128. *A New Method for the Conversion of Acids into Aldehydes.*

By John S. McFadyen and Thomas S. Stevens.

Benzenesulphonphenylhydrazide (I), when warmed with alkali (Escales, *Ber.*, 1885, **18**, 893), yields benzene, nitrogen, and benzenesulphinic acid, probably *via* the unstable intermediate (II) :

$$\text{(I) } NHPh\cdot NH\cdot SO_2Ph \longrightarrow Ph\cdot SO_2K + [Ph\cdot N\colon NH] \text{ (II)} \longrightarrow PhH + N_2$$

It is now shown that aldehydes may be obtained in an analogous manner from benzenesulphonacylhydrazides :

$$R\cdot CO\cdot NH\cdot NH\cdot SO_2Ph \longrightarrow Ph\cdot SO_2K + [R\cdot CO\cdot N\colon NH] \longrightarrow R\cdot CHO + N_2$$

and the generality of the method has been investigated.

The percentage yields of aldehydes obtained from the corresponding benzenesulphon acylhydrazides are recorded in Table I. Those of the aromatic aldehydes are often very good, but the method fails entirely in the aliphatic series. The contrasting behaviour of the benzenesulphon-nitrobenzoylhydrazides recalls the experience of Curtius and Melsbach (*J. pr. Chem.*, 1910, **81**, 524), who found that *m*-nitrobenzhydrazide in weakly alkaline solution yielded *m*-nitrobenz-*m*′-nitrobenzylidenehydrazide, whereas the *p*-isomeride underwent no analogous reaction.

Table I.

A	Benzoic	73	F	*p*-Methoxybenzoic	77	K	† Cinnamic	0
B	* Benzoic	74	G	3 : 4-Methylenedioxybenzoic	87	L	Acetic	0
C	* *p*-Chlorobenzoic	77	H	*m*-Nitrobenzoic	42	M	*iso*Butyric	0
D	*o*-Hydroxybenzoic	55	J	*p*-Nitrobenzoic	0	N	Diphenylacetic	0
E	* *o*-Hydroxybenzoic	42						

* The 2 : 5-dichlorobenzenesulphonacylhydrazide was used.

† The action of benzenesulphonyl chloride on cinnamoylhydrazine yielded a *compound*, white rhombs from alcohol, m. p. 169—171° (decomp.) (Found : N, 9·7, 9·8. $C_{15}H_{14}O_3N_2S$ requires N, 9·3%), from which no cinnamaldehyde could be obtained.

The required benzenesulphonacylhydrazides may be prepared according to the scheme :

$$\begin{tikzcd}
 & R\cdot CO_2Et \arrow[r] & R\cdot CO\cdot NH\cdot NH_2(+ Ph\cdot SO_2Cl) \arrow[dr] & \text{(X)} \\
R\cdot CO_2H \arrow[ur] \arrow[dr] & & & R\cdot CO\cdot NH\cdot NH\cdot SO_2Ph \\
 & R\cdot COCl(+Ph\cdot SO_2\cdot NH\cdot NH_2) \arrow[urr] & & \text{(Y)}
\end{tikzcd}$$

but the action of the acid chloride on benzenesulphonhydrazide in the benzoyl and anisoyl series led to very ready diacylation, and the route (X) was therefore in general preferred to the route (Y). The benzenesulphonacylhydrazides are represented here as having the symmetrical structure, with no free amino-group, since *benzenesulphonbenzoylhydrazide* did not react with benzaldehyde in boiling alcohol.

This type of reaction has also been applied successfully to the replacement, by hydrogen, of a reactive halogen atom in the benzene ring. Thus 2 : 4-dinitrochlorobenzene gave *m*-dinitrobenzene, and picryl chloride yielded *s*.-trinitrobenzene, which may be simply and rapidly prepared by the series of reactions :

$$C_6H_2(NO_2)_3\cdot OH \longrightarrow C_6H_2(NO_2)_3Cl \longrightarrow C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot SO_2Ph \longrightarrow C_6H_3(NO_2)_3$$

Experimental.

The known acid hydrazides were obtained in good yield by published methods. *Piperonoylhydrazine* was prepared by refluxing methyl piperonylate (5 g.), 50% hydrazine hydrate (5·6 c.c.), and alcohol (6 c.c.) for 2 hours. The needles (4 g.; m. p. 170—171°) which separated over-night were collected, and the filtrate and washings (ice-cold alcohol) on concentration and further refluxing yielded 0·6 g. more. The hydrazide crystallised from alcohol in small colourless needles, m. p. 171—172° (Found : N, 15·7. $C_8H_8O_3N_2$ requires N, 15·6%).

The benzenesulphonacylhydrazides (all colourless) were prepared as described for the benzoyl series, usually by method (X) with an average yield of 90%; the descriptions and analytical data are in Table II.

Benzenesulphonbenzoylhydrazide.—(X) Benzenesulphonyl chloride (3·8 c.c.) was added slowly to a stirred, cooled solution of benzhydrazide (4 g.) in pyridine (25 c.c.). After 2 hours the solution was poured into a mixture of ice and hydrochloric acid, and the pale yellow precipitate filtered off, washed with dilute hydrochloric acid and water, and recrystallised from alcohol (80 c.c.). Yield, 7 g. of colourless prismatic needles, m. p. 192—194° (decomp.) (Found: N, 10·4. $C_{13}H_{12}O_3N_2S$ requires N, 10·15%).

(Y) Benzoyl chloride (26·8 c.c.) was added slowly to a stirred, cooled solution of benzenesulphonhydrazide (40 g.) in pyridine (100 c.c.). The solution was poured with stirring into a mixture of ice and hydrochloric acid, and the white precipitate was washed with dilute hydrochloric acid and water. Yield of crude material, 55 g. Recrystallisation from alcohol gave a first crop (2 hours) of colourless prismatic needles (30 g.), m. p. 191—193° (decomp.), not depressed on admixture with the product from method (X) above. After 2 days the mother-liquor deposited a further crop of the above product, together with colourless silky needles. By repeated warming, filtration, and recrystallisation the more easily soluble fine needles were obtained as an apparently homogeneous product, m. p. 192—194° (decomp.), depressed on admixture with benzenesulphonbenzoylhydrazide, but not with ***benzenesulphondibenzoylhydrazide.***

Benzenesulphondibenzoylhydrazide.—Benzenesulphonbenzoylhydrazide (1·1 g.) and benzoyl chloride (0·72 g.) were kept in pyridine (10 c.c.) at 40° for 4 hours. The mixture was poured into water and ligroin, and vigorously shaken. The solid product was filtered off and recrystallised from alcohol, giving silky needles, m. p. 198—200° (decomp.) (Found: N, 7·4. $C_{20}H_{16}O_4N_2S$ requires N, 7·4%).

TABLE II.

Benzenesulphonacylhydrazides.

Acyl.	Solvent.	Description.	M. p.	% N found.	% N required.	Formula.
* Benzoyl	EtOH	Prismatic needles	186—188°‡	8·4	8·1	$C_{13}H_{10}O_3N_2Cl_2S$
* *p*-Chlorobenzoyl	EtOH	Prisms	235—237 ‡	7·5	7·4	$C_{13}H_9O_3N_2Cl_3S$
o-Hydroxybenzoyl	EtOH	Silky needles	161—162	9·8	9·6	$C_{13}H_{12}O_4N_2S$
* *o*-Hydroxybenzoyl	EtOH	Needles	229—230 ‡	7·8	7·8	$C_{13}H_{10}O_4N_2Cl_2S$
p-Methoxybenzoyl	EtOH	Prisms	187—189 ‡	9·3	9·2	$C_{14}H_{14}O_4N_2S$
3 : 4-Methylenedioxybenzoyl	EtOH	Prisms	166—168	8·8	8·8	$C_{14}H_{12}O_5N_2S$
m-Nitrobenzoyl	HOAc	Fibrous needles	222—223 ‡	12·9	13·1	$C_{13}H_{11}O_5N_3S$
† *p*-Nitrobenzoyl	EtOH	Silky needles	197—199 ‡	13·1	13·1	$C_{13}H_{11}O_5N_3S$
Acetyl (Curtius and Lorenzen, *J. pr. Chem.*, 1898, **58**, 173)						
*iso*Butyryl	EtOH	Rhombs	156—158	11·7	11·6	$C_{10}H_{14}O_3N_2S$
Diphenylacetyl	EtOH	Plates	191—193	7·8	7·7	$C_{20}H_{18}O_3N_2S$

* 2 : 5-Dichlorobenzenesulphonacylhydrazides.
† Prepared by route (Y); reaction completed at 50°.
‡ Melting with decomposition.

Decomposition of ***Benzenesulphonacylhydrazides.***—This was brought about by alkaline carbonates; sodium borate or acetate, or organic bases were ineffective. When the aldehyde was steam-volatile and insoluble in alkali, the decomposition, if taking place readily, could conveniently be brought about by steam-distillation from aqueous sodium carbonate. Otherwise ethylene glycol was used as solvent on account of its high b. p., ability to dissolve alkaline carbonates, and miscibility with water, which facilitated isolation of the product. Experiments with other solvents, such as pyridine, quinoline and *cyclo*hexanol, were less encouraging. Benzenesulphinic acid was produced in quantity and identified as 2 : 4-dinitrodiphenylsulphone (mixed m. p.).

Table III contains the results of a few typical experiments. In these, benzenesulphonbenzoylhydrazide was dissolved in glycol heated in an oil-bath at the specified temperature, and anhydrous alkali added in one portion, causing brisk effervescence; after the specified time the reaction was stopped by the addition of hot water. The washed and dried ethereal extract of the resulting solution was evaporated, and the residual aldehyde precipitated and weighed as the dinitrophenylhydrazone. On the preparative scale the percentage yield of redistilled aldehyde was slightly smaller than that of the dinitrophenylhydrazone in the corresponding small-scale experiment.

TABLE III.

Experiment No.	1.	2.	3.	4.	5.	6.	7. †	8. †
Temperature	80→90°	130°	160°	160°	165°	140→190°	110°	‡
Time (secs.)	4000	1000	75	40	60	1000	500	‡
Equivs. alkali	6	4 *	5	2	1 *	4 *	4	6
Yield %	30	40	73	60	46	10	74	65

* Potassium carbonate; in all other cases sodium carbonate.

† Initial material 2 : 5-dichlorobenzenesulphonbenzoylhydrazide.

‡ Carried out by steam-distillation from aqueous sodium carbonate.

Except in experiment 6, the given time of heating is as short as is consistent with complete decomposition.

General Observations.—(a) The quantity of solvent (5 to 20 parts) had little effect on the yield. (b) Sodium carbonate as alkali gave slightly better results than the potassium salt. (c) The optimum temperature was about 160° (1, 2, 3); prolonged heating at a high temperature gave poor results (6). (d) Considerable excess of alkali was necessary (3, 4, 5). (e) The dichlorobenzenesulphonhydrazide decomposed at a lower temperature, giving a very similar yield (7, 8).

The other benzenesulphonacylhydrazides were treated in a similar manner, except that the alkali-soluble salicylaldehyde was steam-distilled from the acidified reaction mixture, and estimated as the dinitrophenylhydrazone. The yields given in Table I were obtained under the following conditions :

Case	C.	D.	E.	F.	G.	H.
Temperature	80→110°	155°	160°	150°	155°	155°
Time (secs.)	900	180	40	120	150	75
Equivs. Na_2CO_3	5	5	4	6	6	6

In case J the only product isolated was a crude, buff-coloured amorphous solid, softening at about 220°, but not completely melted at 290°. The initial materials in cases L and M were heated with sodium carbonate in a variety of high-boiling solvents, the vapours being led by a gentle air stream directly into the dinitrophenylhydrazine reagent, but no aldehyde was detected.

Benzenesulphon-2′ : 4′-dinitrophenylhydrazide.—2 : 4-Dinitrophenylhydrazine (4 g.) was suspended in pyridine (25 c.c.) at 50°, and vigorously stirred during the addition (15 mins.) of benzenesulphonyl chloride (2·8 c.c.). After 2 hours' stirring at room temperature, the product was poured into dilute caustic soda solution, and filtered from unchanged dinitrophenylhydrazine. The filtrate, on acidification, gave a brownish-yellow precipitate, which on recrystallisation from alcohol (animal charcoal) gave a mixture of lemon-yellow laminæ, m. p. 196—198° (decomp.) (Found : N, 16·4. $C_{12}H_{10}O_6N_4S$ requires 16·6%), and fine yellow needles, m. p. 196—198° (decomp.) (Found : N, 16·5%), showing no depression on admixture with one another, but each depressed by dinitrophenylhydrazine. In contact with alcohol, the needles gradually changed to the laminæ at room temperature.

Decomposition. Sodium carbonate (1 g.) was added to *benzenesulphon-2′ : 4′-dinitrophenylhydrazide* (1 g.) in ethylene glycol (10 c.c.) at 150°. After 3 minutes, hot water was added, and the mixture cooled. The chocolate-brown precipitate (0·34 g.; 70%), m. p. 81—83°, was recrystallised from alcohol (animal charcoal), giving pale yellow plates, m. p. 90°, not depressed on admixture with *m*-dinitrobenzene.

Benzenesulphon-2′ : 4′ : 6′-trinitrophenylhydrazide.—Hot alcoholic solutions of picryl chloride (15 g. in 120 c.c.) and benzenesulphonhydrazide (10 g. in 75 c.c.) were mixed and refluxed for a few minutes with shaking. The solid which rapidly separated was filtered off after cooling and washed with hot alcohol. It crystallised from alcohol (1000 parts) in lemon-yellow fibrous needles, m. p. 210—220° (decomp.) (Found : N, 18·3. $C_{12}H_9O_8N_5S$ requires N, 18·3%).

Decomposition. A mixture of *benzenesulphon-2′ : 4′ : 6′-trinitrophenylhydrazide* (9 g.), borax (5 g.), and water (50 c.c.) was heated carefully until the first effervescence was over, and then boiled for 40 minutes. After thorough cooling, the dark brown, amorphous solid (crude trinitrobenzene) was collected. This was recrystallised twice from alcohol (animal charcoal), giving 3 g. of pale yellow plates, m. p. 121—122°, not depressed on admixture with pure 1 : 3 : 5-trinitrobenzene.

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THE UNIVERSITY, GLASGOW. [*Received, March 4th,* 1936.]