) was stirred at room temperature under anhydrous conditions. After about 10 min. the bulk of the solid in the reaction mixture increased considerably. Hence more acetic acid (50 ml.) was added and the mixture stirred for 16 hr. Anhydrous oxalic acid (0·26 g.), dissolved in absolute ether (25 ml.), was added in order to destroy the unused lead tetra-acetate. The resultant white slurry was filtered, and the precipitate (2·6 g.) thoroughly extracted with boiling ethyl acetate. The ethyl acetate extract gave, on concentration and subsequent cooling, shiny white plates (1·10 g., yield 62%), m. p. 190—192°. The product melted at 192° on recrystallization from the same solvent (Found: C, 57·8; H, 4·7; N, 8·4; S, 9·1; Ac, 13·4. $C_{16}H_{16}N_2O_4S$ requires C, 57·8; H, 4·8; N, 8·4; S, 9·6; Ac, 13·0%). Its spectral data have already been mentioned in the introduction.

Lithium Aluminium Hydride Reduction of Compound (I).—The acetoxy-compound (243 mg.), from experiment A, and a slurry of lithium aluminium hydride (315 mg.) in absolute ether (50 ml.) were heated under anhydrous conditions for 8 hr. in such a way that ether refluxed gently. The reaction mixture was cooled and treated with moist ether (20 ml.) and ice-cold water (20 ml.). The resultant mixture was filtered and the precipitate washed with ether (25 ml.). The filtrate and washings were combined, and the ether layer separated. This was washed with water (20 ml.), dried (Na_2SO_4) and the ether removed; a small amount of a gum was obtained. This was not examined. The precipitate and the aqueous layer from the filtrate were combined, and the mixture cooled in ice and then acidified with 6N-hydrochloric acid. The organic material so liberated was thoroughly extracted with ether (150 ml.). The ether extract gave on usual work-up a crystalline solid (194 mg.; yield, 90%), m. p. 160—164°. It crystallized from ethanol in long shiny plates, m. p. 165—167° (Found: C, 58·2; H, 4·9; N, 10·0. $C_{14}H_{14}N_2O_3S$ requires C, 57·9; H, 4·8; N, 9·7%). Its mixed m. p. and infrared and ultraviolet spectra were identical with those of an authentic sample, m. p. 165—167°; $\nu_{max.}$ 3305 and 3220 (NH), 1678 (CO), 1166 and 1328 (SO_2·N) cm.$^{-1}$; $\lambda_{max.}$ 226 mμ (log ε, 4·17), prepared by heating equivalent quantities of benzoyl chloride and tolene-*p*-sulphonylhydrazine in ethanol.

Treatment of Compound (I) *with Sodium Hydrogen Carbonate.*—The acetoxy-compound (203 mg.), from experiment A, was heated with an aqueous saturated solution (50 ml.) of sodium hydrogen carbonate for 10 min., and then steam-distilled. The distillate (75 ml.), possessing a characteristic smell, was treated with a solution of 2,4-dinitrophenylhydrazine (225 mg.) and concentrated sulphuric acid (2 ml.) in absolute ethanol (25 ml.). To the resultant mixture

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[3] P. Grammaticakis, *Bull. Soc. chim. France*, 1952, 446.

aldehyde-free ethanol (400 ml.) was added till a clear red solution resulted. This was then concentrated to about 25 ml. On filtration of the concentrate, and subsequent washing of the precipitate with absolute ethanol (2 × 5 ml.), an orange-red solid (112 mg., yield 98%), m. p. 234—236°, was obtained. It crystallized from ethanol in shiny orange crystals, m. p. 236°, identical with mixed m. p. with an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde.

The alkaline solution, left after steam-distillation, gave on acidification with hydrochloric acid, and subsequent extraction with ether, a white solid (47 mg., yield 79%). This was dissolved in ethanol (5 ml.), neutralized with dilute sodium hydroxide, and then treated with 1-chloro-2,4-dinitrobenzene (61 mg.). The mixture was heated under gentle reflux for 10 min. The solvent was then distilled off, and the residual mixture treated with water (10 ml.) and extracted with ether (75 ml.). The ether extract gave a yellowish white solid (72 mg.), m. p. *ca.* 176°. On recrystallization from ethanol it gave shiny yellowish prisms, m. p. 184—186°; $\nu_{max.}$ 1543 and 1533 (NO_2), 1161 and 1308 (SO_2) cm.$^{-1}$. The m. p. and infrared spectrum of this compound agree with those of the 2,4-dinitro-*p*-tolyl sulphone,[4] m. p. 187°.

Deuterium Exchange.—This was carried out by dissolving the acetoxysulphonylhydrazone (*ca.* 250 mg.) in hot dry dioxan (25 ml.) and then letting the solution stand with deuterium oxide (2 ml.) at room temperature for 1 hr. The deuterated product was obtained by removal of the solvents *in vacuo* (water pump) and subsequent drying of the precipitate over phosphorus pentoxide at 80°/0·2 mm. The product from the acetoxy-compound (I) melted at 186—187°, and that from compound (III) at 178—179°. Both deuterated compounds showed the ND band at 2435 cm.$^{-1}$.

*Lithium Aluminium Hydride Reduction of the Toluene-*p*-sulphonylhydrazone of Benzaldehyde.*—This was carried out under a variety of experimental conditions, and with the aim of reducing the carbon–nitrogen double bond. At 0° no reduction took place and when the reaction mixture was heated to *ca.* 50° an oily product was obtained. The experiment in which di-*p*-tolyl disulphoxide was obtained was carried out as follows. A mixture of the toluene-*p*-sulphonylhydrazone of benzaldehyde (545 mg.), lithium aluminium hydride (865 mg., *ca.* 11 molar equivalent) and absolute ether was stirred under anhydrous conditions at room temperature for 6 hr. The reaction mixture was cooled in ice and treated successively with ice-cooled moist ether (40 ml.) and ice-water (2 ml.). The ether was then removed *in vacuo* (water pump) and the residual mixture acidified with 12N-hydrochloric acid (16 ml.). On extraction with ether (5 × 50 ml.) a yellowish white solid (306 mg.) mixed with some oily product was obtained. This was chromatographed over silica gel, using a mixture of ether and light petroleum (b. p. 40—60°) (in 1 : 3 ratio) for eluating the column. The eluate (200 ml.) gave a solid (250 mg., yield 90·4%) which crystallized from the same solvent mixture in white plates, m. p. 73—75°, which showed a tendency to turn brown on exposure to air (Found: C, 59·8; H, 5·2; N, 0; S, 22·3. Calc. for $C_{14}H_{14}O_2S_2$: C, 60·4; H, 5·1; S, 23·0%). Its elemental analysis, m. p., and infrared spectrum [$\nu_{max.}$ 1308, 1161 (SO_2) cm.$^{-1}$] agree with those of the di-*p*-tolyl disulphoxide,[5] m. p. 76°.

The toluene-*p*-sulphonylhydrazone of salicylaldehyde gave similarly the di-*p*-tolyldisulphoxide.

The Reaction of Lead Tetra-acetate with the Benzenesulphonylhydrazone of Benzaldehyde.—This was carried out just as described in experiment A, with 2 g. of benzenesulphonylhydrazone, 5·4 g. of 95·6% lead tetra-acetate and 50 ml. of glacial acetic acid. The crude acetoxy-compound (2·0 g., yield 82%), m. p. 182—184°, crystallized from ethyl acetate in small shiny prisms, m. p. 186—187°; $\nu_{max.}$ 3276 (NH), 1721 and 1264 (OAc) and 1670 (C:N), 1160 and 1320 (SO_2·N) cm.$^{-1}$; $\lambda_{max.}$ 228 and 268 mμ (log ε, 4·30 and 3·38, respectively) (Found: C, 56·3; H, 4·7; N, 9·1; Ac, 14·0. $C_{15}H_{14}N_2O_4S$ requires C, 56·6; H, 4·4; N, 8·8; Ac, 13·5%).

*The Reaction of Lead Tetra-acetate with the Toluene-*p*-sulphonylhydrazone of Salicylaldehyde.*—Quantitative estimations, performed as described earlier, showed that one mole of the toluene-*p*-sulphonylhydrazone of salicylaldehyde consumed 2·26 moles of lead tetra-acetate in 1 hr. and 3·51 moles in 24 hr.

Attempts to prepare the corresponding acetoxy-compound by the procedure described in experiment A led to a brown intractable gum. Hence the reaction was not studied further.

[4] J. D. Loudon, *J.*, 1935, 537.

[5] R. Otto, J. Lowenthal, and A. von Gruber, *Annalen*, 1869, **149**, 101; see also B. N. Trivedi, *J. Indian Chem. Soc.*, 1956, **33**, 359.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, GLASGOW W.2.
[Present address: DEPARTMENT OF CHEMISTRY AND BIOLOGY, COLLEGE OF TECHNOLOGY, BYROM STREET, LIVERPOOL 3.]

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