

Oxidations of Some Mono- and Bis-(toluene-*p*-sulphonyl)hydrazones with Mercury(II) and Lead(IV) Acetates: Interception of Hydrazono-metallo Intermediates. Reactions of Mercury(II) Acetate with Nitrogen Compounds. Part 2

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Oxidation of benzil bis(toluene-*p*-sulphonyl)hydrazone with either mercury(II) or lead(IV) acetates in acetic acid gave 4,5-diphenyl-1,2,3-triazol-1-yltoluene-*p*-sulphonamide. An unstable hydrazono-mercury acetate intermediate was isolated from the mercury(II) reaction and it provided a model for previously postulated lead-hydrazono intermediates. Treatment of benzil toluene-*p*-sulphonylhydrazone with lead(IV) acetate in acetic acid gave *O*-acetylbenzoin in a reaction involving phenylbenzoyldiazomethane as an intermediate. Treatment of the mono-hydrazone with mercury(II) acetate gave bis[benzil toluene-*p*-sulphonylhydrazino]mercury. Regeneration of the ketone from benzophenone toluene-*p*-sulphonylhydrazone on treatment with lead(IV) acetate in acetic acid was confirmed.

THE mercury(II) and lead(IV) ions constitute a pair of comparable isoelectronic oxidising agents of which the lead species [$E^\circ(\text{Pb}^{2+}/\text{Pb}^{4+}) = -1.6 \text{ v} - 1.75$] is stronger [$E^\circ(\frac{1}{2}\text{Hg}^{2+}/\text{Hg}^{2+}) = -0.91$].¹ The acetate salts of these ions are widely used in organic synthesis and they often give comparable reactions.² A feature of mercury(II) acetate reactions, not common with lead(IV), is the frequent detection of stable organomercury intermediates or compounds. We have previously³ compared the reactions of some aldehyde hydrazones with lead(IV) and mercury(II) acetates in an attempt to isolate mercury intermediates since these should compare with the postulated^{4,5} corresponding lead intermediates which cannot be isolated or directly detected.⁵ However, different reactions were observed with both reagents and a mechanistic comparison was not possible. Herein, we report a cyclisation of a bis(hydrazone) which is effected by both reagents and in which a hydrazono-mercury intermediate has been detected. Bis(hydrazones)^{6,7} and osazones^{8,9} have been oxidised with a variety of metal-containing oxidising agents. These reactions usually result in a cyclisation or a dehydrogenation to a bis(azoethylene)-type product. There are

few mechanistic data on the reactions and metallo-intermediates have not been detected previously¹⁰ for either bis- or mono-hydrazone oxidations.

RESULTS AND DISCUSSION

(a) *Reactions with Benzil Bis(toluene-*p*-sulphonyl)-hydrazone.*—Benzil bis(toluene-*p*-sulphonyl)hydrazone (I) has a number of possible geometric isomers. For the corresponding bis(phenylhydrazone) three forms have been detected.⁸ One form only of biacetyl bis(phenylhydrazone) has been reported.¹¹ A sample of compound (I), prepared either directly from benzil¹² or from the monohydrazone, showed only one form. Its i.r. spectrum showed a sharp NH singlet at 3210 cm^{-1} and its ¹H n.m.r. spectrum (CDCl₃), showed one NH signal at δ 7.52 (confirmed by deuteration). No low-field signals at δ 12–15,^{13,14} or i.r. NH doublet patterns, expected for intramolecular hydrogen-bonded forms were detected. The ¹³C spectrum (CDCl₃) showed one C=N signal at 145.8 p.p.m. The compound is, therefore, assigned structure (I). It may contain imino *E-Z* isomers, which interconvert.

* Part I is ref. 3.

¹ A. Berka, V. Dvorak, I. Nemeč, and J. Zyka, *J. Electroanal. Chem.*, 1962, **4**, 150; S. Glasstone, 'Textbook of Physical Chemistry,' MacMillan and Co. Ltd., London, 1960, p. 950.

² W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 35; R. N. Butler, in 'Synthetic Reagents,' ed. J. S. Pizey, Ellis Horwood Ltd., Chichester, 1977, **3**, 277.

³ R. N. Butler and W. B. King, *J.C.S. Perkin I*, 1976, 986.

⁴ M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone, *J. Chem. Soc. (C)*, 1967, 735; W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc. (C)*, 1969, 2587.

⁵ R. N. Butler and W. B. King, *J.C.S. Perkin I*, 1977, 282.

⁶ (a) N. E. Alexandrou and S. Adamopoulos, *Synthesis*, 1976, 482; (b) N. E. Alexandrou and E. D. Micromastoras, *J. Org. Chem.*, 1972, **37**, 2345.

⁷ H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and V. Vaciago, *J.C.S. Perkin II*, 1972, 662, and references therein.

⁸ R. B. Woodward and C. Winter, *Tetrahedron Letters*, 1969, 2697.

⁹ For a review see H. El Khadem, *Adv. Carbohydrate Chem.*, 1965, **20**, 139.

¹⁰ A preliminary report, R. N. Butler, and A. B. Hanahoe, *J.C.S. Chem. Comm.*, 1977, 622.

¹¹ O. L. Chapman, R. W. King, W. J. Welstead, and T. J. Murphy, *J. Amer. Chem. Soc.*, 1964, **86**, 4968.

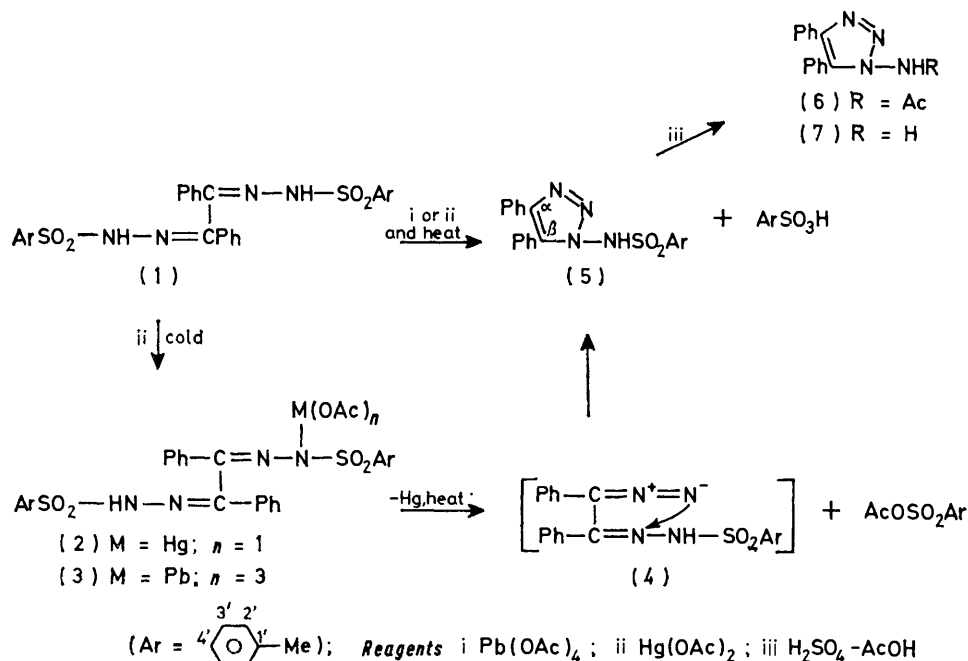
¹² W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.

¹³ A. D. Mitchell and D. C. Nonhebel, *Tetrahedron Letters*, 1975, 3859.

¹⁴ J. Elguero, R. Jacquier, and G. Tarrago, *Bull. Soc. chim. France*, 1966, 2981.

When compound (1) was heated under reflux in acetic acid with an equimolar quantity of mercury(II) acetate, the cyclised product (5) (92%) (Scheme 1) was obtained

anhydride of acetic and toluene-*p*-sulphonic acids, the latter of which would subsequently give the sulphonic acid (Scheme 1). Rapid internal cyclisation of the

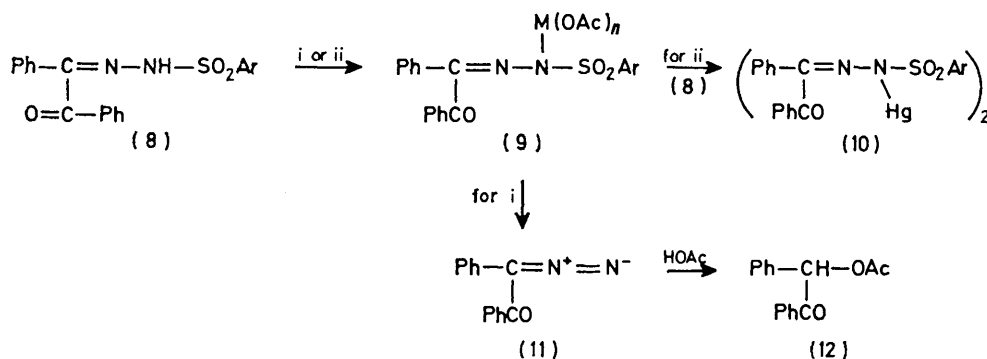


SCHEME 1

along with toluene-*p*-sulphonic acid and mercury. The triazolylsulphonamide (5) (72%), accompanied by lead salts of toluene-*p*-sulphonic acid, was also obtained by heating compound (1) with lead tetra-acetate (LTA) in acetic acid at 60 °C for *ca.* 6 h. When the reaction with mercury(II) acetate was carried out at ambient temperature, an unstable mercurio-intermediate (2) (80%)

intermediate (4) (Scheme 1) gives the triazole (5). Such cyclisations are known and in some cases they have been slowed to measurable rates by special substituents.¹⁵

(b) *Reactions with Benzil Mono(toluene-*p*-sulphonyl)-hydrazone.*—The monohydrazone (8) also showed only one form in solution. The ¹H n.m.r. spectrum (CDCl₃) showed one NH signal at δ 8.32 and the ¹³C spectrum

SCHEME 2 Reagents: i, Pb(OAc)₄; ii, Hg(OAc)₂

was isolated. Separate heating of compound (2) in acetic acid gave the cyclised product (5) (70%) together with mercury and gums containing toluene-*p*-sulphonic acid. These results suggest that the corresponding lead species (3) was an intermediate in the LTA cyclisation. The results for the comparable reactions with the monohydrazone suggest that the conversion of the intermediate (2) into compound (5) involves a fragmentation in which the metal is reduced and the diazo intermediate (4) is generated possibly along with the mixed

(CDCl₃) showed one C=N signal at 144.9 p.p.m. In solution it is comparable to benzil monophenylhydrazone (NH, δ 7.9–8.1, CDCl₃) which is reported¹⁶ to exist in one form only in which there is no intramolecular hydrogen bonding. The form (8), therefore, appears to be that entering the reactions. However, the i.r. spectrum (solid state) showed an NH doublet at 3 200

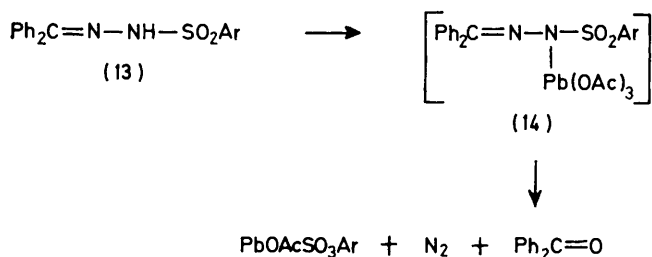
¹⁵ G. Himbert and M. Regitz, *Annalen*, 1973, 1505.

¹⁶ H. S. El Khadem, G. P. Kreishman, and E. H. El Ashry, *J. Org. Chem.*, 1975, **40**, 3149.

and $3\ 220\ \text{cm}^{-1}$ and there may be some intramolecular hydrogen bonding in the solid.

When compound (8) was treated with LTA (1 mol. equiv.) in acetic acid for 1.5 h at $60\ ^\circ\text{C}$, the products were *O*-acetylbenzoin (12) (80%) and lead salts of toluene-*p*-sulphonic acid. In this reaction the diazo-compound (11) was a precursor to compound (12) (Scheme 2). This was proved by removing acetic acid by using as solvent dichloromethane containing 3 mol. equiv. of triethylamine per mol. equiv. of acetic acid expected to be formed. Treatment of the hydrazone (8) with LTA in this solvent gave a deep red solution which, after it had been washed with water and the solvent removed, gave an oily residue showing intense i.r. absorptions at $2\ 080$ and $1\ 750\ \text{cm}^{-1}$; the latter were assigned to compound (11). This residue, when warmed separately in acetic acid, gave compound (12) in a well known¹⁷ reaction of diazo-compounds. These results support the presence of the intermediate (4) in the reactions of compound (1). The reaction of mercury(II) acetate with the hydrazone (8) followed a different path (Scheme 2), presumably due to the greater stability of the intermediate (9; $M = \text{Hg}$; $n = 1$). Instead of fragmentation this intermediate attacked a further molecule of parent hydrazone giving a quantitative yield of the bis(hydrazonomercurial) (10). As expected, compound (10) was obtained in quantitative yield when either a 1 or 0.5 mol. equiv. of mercury(II) acetate was used.

Compound (8) is a ketone toluene-*p*-sulphonylhydrazone and its behaviour with LTA is unusual since such hydrazones are reported¹⁸ to cleave to the parent ketone and an unidentified product containing sulphur and no nitrogen. The reaction was re-examined for benzophenone toluene-*p*-sulphonylhydrazone (13). Treatment of this compound with LTA in acetic acid at ambient temperature caused an immediate and brisk evolution of nitrogen and concomitant separation of lead acetate toluene-*p*-sulphonate (Scheme 3). In agreement



SCHEME 3

with the previous work¹⁸ the solution contained benzophenone in 88% yield. From the present results and those reported,³ it is likely that this reaction involves the intermediate (14) (Scheme 3). This undergoes an interesting fragmentation which is fundamentally different from that of the benzil derivatives. It may involve

¹⁷ A. Stojilkovic, N. Orbovic, S. Sredojevic, and M. Lj. Mihailovic, *Tetrahedron*, 1970, **26**, 1101; D. H. Barton, J. F. McGhie, and P. L. Batten, *J. Chem. Soc. (C)*, 1970, 1033.

an acetoxy-migration to the methine carbon, as suggested,¹⁸ but, however, since replacement of a phenyl by a benzoyl group at this carbon should enhance rather than inhibit such a nucleophilic migration, a solvolytic fragmentation seems more likely.

(c) *Structure Determinations.*—The structure of compound (5) needs to be distinguished from possible dimeric structures and also from a dihydrotetrazine structure since, until recently,^{6,7} oxidation products of some bis(acylhydrazones) were thought to be dihydrotetrazines. The mass spectrum eliminated dimeric products with a strong molecular ion peak, $M^+ 390$, and also an $(M - 1)$ peak both readily identified by the expected satellite intensities due to the sulphur isotopes. A dihydrotetrazine structure was eliminated by its remarkable stability. The compound was recovered from concentrated hydrochloric acid–acetic acid (1 : 1 v/v) after 24 h under reflux and also from a mixture of concentrated sulphuric acid–acetic acid (3 : 5 v/v) after 1 h at $60\ ^\circ\text{C}$, a procedure specially recommended¹⁹ for cleavage of resistant sulphonamides. However, a cleavage giving the acetyl derivative (6) was ultimately achieved when the temperature of the sulphuric acid–acetic acid mixture was held carefully at 120 – $140\ ^\circ\text{C}$ for 45 min. Compound (6), which presumably arose due to the formation of acetic anhydride under the extreme conditions, was separately cleaved, by concentrated hydrochloric acid, to the known amine (7) identified from an authentic sample.^{6a} Compound (12) was identified by comparison with a sample obtained by acetylation of benzoin. Compounds (2) and (10) regenerated the parent hydrazones (1) and (8) respectively when they were stirred in dilute hydrochloric acid at ambient temperatures. I.r. spectra and ^1H and ^{13}C n.m.r. spectra (Experimental section) were consistent with the assigned structures.

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured for KBr discs or mulls with a Perkin-Elmer 377 grating i.r. spectrophotometer. ^1H and ^{13}C n.m.r. spectra were measured at probe temperatures (Me_4Si as reference) with a JEOL JNM-100 or CFT-20 spectrometer. The substrates (1), (8), and (13) were prepared by literature^{12,20} procedures.

(i) *Reactions of Benzil Bis(toluene-*p*-sulphonyl)hydrazone (1).*—(a) A mixture of the hydrazone (1) (546 mg) and acetic acid (20 ml) containing acetic anhydride (0.5 ml) was treated with LTA (487 mg) and stirred at ambient temperature for 1 h and then for 6 h at $60\ ^\circ\text{C}$ after which lead toluene-*p*-sulphonate salts were removed. The yellow solution was brought to 200 ml with water and extracted while cloudy with ether (4×50 ml). The combined ethereal extract, after washing with water and dilute sodium carbonate solution, was dried and on evaporation yielded *N*-(4,5-diphenyl-1,2,3-triazol-1-yl)toluene-*p*-sulphonamide (5) (285 mg, 72%), m.p. 224 – $226\ ^\circ\text{C}$ [from chloroform–pentane (b.p. 40 – $60\ ^\circ\text{C}$)] and a yellow gum (Found:

¹⁸ A. Bhati, *Chem. Comm.*, 1965, 476.

¹⁹ P. D. Carpenter and M. Lennon, *J.C.S. Chem. Comm.*, 1973, 664.

²⁰ F. L. Scott and R. N. Butler, *J. Chem. Soc. (C)*, 1966, 1202.

C, 64.2; H, 4.6; N, 14.35. $C_{21}H_{18}N_4O_2S$ requires C, 64.6; H, 4.6; N, 14.2%; ν_{\max} (mull or KBr disc) 3 400br, vw (NH), 1 160—1 170, and 1 360—1 380 cm^{-1} (SO_2); mass spectrum, m/e (intensity %, obs., calc.), M^+ , 390 (100), 391 (32.5, 32.9), 392 (8.8, 7.5), and 389 (115); 1H n.m.r. $\delta[(CD_3)_2SO]$ 2.40 (3 H, *p*-Me) and 7.28—7.60 (14 H, Ar); ^{13}C n.m.r. [$CDCl_3$: $(CD_3)_2SO$] 3:1 v/v] δ 21.0 (*p*-Me), 126.4—130.0 (Ar), 134.5 (5-Ph, C-1'), 144.5 (tosyl, C-4'), 135.5 (tosyl, C-1'), 142.0 (C $^\alpha$), and 125.7 (C $^\beta$). The compound was unchanged when heated for 24 h under reflux in a mixture of concentrated hydrochloric acid and acetic acid (1:1 v/v).

(b) A mixture of the hydrazone was treated with mercury(II) acetate (318 mg) and heated under reflux for 2 h. The yellow solution was decanted free of mercury, cooled, and then treated with water to give compound (5) (360 mg, 92%). Evaporation of the aqueous filtrate yielded toluene-*p*-sulphonic acid and some gums.

(c) When a similar mixture of the hydrazone (1) and mercury(II) acetate (318 mg) was stirred at ambient temperature for 16 h, a white precipitate of unstable *N*-acetoxymercurio-*N*-toluene-*p*-sulphonylhydrazonobenzil toluene-*p*-sulphonylhydrazone (2), separated (643 mg, 80%), m.p. 173—175 °C (washed with cold ether; mild heating in organic solvents caused partial cyclisation) (Found: C, 45.5; H, 3.65; N, 7.5. $C_{30}H_{28}HgN_4O_6S_2$ requires C, 44.7; H, 3.5; N, 7.0%). ν_{\max} 3 220 (NH), 1 645 (HgOAc, C=O), 1 620, 1 600 (C=N), 1 150—1 170, and 1 360—1 370 cm^{-1} (SO_2). 1H N.m.r. $\delta[(CD_3)_2SO]$ 1.90 (3 H, HgOAc), 2.40 (6 H, *p*-Me), 7.28—7.48 (15 H, Ar including NH), and 7.60 (4 H, ds overlapping, ts HC-3'); ^{13}C n.m.r. $\delta[(CD_3)_2SO]$ 21.05 (OAc, *p*-Me), 126.2—130.3 (Ar), 135.6 and 133.4 (Ph, C-1, C-1'), 136.4 and 133.6 (ts, C-1, C-1'), 143.2 (ts, C-4, C-4'), and 145.8 (C=N). Compound (2) when stirred in dilute hydrochloric acid at ambient temperature gave the hydrazone (1) and a solution containing Hg^{II} ion. Compound (2) (500 mg) was heated for 2 h under reflux in acetic acid (20 ml) and the cooled solution was decanted free of mercury, treated with water (130 ml), and extracted with ether (4 × 40 ml) to give the triazole (5) (172 mg, 70%). Evaporation of the aqueous solution gave toluene-*p*-sulphonic acid and some gums.

(d) *Cleavage of the Diphenyl-1,2,3-triazol-1-ylsulphonamide* (5).—A mixture of compound (5) (500 mg) concentrated sulphuric acid (3 ml) and glacial acetic acid (5 ml) was heated at 120—140 °C for 45 min (higher temperatures caused charring and decomposition), cooled, and treated with water whereupon the acetyl derivative (6) (352 mg, quantitative yield) separated, m.p. 249—251 °C (Found: C, 69.2; H, 4.8; N, 19.85. $C_{16}H_{14}N_4O$ requires C, 69.05; H, 5.0; N, 20.1%). This compound (10 mg) when heated with acetic anhydride (1 ml) and acetic acid (1 ml) gave the diacetyl derivative, m.p. 173—175 °C (Found: C, 67.4; H, 4.7; N, 17.5. $C_{18}H_{16}N_4O_2$ requires C, 67.5; H, 5.0; N, 17.5%) which was also obtained directly by similar acetylation of the amine (7). A mixture of the derivative (6) (90 mg) and concentrated hydrochloric acid (5 ml) was heated under reflux for 3 h, cooled, brought to 40 ml with water, and subsequently to pH 7 with sodium hydroxide (10%); it was then extracted with chloroform (3 × 20 ml). The combined chloroform extracts were evaporated to 6 ml and treated with pentane (40—60 °C) to give the amine (7) (48 mg, 62%), m.p. 126—128 °C (lit.,^{6a} 126—128 °C) (identical i.r. spectrum and mixed m.p. with an authentic sample).

(ii) *Reactions with Benzil Toluene-*p*-sulphonylhydrazone* (8).—(a) A mixture of the hydrazone (8) (500 mg) and acetic acid (20 ml) containing acetic anhydride (0.5 ml) was treated with LTA (724 mg) and stirred at ambient temperature for 1 h, and then at 60 °C for 1 h. Lead toluene-*p*-sulphonate salts (from which toluene-*p*-sulphonic acid was obtained by precipitation of lead with aqueous hydrochloric acid and evaporation of the solution) which separated, were removed and the remaining solution was made up to 200 ml with water and extracted with ether (4 × 50 ml). The combined ethereal extract, after washing with water and dilute sodium carbonate solution, was dried and evaporated to yield *O*-acetylbenzoin (12) (80%), m.p. 83—84 °C [from chloroform-pentane (b.p. 40—60 °C)] (lit.,²¹ 83 °C) (Found: C, 75.4; H, 5.75. Calc. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.75%). This compound was identical (mixed m.p. and i.r. spectra) with a sample prepared by heating benzoin with a 1:1 (v/v) mixture of acetic anhydride-acetic acid and isolated similarly.

(b) A mixture of the hydrazone (8) (790 mg) and dichloromethane (15 ml) containing triethylamine (2.4 ml) was treated with LTA (1.035 g) and stirred at ambient temperature for 1 h. The deep red solution was brought to 50 ml with dichloromethane, washed with water (4 × 10 ml), filtered after 1 h to remove lead salts, and evaporated. The residue, a deep red syrup (containing some triethylamine) was compound (11), ν_{\max} 2 080 (s) (C=N $^+$ =N $^-$) and 1 750 cm^{-1} (C=O). This, when warmed in acetic acid and worked-up as described, gave *O*-acetylbenzoin (12).

(c) A mixture of the hydrazone (8) (546 mg) and acetic acid (30 ml) containing acetic anhydride (0.5 ml) was treated with mercury(II) acetate (459 mg) and stirred at ambient temperature for 16 h. *Bis*(benzil toluene-*p*-sulphonylhydrazine)mercury (10), m.p. 183—185 °C [from chloroform-pentane (b.p. 40—60 °C)], separated. Further crops separated on addition of water (total quantitative yield 718 mg) (Found: C, 52.5; H, 3.6; N, 5.9. $C_{43}H_{34}HgN_4O_6S_2$ requires C, 52.8; H, 3.55; N, 5.85%). ν_{\max} 1 650 (C=O), 1 600 (C=N), and 1 130—1 160 and 1 360—1 370 cm^{-1} (SO_2), no N-H band; 1H n.m.r. ($CDCl_3$) δ 2.46 (3 H, *p*-Me) and 7.08—7.84 (Ar, 14 H); ^{13}C n.m.r. ($CDCl_3$) δ 21.6, (p-Me), 126.3—131.4 (Ar), 135.6 and 132.35 (Ph, C-1, C-1'), 144.3 (ts, C-4'), 136.6 (ts, C-1'), 145.1 (C=N), and 190.0 (C=O). Treatment with dilute hydrochloric acid regenerated the hydrazone (8). A similar reaction was observed using half the quantity of mercury(II) acetate.

(iii) *Cleavage of Benzophenone Toluene-*p*-sulphonylhydrazone*.—A mixture of the hydrazone (13) (700 mg) and acetic acid (25 ml) containing acetic anhydride (0.5 ml) was treated with LTA (1.085 g) and stirred at ambient temperature for 16 h. Brisk evolution of nitrogen occurred immediately accompanied by precipitation of Pb(OAc)-(SO $_3$ C $_6$ H $_4$ Me) (70%) (Found: C, 25.0; H, 2.25. Calc. for $C_9H_{10}O_5PbS$: C, 24.7; H, 2.3%). 1H n.m.r. $\delta[(CD_3)_2SO]$ 7.52 and 7.12 (dd, 4 H, *J* 9 Hz, Ts, A $_2$ B $_2$); 2.28 (3 H, *p*-Me); 1.74 (3 H, PbOAc); ν_{\max} 1 200, 1 120—1 140, 1 040, 1 010, 810, 675, and 655 cm^{-1} [TsO salt pattern from authentic Pb(TsO) $_2$]. Work-up of the solution as described, gave benzophenone (88%) (estimated by direct isolation and by 2,4-DNPH formation) in the ethereal extract.

[7/1678 Received, 23rd September, 1977]

²¹ Z. Rappoport, 'Handbook of Tables for Organic Compound Identification,' The Chemical Rubber Co., Cleveland, 3rd edn., 1967, p. 279.