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

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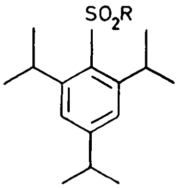
Summary 2,4,6-Tri-isopropylbenzenesulphonyl hydrazide (**1b**) is an effective hydrogenating agent for olefins at relatively low temperatures.

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*-[2]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 amorphous powder, m.p. 121—122° (decomp.), after treating a solution of 2,4,6-tri-isopropylbenzenesulphonyl chloride[4]



(1) a ; R = Cl
b ; R = NHNH$_2$
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 sulphinic acid (**1c**) could be isolated from the products in 60% yield. In CD_3OD 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 ($t_{\frac{1}{2}}$ 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 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	$PhCH\overset{t}{=}CHPh$	2	Dioxan	50	8·0	*ca.* 60[c,d]
3	$PhCH\overset{t}{=}CHPh$	4	THF	65[e]	2·0	*ca.* 60[c,f]
4	$PhCH\overset{t}{=}CHPh$	4	Methylal	42[e]	26·0	*ca.* 90[c]
5	$CH_2{=}CH{-}CH_2OH$	2	THF	65[e]	2·0	100[c]
6	$CH_2{=}CH{-}CH_2OH$	2	Ether	35[e]	24·0	>95[c]
7	$CH_2{=}CH{-}CMe_2OH$	2	THF	65[e]	1·5	100[c]
8	$CH_2{=}CH{-}CMe_2OH$	2	Ether	35[e]	24·0	100[c]
9	$MeCH{=}CHCO_2Et$	2	THF	65[e]	2·0	*ca.* 80[c]
10	$MeCH{=}CHCO_2Et$	2	Ether	35[e]	33·0	*ca.* 90[c]

[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.

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 benzene-[1] 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 at as low a temperature as possible but long reaction times are then necessary. Although other arenesulphonyl hydrazides (notably *o*-nitrobenzenesulphonyl hydrazide[5]) 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 GF_{254} in $CHCl_3$–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.

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[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.

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