Mercurial Derivatives from the Reactions of Substituted Hydrazones with Mercury(II) Acetate and Phenylmercury(II) Hydroxide

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Oxidation of aromatic aldehyde *p*-tolylsulphonylhydrazones with mercury(II) acetate gave *NN*″-mercuriobis-(*N*′-arylmethylenetoluene-*p*-sulphonohydrazide)s. Treatment of aromatic aldehyde 4-nitrophenylhydrazones with mercury(II) acetate resulted in acetoxymercuriation at the 2-position of the 4-nitrophenyl ring. Treatment of both types of hydrazone with phenylmercury(II) hydroxide gave *N*-phenylmercurio-derivatives.

METAL–HYDRAZONE intermediates from the oxidation of hydrazones with metal-containing oxidising agents have not been isolated, although hydrazones have been oxidised with a variety of such reagents.[1-3] The

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[1] For a review, see J. Buckingham, *Quart. Rev.*, 1969, **23**, 37.

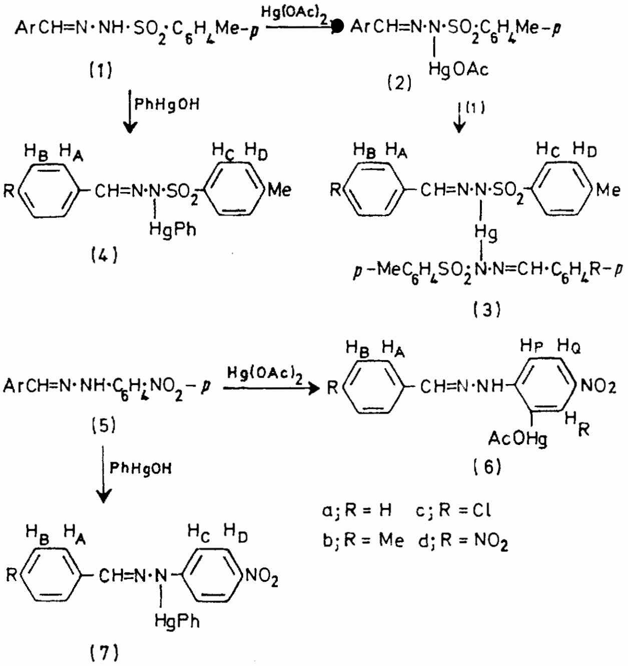
[2] I. Bhatnagar and M. V. George, *Tetrahedron*, 1968, **24**, 1293.

[3] I. Bhatnagar and M. V. George, *J. Org. Chem.*, 1967, **32**, 2252.

oxidation of hydrazones with mercury(II) oxide is reported to lead directly to bis-hydrazone derivatives.[4,5] The isolation of metal hydrazone intermediates would provide worthwhile information on these reactions particularly in relation to determining initial sites of attack. Isolation of such intermediates in the case of oxidation by lead tetra-acetate would be particularly useful.[6-8] Mercury(II) acetate as an oxidising agent often closely parallels lead tetra-acetate in its mode of action,[9] because of the possibility of isolating stable mercurial intermediates for comparison we decided to examine the reaction of mercury(II) acetate with hydrazones.[10] We studied aldehyde *p*-tolylsulphonylhydrazones and 4-nitrophenylhydrazones since each of these gave clean reactions with lead tetra-acetate and led to high yields of *NN'*-diacylhydrazines.[11] However the reactions with mercury(II) acetate were strikingly different.

RESULTS AND DISCUSSION

(i) p-*Tolylsulphonylhydrazones*.—When the aromatic aldehyde *p*-tolylsulphonylhydrazones (1) were treated with equimolar quantities of mercury(II) acetate in slightly warmed glacial acetic acid, the mercuriobis-hydrazones (3) were formed in high yields (Table 1). Compounds (3) may arise *via* anion exchange between two molecules of the intermediates (2) [*i.e.* $2HyHgOAc \longrightarrow HyHgHy + Hg(OAc)_2$ (Hy = hydrazone)] in a reaction requiring equimolar ratios of reactants, or *via* further attack by the intermediates (2) on a molecule of substrate in a reaction requiring only 0.5 mol. equiv. of mercury(II) acetate. The latter process (Scheme) appears to be the favoured route, since identical reactions were observed when only 0.5 mol. equiv. of mercury(II) acetate was used, and no changes were observed when the quantity of mercury(II) acetate was gradually increased from 0.5 to 1.0 mol. equiv. Compounds (3) underwent ready acidolysis to the parent hydrazones when heated briefly under reflux in acetic acid or when treated with cold dilute hydrochloric acid. When the hydrazones (1) were treated similarly with phenylmercury(II) hydroxide, compounds (4) were formed in high yields (Table 1). The bonding site of the mercury atoms in compounds (3) and (4) was established from i.r. spectra, which showed the absence of the sharp N–H band of the parent hydrazones (at 3 230 cm^{-1}), and from ^1H n.m.r. spectra (Experimental section). For each of the compounds (3) and (4) the CH:N signal was shifted downfield from that of the parent hydrazone by 0.3—0.4 p.p.m. Although no bis-hydrazones were encountered in the present reactions, the isolation of products such as (3) suggests that bis- or mono-hydrazone–metal intermediates could be involved in reactions leading to bis-hydrazones with reagents such as mercury(II) oxide,[4,5] and manganese dioxide.[12] However, since the hydrazones (5) behave differently towards mercury(II) acetate (though not towards lead tetra-acetate [11]), the formation of compounds of type (3) could also result from the special reactivity of the sulphonylhydrazone NH group and thus have no further significance. Further studies of this question are in progress.



SCHEME

(ii) p-*Nitrophenylhydrazones*.—When the 4-nitrophenylhydrazones (5) were treated with mercury(II) acetate, the products were, surprisingly, not derived from attack on the hydrazone chain. In this case compounds (6) (Table 1), resulting from attack at the 2-position in the nitrophenyl ring, were obtained. This position is apparently activated to strong electrophiles by the adjacent hydrazone amino-group, but the balance is delicate since the introduction of *para*-electron-withdrawing groups in the benzylidene ring was sufficient to reduce [*e.g.* (5c)] or inhibit the substitution. A reaction could not be achieved with the *p*-nitrobenzaldehyde derivative (5d), even under conditions considerably more vigorous than those giving high yields of products with the hydrazones (5a and b). With the less electrophilic phenylmercury(II) hydroxide, attack occurred on the hydrazone chain at the amino-nitrogen atom and gave compounds (7). The structure of compounds (6) was confirmed from (i) i.r. spectra,

[4] G. Minunni, *Gazzetta*, 1892, **22**, 228.

[5] H. Minato, H. Tateno, and H. Yokokawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 2724.

[6] W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1969, 2589.

[7] P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 4716.

[8] T. A. F. O'Mahony, R. N. Butler, and F. L. Scott, *J.C.S. Perkin II*, 1972, 1319; for a review, see R. N. Butler, T. A. F. O'Mahony, and F. L. Scott, *Chem. Rev.*, 1973, **73**, 93.

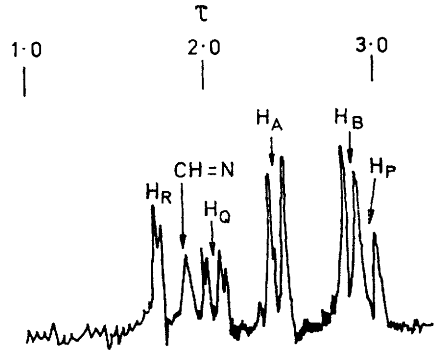
[9] W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 35.

[10] Preliminary report, R. N. Butler and W. B. King, *Chem. and Ind.*, 1975, 647.

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

[12] K. S. Balachandran, I. Bhatnagar, and M. V. George, *J. Org. Chem.*, 1968, **33**, 3891.

which showed an N–H band at 3 240 cm^{-1} as well as C=N and HgOAc carbonyl bands at 1 600—1 640 cm^{-1}; and (ii) ^{1}H n.m.r. spectra (*e.g.* Figure), which showed all the expected signals including the characteristic splitting pattern for H_P, H_Q, and H_R. The assignments in the Figure were confirmed by spin decoupling. The chemical shifts for the series [H_P τ 2.91 ± 0.03 (3.03); H_Q τ 2.03 ± 0.01 (1.92); H_R τ 1.71 ± 0.01 (1.56)] were in good agreement with values calculated (in parentheses) by adding the effects of a 6-amino-substituent to the shifts reported[13,14] for 3-nitrophenylmercury(II) chloride. It was possible with a number of the compounds (6) to observe the weak satellite lines due to ^{199}Hg,H_R-coupling (J 240 Hz) on the low-field side of the H_R signal and also the ^{199}Hg,H_P-coupling (J 88 Hz) on the high-field side of the H_P signal. The value of $J(^{199}\mathrm{Hg},H_R)$ is similar to the value (217.5 Hz) reported for the corresponding coupling in 3-nitrophenylmercury(II) chloride.[13] Values of $J(^{199}\mathrm{Hg},H_{meta})$ previously reported[14] for disubstituted benzenes are generally *ca.* 50 Hz and are lower than the value (88 Hz) observed with compounds (6). The higher values observed here are probably due to the activating effect of the amino-group, which is located between the mercury atom and the *meta*-proton, H_P.



Aromatic region of the ^{1}H n.m.r. spectrum of compound (6b): J_{PQ} 10, J_{QR} 3, J_{AB} 9 Hz; also OAc, τ 8.06, *p*-Me, τ 7.68

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured for KBr discs or mulls with Perkin-Elmer 377 and 457 spectrophotometers. N.m.r. spectra were measured with a JEOL JNM-MH-100 spectrometer [$(CD_3)_2SO$ as solvent]. The hydrazone substrates were prepared by standard procedures.[15]

Reactions with Mercury(II) *Acetate*.—(a) p-*Tolualdehyde* p-*tolylsulphonylhydrazone*. A solution of the hydrazone (1b) (500 mg) in acetic acid (40 ml) containing acetic anhydride (0.7 ml) was treated with mercury(II) acetate (553 mg) and stirred at room temperature for 16 h. The white precipitate of NN″-*mercuriobis*-(N′-p-*methylbenzylidenetoluene*-p-*sulphonohydrazide*) (3b) (498 mg), m.p. 176—177° (Found: C, 46.1; H, 3.85; N, 7.2. $C_{30}H_{30}HgN_4O_4S_2$ requires, C, 46.45; H, 3.9; N, 7.2%), $\nu_{max.}$ 1 600 (C=N) and 1 150 and 1 300 cm^{-1} (SO_2) (no N–H bands); τ 2.60 (H_A) and 2.88 (H_B) (A_2B_2, J_{AB} 8 Hz), 2.16 (H_C) and 2.66 (H_D) (A_2B_2, J_{CD} 9 Hz), 1.84 (1 H, CH=N), 7.64 (3 H, *p*-Me), and 7.72 (3 H, *p*-Me), was removed and washed with water. The filtrate was treated with water and on standing yielded a further crop (20 mg) (total 518 mg, 77%). Fractional evaporation and further work-up of the filtrate gave 14% recovery of compound (1b).

Similar treatment of the other hydrazones (1) gave the products described in Tables 1 and 2. When compounds (3) were stirred in cold dilute hydrochloric acid or briefly heated under reflux in acetic acid, the hydrazones (1) were recovered quantitatively. Prolonged heating in acetic acid led to decomposition. It was not possible to identify unambiguously the i.r. frequency of the Hg–N bond[16,17] in compounds (3) because of the complexity of the absorptions of the parent hydrazones in the range 400—700 cm^{-1}.

TABLE 1

Reactions of hydrazones with $Hg(OAc)_2$ and with PhHgOH

	Product from $Hg(OAc)_2$ [a]			Product from PhHgOH [b]		
Hydrazone	Cpd.	Yield (%)	M.p. (°C)	Cpd.	Yield (%)	M.p. (°C)
(1a)	(3a)	80	171—172	(4a)	95	178—179
(1b)	(3b)	77 [c]	176—177	(4b)	91	171—172
(1c)	(3c)	83	182—183	(4c)	94.5	183—184
(1d)	(3d)	93	179—180	(4d)	90	177—178
(5a)	(6a)	78	203—205	(7a)	90 [d]	192—193
(5b)	(6b)	78	194—196	(7b)	93.5	193—194
(5c)	(6c)	35 [e]	201—203	(7c)	94 [f]	201—202
(5d) [g]	(6d)	<0.5		(7d)	95	213—215

[a] Solvent acetic acid. [b] Solvent isopropyl alcohol. [c] Hydrazone recovered (14%). [d] Hydrazone recovered (7%). [e] Hydrazone recovered (50%). [f] Hydrazone recovered (3%). [g] No reaction was observed with this hydrazone (*cf.* Experimental section).

TABLE 2

Analytical data

	Found (%)				Required (%)		
Cpd.	C	H	N	Formula	C	H	N
(3a)	45.2	3.5	7.25	$C_{28}H_{26}HgN_4O_4S_2$	45.0	3.5	7.5
(3c)	41.0	2.75	6.95	$C_{28}H_{24}ClHgN_4O_4S_2$	41.2	2.95	6.85
(3d)	39.8	2.85	9.9	$C_{28}H_{24}HgN_6O_8S_2$	40.15	2.85	10.05
(4a)	43.75	3.45	5.1	$C_{20}H_{18}HgN_2O_2S$	43.6	3.25	5.1
(4c)	41.05	2.95	4.65	$C_{20}H_{17}ClN_2O_2S$	41.0	2.9	4.8
(4d)	40.3	2.85	7.05	$C_{20}H_{17}HgN_3O_4S$	40.3	2.85	7.05
(6a)	35.85	2.55	8.4	$C_{15}H_{13}HgN_3O_4$	36.05	2.60	8.4
(6c)	33.3	2.35	7.5	$C_{15}H_{12}ClHgN_3O_4$	33.7	2.25	7.85
(7a)	43.7	2.8	7.85	$C_{19}H_{15}HgN_3O_2$	44.05	2.9	8.1
(7b)	45.0	3.15	7.85	$C_{20}H_{17}HgN_3O_2$	45.15	3.2	7.9
(7c)	41.55	2.55	7.5	$C_{19}H_{14}ClHgN_3O_2$	41.3	2.55	7.6

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[13] V. S. Petrosyan and O. A. Reutov, *Izvest. Akad. Nauk. Ser. khim.*, 1968, 1962.

[14] V. S. Petrosyan and O. A. Reutov, *J. Organometallic Chem.*, 1974, **76**, 123.

[15] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1962, p. 722.

[16] D. Breitinger and K. Brodersen, *Angew. Chem. Internat. Edn.*, 1970, **9**, 357.

[17] D. Breitinger, K. Brodersen, and J. Limmer, *Chem. Ber.*, 1970, **103**, 2388.

However, each of the compounds (3) showed a strong band in the range 580—620 cm^{-1}, in which some of the parent hydrazones did not absorb.

(b) p-*Tolualdehyde* p-*nitrophenylhydrazone*. A solution of the hydrazone (5b) (500 mg) in acetic acid (40 ml) containing acetic anhydride (0.8 ml) was treated with mercury(II) acetate (625 mg) and the mixture was stirred at room temperature for 70 min followed by 1.5 h at 55—60 °C and 15 h at 40—45 °C. p-*Tolualdehyde* o-*acetoxymercurio*-p-*nitrophenylhydrazone* (6b) which separated was removed and recrystallised from chloroform; yield 762 mg (78%), m.p. 194—196° (Found: C, 37.1; H, 3.1; N, 8.4. $C_{16}H_{15}HgN_3O_4$ requires C, 37.4; H, 2.9; N, 8.2%), $\nu_{max.}$ 3 240 (N–H) and 1 600—1 640 cm^{-1} (C=N and HgOAc carbonyl); for ^1H n.m.r. see Figure. The other compounds (6) (Tables 1 and 2) were prepared similarly. When the hydrazone (5d) was treated as described or under the more vigorous conditions of (i) stirring at 80—90 °C for 14 h or (ii) heating under reflux for 1.5 h, it was unchanged (90%) and compound (6d) was not encountered.

Reactions With Phenylmercury(II) *Hydroxide*.—(a) p-*Tolualdehyde* p-*tolylsulphonylhydrazone*. A solution of the hydrazone (1b) (300 mg) in isopropyl alcohol (1.5 ml) was treated with phenylmercury(II) hydroxide (307 mg) in the same solvent (3 ml), and the mixture was stirred at ambient temperature for 5.5 h. p-*Tolualdehyde* N-*phenylmercurio*-N-p-*tolylsulphonylhydrazone* (4b) (536 mg, 91%), m.p. 171—172° (Found: C, 44.3; H, 3.3; N, 4.85. $C_{21}H_{20}HgN_2O_2S$ requires C, 44.65; H, 3.55; N, 4.95%), $\nu_{max.}$ 1 600 (C=N) and 1 150 and 1 300 cm^{-1} (SO_2) (no NH bands); τ 1.78 (1 H, CH=N), 2.22 (2 H, H_C part of A_2B_2, J_{CD} 8 Hz), 2.44—2.80 (9 H, overlapping m, H_A, H_B, Ph), 2.92 (2 H, H_B part of A_2B_2, J_{AB} 7 Hz), 7.68 (3 H, s, *p*-Me), and 7.73 (3 H, s, *p*-Me), which separated was removed and washed thoroughly with water. The remaining compounds (4) (Tables 1 and 2) were similarly obtained from the appropriate hydrazones. Compounds (4) were also formed when acetic acid was used as solvent but the yields were lower (*ca.* 60%). In ^1H n.m.r. spectra the CH=N signal of compounds (3) and (4) was at τ 1.66—1.80; *cf.* 2.04—2.16 for the hydrazones (1).

(b) p-*Nitrobenzaldehyde* 4-*nitrophenylhydrazone*. The hydrazone (5d) (400 mg) in isopropyl alcohol (20 ml) was treated with phenylmercury(II) hydroxide (413 mg) in the same solvent (15 ml) and the mixture was stirred at 60—65 °C for 1 h followed by 12 h at ambient temperature. p-*Nitrobenzaldehyde* N-p-*nitrophenyl*-N-*phenylmercuriohydrazone* (7d) (753 mg, 95%), m.p. 213—215° (Found: C, 40.2; H, 2.4; N, 9.9. $C_{19}H_{14}HgN_4O_4$ requires C, 40.5; H, 2.5; N, 9.95%), $\nu_{max.}$ 1 600 cm^{-1} (C=N) (no N–H band); τ 1.32 (1 H, s, CH=N), 1.86 (2 H, H_B) and 2.16 (2 H, H_A) (A_2B_2, J_{AB} 8 Hz), 2.00 (2 H, H_D) and 2.66 (2 H, H_C) (A_2B_2, J_{CD} 10 Hz), and 2.40—2.64 (5 H, m, Ph), was removed and washed with water. The reactions with the other hydrazones (5) were similar. In ^1H n.m.r. spectra the methine proton signal was at τ 1.30—1.39 for compounds (7) and at 1.86—1.90 for compounds (6); *cf.* τ 2.00—2.08 for the hydrazones (5).

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