

2,4,6-Tri-isopropylbenzenesulphonyl Hydrazide as a Hydrogenating Agent

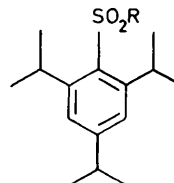
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Summary 2,4,6-Tri-isopropylbenzenesulphonyl hydrazide (**1b**) is an effective hydrogenating agent for olefins at relatively low temperatures.

phous powder, m.p. 121–122° (decomp.), after treating a solution of 2,4,6-tri-isopropylbenzenesulphonyl chloride⁴

In 1961, it was reported^{1,2} that olefins could be reduced to the corresponding saturated hydrocarbons by heating them in solution with benzene-¹ or toluene-*p*-sulphonyl hydrazide. This hydrogenation process is believed to involve di-imide (HN=NH),³ a thermal decomposition product of the arenesulphonyl hydrazide. We now report that 2,4,6-tri-isopropylbenzenesulphonyl hydrazide (**1b**) undergoes thermal decomposition much more readily than benzene- or toluene-*p*-sulphonyl hydrazide and that it is an effective reagent for the hydrogenation of olefins at relatively low temperatures. (**1b**) was isolated as an amor-



- (1) a ; R = Cl
 b ; R = NHHN₂
 c ; R = H

(1a) in tetrahydrofuran with hydrazine hydrate. A satisfactory yield (ca. 80%) of good quality reagent† was obtained when the reaction and work-up temperatures were kept close to 0°. A sample of (1b) remained virtually unchanged after it had been stored at 0°, in the dark, for several weeks. However, it underwent complete decomposition when it was heated, under reflux, in aqueous methanol (1:2, v/v) solution for 1 h and the corresponding

From the results in the Table, it can be seen that hydrogenation can be carried out at a much lower temperature with (1b) than with benzene¹ or toluene-*p*-² sulphonyl hydrazide. (1b) has the advantage of being freely soluble in most organic solvents and its decomposition product (1c) can be removed by extraction with dilute alkali. Preliminary results suggest that it is more economical, from the standpoint of the amount of (1b) required, to carry out

Hydrogenations with 2,4,6-tri-isopropylbenzenesulphonyl hydrazide

Experiment No.	Substrate	Mol equiv. of (1b)	Solvent ^a	Temperature (°C)	Reaction time (h)	% Substrate reduced
1	PhN=NPh	2	Methanol	50	0.2	100 ^b
2	PhCH=CHPh	2	Dioxan	50	8.0	ca. 60 ^{c,d}
3	PhCH=CHPh	4	THF	65 ^e	2.0	ca. 60 ^{e,t}
4	PhCH=CHPh	4	Methylal	42 ^e	26.0	ca. 90 ^e
5	CH ₂ =CH-CH ₂ OH	2	THF	65 ^e	2.0	100 ^e
6	CH ₂ =CH-CH ₂ OH	2	Ether	35 ^e	24.0	>95 ^e
7	CH ₂ =CH-CMe ₂ OH	2	THF	65 ^e	1.5	100 ^e
8	CH ₂ =CH-CMe ₂ OH	2	Ether	35 ^e	24.0	100 ^e
9	MeCH=CHCO ₂ Et	2	THF	65 ^e	2.0	ca. 80 ^e
10	MeCH=CHCO ₂ Et	2	Ether	35 ^e	33.0	ca. 90 ^e

^a Initial concentrations of substrate were ca. 0.1M. No base was added. ^b Estimated by t.l.c. Crystalline hydrazobenzene was isolated from the products in 85% yield. ^c Percentages of dibenzyl (expts. nos. 2–4), *n*-propyl alcohol (expts. nos. 5, 6), *t*-pentyl alcohol (expts. nos. 7, 8), and ethyl butyrate (expts. nos. 9, 10) were estimated by g.l.c. ^d Under the same conditions, no detectable reduction occurred with the equivalent amount of toluene-*p*-sulphonyl hydrazide. ^e Boiling point of solvent. ^f If (1b) (4 mol. equiv.) is added in 4 equal portions at hourly intervals to a solution of *trans*-stilbene in boiling THF, ca. 80% reduction is effected.

sulphinic acid (1c) could be isolated from the products in 60% yield. In CD₃OD solution (n.m.r. tube) at 35°, initial decomposition of (1b) was rapid and, after 1 h, less than 50% of it remained; under the same conditions but in the presence of one molecular equivalent of triethylamine, decomposition of (1b) was even more rapid and first-order kinetics ($t_{1/2}$ 19 min) were observed. In contrast, toluene-*p*-sulphonyl hydrazide was virtually unchanged after it had been heated at 50° in methanol solution for 16 h. Decomposition of (1b) occurred rather more slowly in the other solvents (dimethyl sulphoxide, dioxan, tetrahydrofuran, and chloroform) examined.

hydrogenations at as low a temperature as possible but long reaction times are then necessary. Although other arenesulphonyl hydrazides (notably *o*-nitrobenzenesulphonyl hydrazide⁵) are also known to undergo thermal decomposition very readily, it is not evident from the literature^{3a} that they are practically useful hydrogenating agents.

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† T.l.c. on Merck Kieselgel GF₂₅₄ in CHCl₃-MeOH (9:1 v/v)] of this material indicated that it was at least 90% pure. (1b) was characterized as its analytically pure acetone and cyclohexanone derivatives, m.p.s. 126–130° (decomp.) and 142–143° (decomp.) respectively. A noteworthy and potentially useful aspect of the chemistry of (1b) lies in the comparative facility with which it reacts with aldehydes and ketones.

¹ S. Hünig, H. R. Müller, and W. Thier, *Tetrahedron Letters*, 1961, 353.

² E. E. van Tamelen and R. S. Dewey, *J. Amer. Chem. Soc.*, 1961, **83**, 3729.

³ For reviews on di-imide see: (a) S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271; (b) C. E. Miller, *J. Chem. Educ.*, 1965, **42**, 254.

⁴ R. Lohrmann and H. G. Khorana, *J. Amer. Chem. Soc.*, 1966, **88**, 829.

⁵ A. T. Dann and W. Davies, *J. Chem. Soc.*, 1929, 1050; W. Davies, F. R. Storrie, and S. H. Tucker, *ibid.*, 1931, 624.