

Vacuum Pyrolysis of Salts of 1-Acyl-2-arylsulphonylhydrazines; a General McFadyen–Stevens Aldehyde Synthesis

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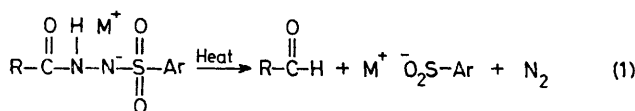
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Summary Vacuum pyrolysis of alkali metal salts of 1-acyl-2-arylsulphonylhydrazines is an efficient general method for synthesising aldehydes.

TABLE. Aldehydes from salts (**1a,c**; Ar = C₆H₄Me-*p*) of 1-acyl-2-*p*-tosylhydrazines.^a

DECOMPOSITION of salts (**1a,b**) of 1-acyl-2-arylsulphonylhydrazines yields aldehydes (**2**), arylsulphinic acid salts (**3**), and nitrogen (equation 1).^{1,2} The aldehyde synthesis is

Aldehyde	Salt precursor (1)	Yield/% ^{b,c}
Me[CH ₂] ₃ CHO	a (c)	68 (70)
Me ₂ CHCHO	a (c)	71 (68)
Me ₃ CCHO	a (c)	84 (60)
Me[CH ₂] ₃ CHO	a (c)	70 (72)
Ph[CH ₂] ₂ CHO	a (c)	85 (85)
CH ₂ :CH[CH ₂] ₈ CHO	a (c)	60 (56)
PhCHO	c	83
<i>p</i> -MeC ₆ H ₄ CHO	c	80
<i>p</i> -MeOC ₆ H ₄ CHO	c	75
2,4-Dimethyloxazole-5-carbaldehyde ^d	a (c)	70 (68)



(1) (2) (3)

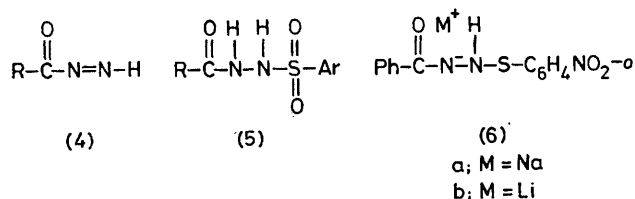
a, M = Na

b, M = K

c, M = Li

^aPrepared from acid chlorides and *p*-tosylhydrazine or from acid hydrazides and *p*-tosyl chloride. The hydrazines (**5**) either have melting points similar to those reported in the literature or give correct analyses. ^bAnalysed on 10% Carbowax 20 M or SE 30–20% Chromosorb W GC columns. ^cThe yields are lower if excess of base is used. ^dThis compound gave correct analysis.

known as the McFadyen–Stevens method and has usually involved decomposition of 1-acyl-2-arylsulphonylhydrazines by sodium or potassium carbonate (4–6 equiv.) in ethylene glycol or ethylene glycol–water at *ca.* 160 °C.^{1,2} Surfaces, in particular powdered glass, accelerate and improve the conversions of (**1a,b**) into (**2**).³ The McFadyen–Stevens method is presumed to involve intermediate acylimides (**4**) and has been widely used for synthesis of stable aromatic and heterocyclic aldehydes.^{1–3} Aliphatic, alicyclic, or other base-sensitive aldehydes have not been obtained efficiently, however, because they undergo aldol condensation, Cannizzaro reactions, or other changes in the hot alkaline environments.^{2,4,5} Some progress has been made in synthesis of alkali-sensitive aldehydes from (**1a,b**) by careful control of the reaction temperature, time, solvent, and the amounts of base and by rapid distillation of the product from the reaction medium.^{4,5}



We now report that vacuum pyrolysis (0.5–2.0 mmHg) of dry sodium or lithium salts (**1a** or **1c**; Ar = *p*-tolyl) of 1-acyl-2-*p*-tosylhydrazines (**5**; Ar = *p*-tolyl) is an effective simple method for preparing sensitive aldehydes (Table). Sodium salts (**1a**; Ar = *p*-tolyl), obtained by neutralization of (**5**; Ar = *p*-tolyl) with fresh sodium methoxide in abso-

lute methanol and removal of methanol under reduced pressure, decompose rapidly at 140–155 °C. Lithium salts (**1c**; Ar = *p*-tolyl), though more expensive, are conveniently prepared from (**5**; Ar = *p*-tolyl) and *n*-butyllithium in tetrahydrofuran (THF) and thermolyse smoothly at 180–200 °C. Potassium salts (**1b**, decomposition range: 130–140 °C) and 1-acyl-2-arylsulphonylhydrazines (**5**) with possibly better leaving groups (Ar = *p*-methoxyphenyl, 2,5-dichlorophenyl, or 2,4,6-tri-isopropylphenyl, respectively) are also satisfactory but are of no particular advantage. Present efforts to develop an efficient low-temperature aldehyde synthesis by decomposition of salts (**6a** or **6b**) of 1-benzoyl-2-*o*-nitrophenylsulphenylhydrazine⁶ either in the absence of solvent (70 °C) or in THF (0–30 °C) have been unsuccessful.

Vacuum pyrolysis of (**1a–c**) provides an excellent small-scale synthesis of pure, volatile aldehydes (**2**). Of note is the efficient preparation of 2,4-dimethyloxazole-5-carbaldehyde, the first oxazole-5-carbaldehyde to be reported. As yet compounds (**4**) have not been detected. Since compounds (**3**) are involatile and thermally stable below 180 °C, compounds (**2**) as condensed directly from the thermolyses are quite pure. The pyrolytic method has been used conveniently for preparing (**2**) in 0.05 mol quantities. Decomposition of larger amounts of (**1a–c**) is feasible if the vacuum system can handle the large volumes of nitrogen produced rapidly.†

A typical procedure for conversion of (**5**) into (**2**) is as follows. *n*-Butyllithium (0.01 mol) in hexane (5 ml), or sodium methoxide (0.01 mol) in methanol (10 ml), was added to (**5**) (0.01 mol) in THF (30 ml) at 0 °C. The stirred mixture was warmed to room temperature and

† A large Pyrex flask connected to the vacuum pyrolysis system will usually handle the pressure surges that may occur.

stored for 0.5 h. The solvents were evaporated under reduced pressure and the residue was pyrolysed (0.1 mmHg) at 190–200 °C. The aldehyde (2) produced was collected at –78 °C and analysed by g.l.c.

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⁶ See also, S. Cacchi and G. Paolucci, *Gazzetta*, 1974, **104**, 221.