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2,4,6-TRI-ISOPROPYLBENZENESULPHONYL HYDRAZIDE: A CONVENIENT SOURCE OF DI-IMIDE

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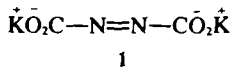
Abstract—2,4,6-Tri-isopropylbenzenesulphonyl hydrazide (TPSH, **3a**) undergoes thermal decomposition in d_4-methanol solution at 35°, in the presence of triethylamine, at a rate *ca.* 380 times that of *p*-toluenesulphonyl hydrazide (**2b**). **3a** has been found to be a convenient and effective hydrogenating agent for azobenzene and a number of olefins in methanol solution at 20° and in boiling ether and tetrahydrofuran solutions. Reductions in ether solution appear to be facilitated by the addition of base. 2,4,6-Trimethylbenzenesulphonyl hydrazide (MSH, **4a**) undergoes thermal decomposition at a rate *ca.* 24 times that of **2b**; **4a** is also a useful hydrogenating agent.

Following pioneering studies in several laboratories[1-4] some 15 years' ago, di-imide reduction of alkenes and alkynes has become established as an important organic reaction. Di-imide (HN=NH) has been generated in a number of ways but an examination of the literature[5] suggests that the procedures which have been most widely used are (a) the oxidation of hydrazine,[1,2,3a,4] usually in the presence of a catalytic amount of copper(II) ions, (b) the decarboxylation of potassium azodicarboxylate[1,2,3a] (**1**) in the presence of a proton source and (c) the decomposition of benzenesulphonyl[2] (**2a**) or, more commonly, *p*-toluenesulphonyl hydrazide[3b] (**2b**) both in the presence and absence of additional base.

It is difficult to ascertain from the literature which procedure is the most convenient or useful but House[6] concluded that potassium azodicarboxylate (**1**), the conjugate acid of which undergoes decarboxylation at or even below room temperature, appeared to be the most useful source of di-imide. Although it is apparently unnecessary to use a large excess of potassium azodicarboxylate, relatively freshly prepared reagent should be used if reproducible results are to be obtained.[7] An obvious advantage of procedure (a) (see above) over procedure (b) is that hydrazine is much more readily accessible than (**1**). However, di-imide generated directly from hydrazine appears to be required in a much larger excess.[8] Procedure (c) has a distinct disadvantage over both procedures (a) and (b) in that the decomposition rates of **2a** and **2b** are very slow below 80–100°. Indeed Dewey and van Tamelen[3b] carried out their original reductions with *p*-toluenesulphonyl hydrazide (**2b**) in boiling diglyme solution (i.e. at 162°). Clearly this disadvantage could be removed if an arenesulphonyl hydrazide which underwent thermal decomposition more readily than **2a** or **2b** were available.

It has been known[9] for many years that *o*-nitro- and 2,4-dinitro-benzenesulphonyl hydrazides (**2c** and **2d**, respectively) are both very labile thermally. Hünig *et al.* stated[5a] that di-imide could be generated from **2c** at a rate suitable for preparative use at 25° but have not reported examples of its use in practice; indeed these authors cited only[5a] an example in which **2c** was a very inefficient hydrogenating agent at 39.1°. In connection with our work in the field of polynucleotide synthesis,[10] we undertook the preparation of 2,4,6 - tri - isopropylbenzenesulphonyl hydrazide (**3a**, TPSH) and found, to our surprise, that it was considerably more labile to heat than **2b**. We subsequently examined the potential use of TPSH as a source of di-imide and now report our findings in full.‡ We have also investigated the properties of 2,4,6-trimethylbenzenesulphonyl hydrazide (**4a**, MSH) from the same standpoint.



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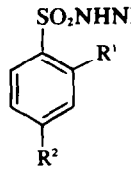
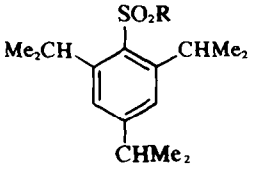


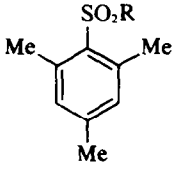
2

a: $R^1 = R^2 = H$
b: $R^1 = H$, $R^2 = Me$
c: $R^1 = NO_2$, $R^2 = H$
d: $R^1 = R^2 = NO_2$



3

a: $R = NHNH_2$
b: R = Cl
c: R = H



4

a: $R = NHNH_2$
b: R = Cl
c: R = H

TPSH (**3a**) may be prepared as a colourless solid in nearly quantitative yield by treating a solution of 2,4,6 - tri - isopropylbenzenesulphonyl chloride[11] (**3b**) in tetrahydrofuran with hydrazine hydrate at or below 0° (Experimental). If reasonable care is taken to control the temperature during the preparation and work-up, a product of high quality may be obtained. As **3b** itself may be prepared in high yield from practical grade 1,3,5 - tri -

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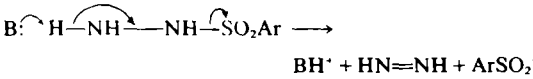
‡For a preliminary account of some of this work, see N. J. Cusack, C. B. Reese and B. Roozpeikar, *J. Chem. Soc. Chem. Comm.* 1132 (1972).

isopropylbenzene, a relatively cheap commercially-available hydrocarbon, TPSH (**3a**) may be regarded as an inexpensive, readily accessible reagent. MSH (**4a**) may similarly be prepared in high yield from 2,4,6 - trimethylbenzenesulphonyl chloride (**4b**);[12] it is more stable to heat than TPSH and may be obtained as an analytically pure crystalline solid.

TPSH (**3a**) is a relatively stable compound; thus not more than *ca.* 5% decomposition was detected after the dry solid had been stored in a dark bottle at 4° for 9 months. When similar precautions were taken at room temperature, decomposition appeared to be slightly more rapid. If necessary TPSH can readily be freed from its decomposition products (Experimental). When TPSH was heated in aqueous methanol solution, under reflux, it decomposed rapidly and the corresponding sulphinic acid (**3c**) was isolated from the acidified products. MSH (**4a**) was similarly converted into 2,4,6-trimethylbenzenesulphinic acid (**4c**).

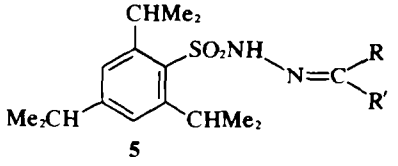
An attempt was then made to obtain a quantitative estimate of the rate of decomposition of TPSH. NMR spectroscopy seemed to be a suitable technique for this purpose as the chemical shifts of the resonance signals of the aryl protons of TPSH (**3a**) and its aromatic decomposition product [possibly a mixture of **3c** and its conjugate base] in d_4-methanol solution were separated by more than 0.2 ppm. The first kinetic study was carried out with *ca.* 0.2 M TPSH in d_4-methanol solution at 35°, the ambient temperature of the spectrometer. Under these conditions, TPSH underwent *ca.* 50% decomposition after 50 min but only *ca.* 70% decomposition after 190 min. However, when one molecular equivalent of triethylamine was added to the reaction solution, the decomposition of TPSH displayed first order kinetics with a half-time ($t_{1/2}$) of 19 min. Under the same conditions (i.e. at 35°, in the presence of one molecular equivalent of triethylamine), the decomposition of MSH (**4a**) was also found to display first order kinetics with $t_{1/2} = 300$ min. In the case of *p*-toluenesulphonyl hydrazide (**2b**), a less satisfactory first order plot was obtained with $t_{1/2} = ca.$ 120 hr. It follows from these results that TPSH (**3a**) decomposes *ca.* 16 times as fast as MSH (**4a**) and *ca.* 380 times as fast as *p*-toluenesulphonyl hydrazide (**2b**) in d_4-methanol solution in the presence of triethylamine at 35°.



Scheme 1.

It is not surprising that the kinetics of decomposition of TPSH (**3a**) are complex in the absence of triethylamine as the medium would then be expected to become more acidic as the reaction proceeds: two molecules of TPSH should give rise to two molecules of sulphinic acid (**3c**) [pK_a (see below) probably in the region 2–3] and *at most* one molecule of hydrazine (pK_a − 0.88, 8.11),[13a] formed by the disproportionation of two molecules of di-imide. It is possible that the thermal decomposition of arenesulphonyl hydrazides is base-catalyzed as indicated in Scheme 1. However, the results obtained for TPSH (**3a**) can also be explained in terms of the decomposition being retarded unless sufficient base is added to neutralize the sulphinic acid (**3c**) formed. The reason why TPSH (**3a**) and, to some extent, MSH (**4a**) are more labile than **2b** is less clear. It is not due to the more hindered sulphinic acids (**3c** and **4c**, respectively) being stronger than *p*-toluenesulphinic acid and hence to the corresponding sulphinate ions being better leaving groups.† Indeed the reverse would appear to be true: the pK_a's of **3c**, **4c** and *p*-toluenesulphinic acid in ethanol–water (3:2 v/v) were found to be 4.3, 3.8 and 3.4, respectively. The reported[13b] pK_a of *p*-toluenesulphinic acid is 1.7 but it was necessary to carry out the present determinations in an ethanol-rich medium to solubilize **3c**. It is nevertheless reasonable to conclude that the ease of decomposition of **3a** and **4a** is a consequence of the bulky *ortho*-substituents. Possibly release of steric compression in the transition state is a significant factor in the decomposition of arenesulphonyl hydrazides.

Before proceeding with a discussion of the use of TPSH (**3a**) as a hydrogenating agent, it is appropriate to consider briefly a few other aspects of its chemistry. First, it is freely soluble in most organic solvents other than hydrocarbons. This adds considerably to its utility as an organic reagent. Secondly, its rate of decomposition in solution is solvent-dependent and decreases in the series: methanol, dimethyl sulphoxide, dioxan, chloroform. Thirdly, it reacts very rapidly with a wide range of aldehydes and ketones, *in the absence of an acid catalyst*, to give the corresponding 2,4,6 - tri - isopropylbenzenesulphonyl hydrazones (**5**). For example, treatment of cyclohexanone with a small excess of TPSH in tetrahydrofuran solution for 10 min at 20° gave **5** (R^1, R^2 = −$(CH_2)_5$−) as a crystalline compound in 90% yield. As a consequence of its ease of reaction with aldehydes and ketones, it is possible that TPSH will find application as a reagent in several useful synthetic reactions.



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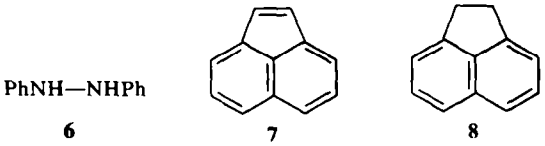
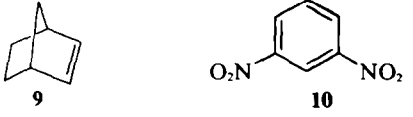


6 **7** **8**



9 **10**

a: R = CH_2=$CHCMe_2$–
b: R = $EtCMe_2$–

The results of the hydrogenation studies with TPSH (**3a**) are indicated in Table 1. It is clear from the literature[5] and especially from the studies of Garbisch *et al.*[14] that certain olefins are better substrates for di-imide than others. It is also apparent[5] that azo-compounds (including

†It is nevertheless possible that the reported[9] high labilities of *o*-nitro- and 2.4 - dinitro - benzenesulphonyl hydrazides (**2c** and **2d**, respectively) are due to the sulphinate ions being particularly good leaving groups.

Table 1. Hydrogenations with 2,4,6 - tri - isopropylbenzenesulphonyl hydrazide (**3a**, TPSH)

Experiment No.	Substrate	Mol. Equiv. of (3a)	Added Base[a]	Solvent	Temperature (°C)	Reaction time (hr)	% Substrate reduced
1	PhN=NPh	2	-	MeOH	20	1.5	100[b]
2	PhN=NPh	2	A	MeOH	20	1.25	100[b]
3	PhN=NPh	2	-	Et_2O	36	11.5	100[b]
4	PhN=NPh	2	A	Et_2O	36	4.5	100[b]
5	PhN=NPh	2	B	Et_2O	36	1.9	100[b]
6	PhN=NPh	2	-	THF	67	2.0	100[b]
7	PhN=NPh	2	A	THF	67	1.5	100[b]
8	PhN=NPh	2	-	MeOH	50	0.2	100[b] (85[c])
9	acenaphthylene (7)	2.5	-	MeOH	20	16[d]	99[c]
10	norbornene (9)	2	A	D_4-MeOH	35	2.5	100[e]
11	CH_2=CH-CH_2OH	2	-	Et_2O	36	24	98[f]
12	CH_2=CH-CH_2OH	2	-	THF	67	2.0	100[f]
13	CH_2=CH-CMe_2OH	2	-	Et_2O	36	9.0	100[f]
14	CH_2=CH-CMe_2OH	2	-	THF	67	1.5	100[f]
15	(10a)	2	-	THF	67	2.0	61[c]
16	MeCH=CH-CO_2Et	2	-	Et_2O	36	33	90[f]
17	PhCH=CHPh	4	-	Et_2O	36	33	70[f]
18	PhCH=CHPh	4	-	$(MeO)_2CH_2$	42	26	90[f]

[a] A = triethylamine, B = piperidine; ca. 1 molecular equivalent of base with respect to TPSH (3a) was usually added.

[b] As indicated by the disappearance of absorption at 445 nm.

[c] Isolated crystalline product, identical to authentic material.

[d] The reaction was probably complete after 360 min. Piperidine (base B) appeared to have no effect on the reaction rate.

[e] N.m.r. spectroscopy indicated that no substrate remained.

[f] As estimated by g.l.c.

di-imide itself) are especially good substrates and, for this reason, we carried out our initial studies (Table 1, experiments Nos. 1–8) with azobenzene. The latter is also a particularly convenient substrate to work with in that its orange colour disappears when it is hydrogenated. When a 0.1 M solution of azobenzene in methanol was treated with a twofold excess of TPSH at 20° (experiment No. 1), hydrogenation was complete after 90 min. Although triethylamine has a notable effect on the decomposition of TPSH in d_4-methanol solution at 35° (see above), the rate of hydrogenation was not significantly increased by the addition of base (experiment No. 2). Although hydrogenation was much slower in ether solution (experiment No. 3), the addition of triethylamine (experiment No. 4) and especially of piperidine (experiment No. 5) increased the reaction rate appreciably. The effect of additional base was less noticeable when hydrogenations were carried out in boiling tetrahydrofuran solution (experiments Nos. 6 and 7). Finally, in a preparative experiment (No. 8), azobenzene was quantitatively reduced by two molecular equivalents of TPSH in methanol solution in 12 min at 50° and hydrazobenzene (**6**) was isolated from the products as a pure crystalline solid in 85% yield. It should be emphasized that TPSH reductions are particularly easy to work-up (see experimental section) as 2,4,6 - tri - isopropylbenzenesulphinic acid (**3c**) may readily be removed by extracting an ethereal solution of the products with dilute aqueous alkali.

TPSH proved to be an effective reagent for the hydrogenation of olefins. When acenaphthylene (**7**) was treated with 2.5 molecular equivalents of TPSH in methanol solution at 20° (experiment No. 9), the reaction appeared to go to completion after 6 hr. The products were worked-up after a further 10 hr to give acenaphthene (**8**) as a crystalline solid in 99% isolated yield. The reduction of norbornene (**9**) in d_4-methanol solution at 35° (experiment No. 10) was monitored by NMR spectroscopy and appeared to be complete after 150 min. The hydrogenations of allyl alcohol (experiments Nos. 11 and 12) and 3 - methylbut - 1 - en - 3 - ol (experiments Nos. 13 and 14) were then undertaken. The reduction of each substrate was carried out both in boiling ether and boiling tetrahydrofuran solutions and a twofold excess of TPSH was used in each experiment. 3 - Methylbut - 1 - en - 3 - ol, which appeared to be the better substrate, was completely hydrogenated in boiling ether solution in 9 hr (experiment No. 13); reduction of the 3,5-dinitrobenzoyl derivative (**10a**) of the latter alcohol (experiment No. 15) proceeded smoothly in boiling tetrahydrofuran solution and crystalline t-pentyl 3,5-dinitrobenzoate (**10b**) was isolated from the products in 61% yield. Ethyl crotonate, a comparatively polar olefin, was *ca.* 90% hydrogenated by a twofold excess of TPSH in boiling ether solution after 33 hr (experiment No. 16). However, *trans*-stilbene was only *ca.* 70% hydrogenated by a fourfold excess of TPSH under the same conditions (experiment No. 17). A somewhat better result (experiment No. 18) was obtained by carrying out the reaction in boiling methylal. In contrast to the results of the last two experiments, it was found that no detectable hydrogenation of *trans*-stilbene occurred when it was heated with a twofold excess of *p*-toluenesulphonyl hydrazide (**2b**) in dioxan solution for 8 hr at 50°.

MSH (**4a**) was also found to be a convenient source of di-imide. When azobenzene was heated with a twofold excess of MSH in methanol solution, under reflux, complete reduction to hydrazobenzene (**6**) had occurred after 22 min. In the presence of piperidine (*ca.* one molecular equivalent with respect to MSH), the reaction went to completion after 12 min. In another experiment, acenaphthylene (**7**) was heated in the absence of additional base with *ca.* 2.2 molecular equivalents of MSH

(4a) in methanol solution, under reflux, for 2 hr. Acenaphthene (8) was isolated from the products as a crystalline solid in 98% yield.

It may be concluded from the above experiments that TPSH (3a) is a much more convenient source of di-imide than *p*-toluenesulphonyl hydrazide (2b) and that, under certain conditions, it is an effective hydrogenating agent at room temperature. TPSH may, due to its apparently greater stability, also prove to be a more convenient source of di-imide than potassium azodicarboxylate (1). It is not normally necessary to use more than a two-fold excess of TPSH and, especially in less polar solvents, it appears to be advantageous to add an equivalent amount of a base such as triethylamine. The order of substrate affinity and the stereochemistry of reduction have not been investigated for TPSH but its chemistry would not be expected to differ significantly from that of other sources of di-imide in these two respects. It seems that di-imide may be generated from TPSH (3a) at a convenient rate in methanol solution at room temperature and in tetrahydrofuran (and perhaps also in ether) solution under reflux. Under these conditions, the ratio of the substrate and di-imide concentrations appears to be high enough to prevent disproportionation of the latter becoming an unduly wasteful side reaction. It may also be concluded that di-imide may conveniently be generated from MSH (4a) in boiling methanol solution. The conclusion of Hünig *et al.*[5a] that arenesulphonyl hydrazides are less efficient hydrogenating agents (i.e. that the disproportionation of di-imide to give nitrogen and hydrazine becomes more predominant) at lower temperatures is not substantiated by our observations.

EXPERIMENTAL

NMR spectra were measured at 60 MHz with a Perkin-Elmer R12B spectrometer and at 100 MHz with a Varian HA 100 spectrometer; chemical shifts are given in PPM on a τ scale and tetramethylsilane was used as an internal standard. UV spectra were measured with a Unicam SP 800 spectrophotometer. IR spectra were measured with Unicam SP 1000 and Perkin-Elmer 257 spectrometers. Mass spectra were measured with a MS 902 spectrometer. GLC was carried out with an F. & M. Model 720 and a Perkin-Elmer F11 chromatograph; Carbowax 20 M, Apiezon L and LAC were used as stationary phases. TLC was carried out on glass plates coated with Merck Kieselgel GF_{254}.

2,4,6 - *Tri - isopropylbenzenesulphonyl hydrazide* (*TPSH* 3a) A magnetically-stirred solution of 2,4,6 - tri - isopropylbenzenesulphonyl chloride† (30.3 g, 0.10 mole) in THF (60 ml) was cooled to −10° in an ice-salt freezing mixture and 100% hydrazine hydrate (10.2 g, 0.22 mole) was added dropwise over a period of 15 min. The temp rose to 0° and after stirring at 0° for 3 hr, water (*ca.* 2 ml) was added dropwise to dissolve the precipitated solids. The products were then transferred to a separating funnel and the lower aqueous layer discarded. The organic layer was washed with ice-cold brine (3 × 20 ml), dried (Na_2SO_4) for 3 hr, filtered through hyflo-supercel and then concentrated under reduced pressure below room temp. Petroleum ether (b.p. 30–40°, 100 ml) was added to the crystalline mass so obtained. The material was collected by filtration, washed several times with petroleum ether and any remaining solvent removed by evaporation under reduced pressure at room temp. The product was then triturated with ice-cold water (3 × 100 ml) and finally dried *in vacuo* over P_2O_5 at room temp. for 24 hr to give 2,4,6 - *tri - isopropylbenzenesulphonyl hydrazide* as a colourless solid, m.p. 118–120° dec., yield 28.9 g (96%); R_F [$CHCl_3$–MeOH (9:1 v/v) 0.7; τ($CDCl_3$): 2.76 (2H, s), 5.81 (2H, heptuplet, J = 7 Hz), 7.08 (1H, heptuplet, J = 7 Hz), 8.72 (18H, d, J = 7 Hz).

†Prepared[11] from practical quality 1,3,5 - tri - isopropylbenzene, supplied by Koch–Light Limited.

Stability of solid TPSH. TPSH should be stored in a dark bottle, preferably at 4°. Under these conditions, decomposition occurs to only a small extent (*ca.* 5%) in 9 months. Decomposition occurs slightly more rapidly at room temp. The purity of a specimen of TPSH may be examined by TLC [$CHCl_3$–MeOH (9:1 v/v)] or by NMR spectroscopy (in $CDCl_3$, the aromatic protons of 2,4,6 - tri - isopropylbenzenesulphinic acid (see below), the decomposition product, resonate as a singlet at τ 2.90).

Purification of partially-decomposed TPSH. Impure TPSH (60 g) was dissolved in ether (600 ml) and the solution washed first with aqueous sodium hydroxide (0.75 M, 3 × 50 ml) and then with water (25 ml). Petroleum ether (b.p. 30–40°, 1 litre) was added to the dried ($MgSO_4$) organic layer. The precipitated TPSH (50 g) was collected by filtration and dried *in vacuo* over P_2O_5 for 24 hr at room temp.

2,4,6 - *Tri - isopropylbenzenesulphinic acid* (3c). A soln of TPSH (2.0 g, 6.7 mmole) in MeOH (65 ml) and water (35 ml) was heated, under reflux, for 1 hr. The products were cooled and treated with dil. HCl (50 ml). The colourless crystalline precipitate (1.07 g, 60%) was recrystallized from aqueous methanol to give 2,4,6 - *tri - isopropylbenzenesulphinic acid* [Found: C, 67.2; H, 8.8; S, 12.1. $C_{15}H_{24}O_2S$ requires: C, 67.1; H, 8.95; S, 11.9%], m.p. 88–90°; τ ($CDCl_3$): 2.90 (2H, s), 5.88 (2H, m), 7.10 (1H, m), 8.70 (12 H, d, $J \sim 7$ Hz), 8.77 (6H, d, $J \sim 7$ Hz); pK_a [ethanol–water (3:2 v/v)] 4.3.

2,4,6-*Trimethylbenzenesulphonyl hydrazide* (*MSH* 4a). A magnetically-stirred solution of 2,4,6-trimethylbenzenesulphonyl chloride[12] (11.0 g, 50 mmole) in tetrahydrofuran (40 ml) was cooled to −10° (ice-salt freezing mixture) and 100% hydrazine hydrate (5.5 g, 0.11 mole) was added over a period of 30 min. The temp. rose to 0° and after stirring at 0° for 2 hr, water (7 ml) was added to dissolve the precipitated solids. The products were then transferred to a separating funnel and the lower aqueous layer discarded. The organic layer was washed with ice-cold brine (3 × 30 ml), dried (Na_2SO_4) for 1.5 hr at 0°, filtered through hyflo-supercel and then concentrated under reduced pressure below 15°. Petroleum ether (b.p. 30–40°) was added to the solid residue which was collected by filtration, washed several times with petroleum ether and any remaining solvent removed by evaporation under reduced pressure at room temp. The product was then triturated with ice-cold water (3 × 100 ml) and finally dried *in vacuo* over P_2O_5 at room temp. to give 2,4,6-*trimethylbenzenesulphonyl hydrazide* as a colourless solid, m.p. 115–116° dec; yield 10.3 g (96%). A portion of this material was crystallised from di-n-butyl ether [Found, in material dried *in vacuo* over P_2O_5 at 20°: C, 50.8; H, 6.5; N, 13.3. $C_9H_{14}N_2O_2S$ requires: C, 50.5; H, 6.5; N, 13.1%], τ($CDCl_3$): 3.02 (2H, s), 4.2–4.5 (1H, m), 6.4–6.8 (2H, m), 7.36 (6H, s), 7.70 (3H, s).

2,4,6-*Trimethylbenzenesulphinic acid* (4c). A soln of MSH (0.80 g, 3.7 mmole) in MeOH (5 ml) and water (10 ml) was heated under reflux for 2 hr. The cooled products were basified (to pH 10) with dil. NaOHaq and extracted with chloroform (3 × 25 ml). The aqueous layer was separated, neutralized with dil. H_2SO_4, concentrated under reduced pressure (to *ca.* 10 ml) and then acidified with dilute sulphuric acid. The precipitated 2,4,6-*trimethylbenzenesulphinic acid* (0.50 g, 68%) was collected by filtration and recrystallised from aqueous methanol [Found: C, 58.0; H, 6.5. $C_9H_{12}O_2S$ requires: C, 58.6; H, 6.5%]; m.p. 92–96°; τ(CD_3OD): 3.10 (2H, s), 7.40 (6H, s), 7.72 (3H, s); pK_a [ethanol–water (3:2) v/v] 3.8.

Decomposition of TPSH in the absence of base in various solvents

(a) In d_4-MeOH solution (*ca.* 10% w/v) at 35°, TPSH undergoes *ca.* 50% decomposition (as indicated by NMR spectroscopy) in *ca.* 50 min. Under these conditions, 70% decomposition occurs in 190 min.

(b) In d_6-DMSO solution (*ca.* 10% w/v) at 35°, TPSH undergoes *ca.* 55% decomposition in 145 min.

(c) In $CDCl_3$ solution (*ca.* 10% w/v) at 35°, TPSH undergoes *ca.* 40% decomposition in 22.5 hr.

(d) In dioxan solution (*ca.* 10% w/v) at 35°, TPSH undergoes *ca.* 60% decomposition in 23 hr.

(e) In THF solution (*ca.* 10% w/v), under reflux (at 67°), TPSH undergoes *ca.* 35% decomposition in 35 min.

Kinetics of decomposition of arenesulphonyl hydrazides in the presence of triethylamine in d_4-methanol solution

A soln of the arenesulphonyl hydrazide (30–45 mg) and triethylamine (*ca.* 1 molecular equiv with respect to the arenesulphonyl hydrazide) in d_4-MeOH (*ca.* 0.5 ml) was maintained at the ambient temp. (35°) of the NMR spectrometer. Appropriate regions of the spectra (the Me proton resonance signals in the case of tosyl hydrazide and the aromatic ring proton resonance signals in the cases of MSH and TPSH) were measured after suitable intervals of time. The percentage of remaining arenesulphonyl hydrazide was estimated by measuring the peak heights of the signals (singlets) assignable to starting material and product (arenesulphinate). It was assumed that the amounts of these two components in a mixture were proportional to the corresponding peak heights. Straight lines were obtained by plotting $\log_{10}$ (% of remaining starting material) against time for both TPSH and MSH. In the case of tosyl hydrazide, a reasonably good straight line plot was obtained. The half-time of decomposition of TPSH, MSH and tosyl hydrazide were found to be 19 min, 300 min and *ca.* 120 hr, respectively.

Acetone 2,4,6 - tri - isopropylbenzenesulphonyl hydrazone (5; R=R'=Me). A soln of TPSH (0.70 g, 2.3 mmole) in acetone (9 ml) was stirred for 30 min at 20° and then evaporated under reduced pressure. Crystallization of the residue from aqueous methanol gave *acetone 2,4,6 - tri - isopropylbenzenesulphonyl hydrazone* [Found, in material dried at 60° *in vacuo* over P_2O_5: C, 64.0; H, 8.95; N, 8.1. $C_{18}H_{30}N_2O_2S$ requires: C, 63.9; H, 8.9; N, 8.3%], m.p. 128–134° dec.; yield, 0.70 g (95%); τ($CDCl_3$): 2.90 (2H, s), 5.77 (2H, m), 7.13 (1H. m), 8.12 (3H, s), 8.23 (3H, s), 8.84 (18H, d, J = 7 Hz).

Cyclohexanone 2,4,6 - tri - isopropylbenzenesulphonyl hydrazone (5; R=R'= $-(CH_2)_5-$). TPSH (1.12 g, 3.75 mmole) was added to a stirred soln of cyclohexanone (0.28 ml, 2.7 mmole) in THF (10 ml) at 20°. After 10 min, the products were concentrated under reduced pressure and the residue crystallized from aqueous MeOH to give *cyclohexanone 2,4,6 - tri - isopropylbenzenesulphonyl hydrazone* [Found: C, 66.85; H, 9.2; N, 7.4. $C_{21}H_{34}N_2O_2S$ requires: C, 66.6; H, 9.0; N, 7.4%] as colourless crystals (0.96 g, 90%), m.p. 142–144° dec.; τ($CDCl_3$): 2.83 (2H, s), 5.73 (2H, m), 7.08 (1H, m), 7.6–8.0 (4H, m), 8.1–8.6 (6H, m), 8.74 (18H, d, J = 7 Hz).

General procedure for preparation of 2,4,6 - tri - isopropylbenzenesulphonyl hydrazones

A soln of the aldehyde or ketone substrate and TPSH (*ca.* 1.1 molecular equivalents) in methanol or THF (*ca.* 10 ml/g TPSH) was stirred at 20°. Hydrazone formation was followed by TLC [$CHCl_3$–MeOH (9:1 v/v)]. When the reaction had gone to completion (after as little as 5 min for some unhindered substrates), the product was precipitated (if necessary) by the addition of water and crystallized from aqueous MeOH or some other suitable solvent. Except in the cases of hindered substrates, high yields of products were usually obtained.

Acetone 2,4,6-trimethylbenzenesulphonyl hydrazone. A soln of MSH (1.0 g, 4.67 mmole) in acetone (10 ml) was stirred for 20 min at 20° and then evaporated under reduced pressure. Crystallization of the residue from aqueous methanol gave *acetone 2,4,6-trimethylbenzenesulphonyl hydrazone* [Found, in material dried *in vacuo* over P_2O_5: C, 56.9; H, 7.2; N, 10.8. $C_{12}H_{18}N_2O_2S$ requires: C, 56.7; H, 7.1; N, 11.0%] as colourless crystals (1.04 g, 87%), m.p. 160–161° dec.; τ($CDCl_3$): 3.05 (2H, s), 7.33 (6H, s), 7.71 (3H, s), 8.12 (3H, s), 8.20 (3H, s).

Reduction of azobenzene with TPSH. A soln of azobenzene (0.091 g, 0.50 mmole) and TPSH (0.30 g, 1.0 mmole) in MeOH (5 ml) was allowed to stand at 20°. After 90 min, the yellow colour of the solution was discharged and no absorption at 445 nm was detectable.

The reaction between azobenzene and TPSH was similarly examined in the presence of triethylamine and in other solvents, both in the absence and presence of base. For results, see Table 1 (experiments Nos. 2–8).

Hydrazobenzene. TPSH (3.0 g, 10.1 mmole) was added to a stirred soln of azobenzene (0.91 g, 5.0 mmole) in methanol (50 ml), maintained at 50°. After 12 min, when the yellow colour of the soln was discharged, the products were concentrated under reduced pressure, redissolved in ether (75 ml) and the soln extracted with 2% NaOHaq (3 × 100 ml). The dried (Na_2SO_4) organic layer was evaporated to give a nearly colourless crystalline mass (0.80 g, 85%). Crystallization of this material from EtOH gave hydrazobenzene, m.p. 126–127°, identical (mixed m.p., ultraviolet and IR spectra) to authentic material.

Reduction of acenaphthylene with TPSH

TPSH (4.12 g, 13.8 mmole) was added to a stirred soln of acenaphthylene (0.835 g, 5.5 mmole) in MeOH (50 ml) at 20°. After 16 hr (the discharge of the yellow colour suggested that the reaction had gone to completion in *ca.* 6 hr), 5% aqueous sodium hydroxide solution (50 ml) was added and the colourless crystalline ppt collected by filtration. After this material had been washed with cold water and dried *in vacuo* over P_2O_5, it had m.p. 94–95°; it was identified (UV and NMR spectra) as acenaphthene (lit.[15] m.p. 95°); yield 0.835 g (99%). There was no indication that the rate of reduction could be increased by the additon of piperidine.

Reduction of norbornene with TPSH

A soln of norbornene (0.005 g, 0.05 mmole), TPSH (0.03 g, 0.1 mmole) and triethylamine (14 μl, 0.1 mmole) in d_4-MeOH (0.5 ml), contained in an NMR tube, was maintained at the ambient temperature (35°) of the NMR spectrometer. After 75 min, the intensity of the norbornene olefinic proton resonance signal (at *ca.* τ 4) was weak and, after 150 min, the latter signal could not be detected.

Reduction of allyl alcohol and 3-methylbut - 1 - en - 3 - ol with TPSH

(a) A soln of allyl alcohol (0.15 ml, 2.2 mmole) and TPSH (1.33 g, 4.46 mmole) in ether (20 ml) was heated under reflux. After suitable intervals of time, aliquots (1 ml) of the reaction solution were removed, treated with acetone (0.5 ml) and, after *ca.* 15 min, examined by GLC. After 24 hr, *ca.* 98% reduction of the substrate to n-propanol was found to have occurred. The reduction was repeated in boiling THF soln (Table, experiment No. 12).

(b) The reaction between 3 - methylbut - 1 - en - 3 - ol (0.1 ml, 1.0 mmole) and TPSH (0.60 g, 2.0 mmole) was carried out in boiling ether (10 ml) and boiling THF (10 ml) solutions (Table, experiments Nos. 13 and 14).

Reduction of 3,5-dinitrobenzoate ester of 3 - methylbut - 1 - en - 3 - ol with TPSH

A soln of 3 - methylbut - 1 - en - 3 - yl 3,5-dinitrobenzoate (0.70 g, 2.5 mmole) and TPSH (1.50 g, 5.0 mmole) in THF (50 ml) was heated, under reflux, for 2 hr. The cooled products were evaporated under reduced pressure, the residue dissolved in ether (100 ml) and the solution extracted with 2% NaOHaq (3 × 100 ml). The dried (Na_2SO_4) organic layer was evaporated to give t-pentyl 3,5-dinitrobenzoate (0.55 g, 61%) as a crystalline mass. After recrystallization from ethanol, the product had m.p. 115.5–116° (lit.[16] 117°); τ($CDCl_3$): 0.7–1.0 (3H, m), 7.97 (2H, quart., J ~ 7.5 Hz), 8.36 (6H, s), 8.99 (3H, t, J ~ 7.5 Hz).

Reduction of ethyl crotonate with TPSH

The reduction of ethyl crotonate (0.123 ml, 1.0 mmole) by TPSH (0.60 g, 2.0 mmole) to give ethyl butyrate was carried out in boiling ether (15 ml) solution (see Table 1, experiment No. 16); it was monitored as in the above reduction of allyl alcohol.

Reaction between trans-stilbene and tosyl hydrazide

A soln of *trans*-stilbene (0.10 g, 0.55 mmole) and tosyl hydrazide (0.21 g, 1.1 mmole) in dioxan (6 ml) was maintained at 50°. After 8 hr, an aliquot (1 ml) of this solution was treated with acetone (1 ml) at 20° for 20 hr. GLC analysis revealed no dibenzyl in the products.

Reduction of trans-stilbene with TPSH

The reduction of *trans*-stilbene (0.30 g, 1.67 mmole) by TPSH (2.0 g, 6.7 mmole) to give dibenzyl was carried out in (a) boiling ether (17 ml) and (b) boiling dimethoxymethane solutions (see Table 1, experiments Nos. 17 and 18).

Reductions with MSH

(a) *Azobenzene.* A soln of azobenzene (0.090 g, 0.49 mmole) and MSH (0.228 g, 0.94 mmole) in MeOH (5 ml) was heated under reflux. After 22 min, the solution became colourless. When the experiment was repeated but with the addition of piperidine (0.1 ml, 1 mmole), the reaction soln became colourless ater 12 min.

(b) *Acenaphthylene.* A soln of acenaphthylene (0.979 g, 6.44 mmole) and MSH (3.0 g, 14.0 mmole) in MeOH (30 ml) was heated, under reflux, for 2 hr, cooled and then worked-up as in the above reduction of acenaphthylene with TPSH. Acenaphthene (0.977 g, 98%), identical (NMR and UV spectra) to authentic material, was obtained.

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