290. *The Reactions of Nitrosulphonyl Chlorides. Part III. Identification and Characterisation of Aldehydes and Ketones as Nitrobenzenesulphonhydrazones.*

By JAMES M. L. CAMERON and FREDERICK R. STORRIE.

CERTAIN mononitrobenzenesulphonhydrazones of aldehydes and ketones

$$(NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}N{:}CR_1R_2)$$

have been described by Davies, Storrie, and Tucker (J., 1931, 624) and by Witte (*Rec. trav. chim.*, 1932, **51**, 299). We describe below some more of these derivatives and give in Table I the melting points of those which have so far been prepared. We are indebted to Miss M. C. Nelmes for the observation that acetone-*p*-nitrobenzenesulphonhydrazone (*loc. cit.*) is dimorphic, and since these compounds sometimes exhibit dimorphism, the solvent used in crystallisation is stated in each case.

TABLE I.

Mononitrobenzenesulphonhydrazones.

Aldehyde or ketone.	Ortho-.	Meta-.	Para-.
1. Acetaldehyde	—	—	121—122°
2. Acetone	147—148° *a*	148—150° *a*	169—171 *a*
3. Methyl ethyl ketone	143—144	124—125 *a*	155—156
4. Furfuraldehyde	118—120	156—157	152
5. *iso*Valeraldehyde	—	—	132—133
6. Methyl *n*-propyl ketone	—	115	—
7. Methyl *iso*propyl ketone	113—114	129—130	160—161
8. Diethyl ketone	99—101	—	—
9. Mesityl oxide	139—140	128—130	127—128
10. *cyclo*Hexanone	135—136	152—153	162
11. Methyl *iso*butyl ketone	73—74 ‡	102	155—156
12. Dextrose	—	149—150	—
13. *p*-Bromobenzaldehyde	—	175—176	186—187
14. *o*-Nitrobenzaldehyde	190—192	179—180	199—200
15. *m*- ,,	185—186	182—183	195—196
16. *p*- ,,	194—196	162—163	197—198
17. Benzaldehyde	170—171	150—151 *a*	142—144 *a*
18. Salicylaldehyde	195—196	167—168	192 †
19. Bromopiperonal	169—171	—	197
20. Piperonal	177—179 *a*	173—175 *a*	189—190 *a*
21. Acetophenone	138—140	175	192
22. Anisaldehyde	116—118	134 *b* * ‡	160 *b*
23. Vanillin	168—169	159—160	166—167
24. Cinnamaldehyde	153—155	188 *b*	—
25. Veratraldehyde	—	181—182	188—189
26. Benzylideneacetone	—	176—177	173—174
27. Benzylacetone	95—96	131—132	153—154
28. Benzophenone	138—140	146—147	—
29. Phenyl *p*-tolyl ketone	128—130 ‡	—	—
30. Benzoin	—	159—160	—
31. Benzil (dihydrazone)	—	166—167	—

a. Prepared by Davies, Storrie, and Tucker. *b*. Prepared by Witte.
* We find m. p. 130—131°. † Witte gives 178—179°. ‡ All melt with decomposition except those marked thus.

We also describe certain 2-chloro-5-nitrotoluene-4-sulphonhydrazones (some of which have already been prepared by Dann and Davies, J., 1929, 1050) and 2 : 4-dinitrobenzenesulphonhydrazones, and intend to prepare more of these derivatives. We are investigating a rapid method of analysing these substances, which should increase their importance in the identification and characterisation of aldehydes and ketones.

EXPERIMENTAL.

The *o*-, *m*-, and *p*-nitrobenzenesulphonhydrazones are prepared by the method described earlier (Davies, Storrie, and Tucker, *loc. cit.*), except that it has since been found that the *o*-nitrobenzenesulphonhydrazide can be isolated and dried without decomposition. Where acetone is mentioned as the crystallising solvent, it is not, of course, the solvent used in the preparation of the derivative.

The number preceding each compound corresponds to that in Table I.

o-*Nitrobenzenesulphonhydrazones.*

No.	Appearance.	Solvent.	Formula.	N, %. Found.	N, %. Calc.
3	Slightly yellow hexagonal prisms	EtOH	$C_{10}H_{13}O_4N_3S$	15·7	15·5
4	Brownish rectangular laminæ	MeOH	$C_{11}H_9O_5N_3S$	14·3	14·2
7	White leaflets	EtOH	$C_{11}H_{15}O_4N_3S$	14·6	14·7
8	Colourless rhombohedra	MeOH	$C_{11}H_{15}O_4N_3S$	14·8	14·7
9	White hexagonal prisms	$COMe_2$	$C_{12}H_{15}O_4N_3S$	14·1	14·1
10	White rhombs	$COMe_2$	$C_{12}H_{15}O_4N_3S$	14·3	14·1
11	Slightly yellow prisms	MeOH	$C_{12}H_{17}O_4N_3S$	14·4	14·1
14	Stout white prisms	$COMe_2$	$C_{13}H_{10}O_6N_4S$	16·1	16·0
15	Short white needles	$COMe_2$	$C_{13}H_{10}O_6N_4S$	15·8	16·0
16	White prisms	$COMe_2$	$C_{13}H_{10}O_6N_4S$	15·9	16·0
17	Stout yellow rhombs	MeOH	$C_{13}H_{11}O_4N_3S$	14·0	13·8
18	Pale yellow nodules	$COMe_2$–EtOH	$C_{13}H_{11}O_5N_3S$	13·3	13·1
19	Pale yellow microcrystals	EtOH	$C_{14}H_{10}O_6N_3S$	10·1	9·8
21	White quadrilateral prisms	$COMe_2$	$C_{14}H_{13}O_4N_3S$	13·2	13·1
22	Pale yellow plates (parallelograms)	EtOH	$C_{14}H_{13}O_5N_3S$	12·5	12·5
23	Pale yellow microcrystals	EtOH	$C_{14}H_{13}O_6N_3S$	12·2	12·0
24	Yellow prisms	EtOH	$C_{15}H_{13}O_4N_3S$	12·9	12·7
27	Stout white prisms	EtOH	$C_{16}H_{17}O_4N_3S$	12·1	12·1
28	Long thin white needles	$COMe_2$–EtOH	$C_{19}H_{15}O_4N_3S$	10·9	11·0
29	White microcrystals	EtOH	$C_{20}H_{17}O_4N_3S$	10·6	10·6

m-*Nitrobenzenesulphonhydrazones.*

No.	Appearance.	Solvent.	Formula.	N, %. Found.	N, %. Calc.
4	Pale yellow leaflets	EtOH	$C_{11}H_9O_5N_3S$	14·2	14·2
6	Small white needles	EtOH	$C_{11}H_{15}O_4N_3S$	14·8	14·7
7	White prisms	EtOH	$C_{11}H_{15}O_4N_3S$	15·0	14·7
9	White microcrystals	EtOH	$C_{12}H_{15}O_4N_3S$	14·0	14·1
10	Long white prisms	MeOH	$C_{12}H_{15}O_4N_3S$	14·1	14·1
11	White microcrystals	EtOH	$C_{12}H_{17}O_4N_3S$	14·2	14·1
12	Small white needles	EtOH	$C_{12}H_{17}O_9N_3S$	11·3	11·1
13	Small white needles	MeOH	$C_{13}H_{10}O_4N_3BrS$	10·9	11·0
14	Pale yellow microcrystals	H_2O–MeOH	$C_{13}H_{10}O_6N_4S$	16·3	16·0
15	Small white needles	$COMe_2$–EtOH	$C_{13}H_{10}O_6N_4S$	16·0	16·0
16	White microcrystals	EtOH	$C_{13}H_{10}O_6N_4S$	15·7	16·0
18	White plates	EtOH	$C_{13}H_{11}O_5N_3S$	13·1	13·1
21	White microcrystals	EtOH	$C_{14}H_{13}O_4N_3S$	13·5	13·1
22	Pale buff glistening leaflets	EtOH	$C_{14}H_{13}O_5N_3S$	12·5	12·5
23	Small yellow needles	EtOH	$C_{14}H_{13}O_6N_3S$	11·7	12·0
25	Bright yellow needles	EtOH	$C_{15}H_{15}O_6N_3S$	11·5	11·5
26	White plates	EtOH	$C_{16}H_{15}O_4N_3S$	12·1	12·2
27	Short white prisms	EtOH	$C_{16}H_{17}O_4N_3S$	12·3	12·1
28	Small white plates	EtOH	$C_{19}H_{15}O_4N_3S$	11·1	11·0
30	Small white matted needles	EtOH	$C_{20}H_{17}O_5N_3S$	10·1	10·2
31	Pale yellow microcrystals	EtOH	$C_{26}H_{20}O_8N_6S_2$	13·6	13·8

p-*Nitrobenzenesulphonhydrazones.*

No.	Appearance.	Solvent.	Formula.	N, %. Found.	N, %. Calc.
1	Small fine white needles	H_2O–MeOH	$C_8H_9O_4N_3S$	17·1	17·3
3	White needles	EtOH	$C_{10}H_{13}O_4N_3S$	15·3	15·5
4	Yellow needles	EtOH	$C_{11}H_9O_5N_3S$	14·5	14·2
5	White plates	MeOH	$C_{11}H_{15}O_4N_3S$	14·5	14·7
7	Small white needles	MeOH	$C_{11}H_{15}O_4N_3S$	14·7	14·7
9	Pale yellow microcrystals	EtOH	$C_{12}H_{15}O_4N_3S$	14·3	14·1
10	Small white needles	EtOH	$C_{12}H_{15}O_4N_3S$	13·9	14·1
11	White plates	EtOH	$C_{12}H_{17}O_4N_3S$	14·3	14·1
13	Stout colourless prisms	EtOH	$C_{13}H_{10}O_4N_3BrS$	11·0	11·0
14	Fine white needles	$COMe_2$	$C_{13}H_{10}O_6N_4S$	15·9	16·0
15	Small white rhombs	EtOH	$C_{13}H_{10}O_6N_4S$	16·2	16·0
16	Small white needles	EtOH	$C_{13}H_{10}O_6N_4S$	15·9	16·0
18	Pale yellow plates	EtOH	$C_{13}H_{11}O_5N_3S$	13·0	13·1
19	Thin white plates	EtOH	$C_{14}H_{10}O_6N_3S$	9·7	9·8
21	White microcrystals	EtOH	$C_{14}H_{13}O_4N_3S$	13·2	13·1
23	Pale yellow needles	EtOH	$C_{14}H_{13}O_6N_3S$	12·2	12·0
25	Small yellow nodules	EtOH	$C_{15}H_{15}O_6N_3S$	11·6	11·5
26	Yellow needles	$COMe_2$	$C_{16}H_{15}O_4N_3S$	12·1	12·2
27	Small white needles	MeOH	$C_{16}H_{17}O_4N_3S$	12·2	12·1

All the following hydrazones melt with decomposition. 2 : 4-Dinitrobenzenesulphonhydrazide is prepared as described by Davies, Storrie, and Tucker (*loc. cit.*), and its derivatives are prepared in the same manner as the mononitro-derivatives, except that the temperature must be kept below − 10° on account of the increased instability of the hydrazide. 2 : 4-*Dinitrobenzenesulphonhydrazones of*: (2) colourless, silky needles from acetone, m. p. 148° (Found: N, 18·8. $C_9H_{10}O_6N_4S$ requires N, 18·6%); (17) yellow micro-crystals from acetone, m. p. 188° (Found: N, 16·0. $C_{13}H_{10}O_6N_4S$ requires N, 16·0%); (19) yellow micro-crystals from acetone, m. p. 177° (Found: N, 11·6. $C_{14}H_9O_8N_4BrS$ requires N, 11·6%); (20) orange needles from acetone, m. p. 172—173° (Found: N, 14·5. $C_{14}H_{10}O_8N_4S$ requires N, 14·2%); (28) yellowish micro-crystals from acetone, m. p. 132—133° (Found: N, 12·8. $C_{19}H_{14}O_6N_4S$ requires N, 13·1%).

2-Chloro-5-nitrotoluene-4-sulphonhydrazide is described by Dann and Davies (*loc. cit.*); the hydrazones are prepared as for the nitrobenzenesulphonhydrazones. *Acetone*-2-*chloro*-5-*nitrotoluene*-4-*sulphonhydrazone*, stout, colourless, hexagonal prisms from acetone, m. p. 156—157° (Found: N, 14·1. $C_{10}H_{12}O_4N_3ClS$ requires N, 13·8%). *Benzaldehyde*-2-*chloro*-5-*nitrotoluene*-4-*sulphonhydrazone*, stout, colourless prisms from alcohol, m. p. 158—160° (Found: N, 11·8. $C_{14}H_{12}O_4N_3ClS$ requires N, 11·6%).

The acetone-*p*-nitrobenzenesulphonhydrazone described by Davies, Storrie, and Tucker (*loc. cit.*) as melting at 169—171° when crystallised from acetone, has m. p. 183—184° when crystallised from alcohol, the latter being the more stable form.

The authors thank Miss M. E. C. Anderson, and Messrs. R. B. Carswell, R. L. Jones, and J. Lindsay for preparing some of the compounds described above.

THE UNIVERSITY OF GLASGOW. [*Received, June* 18*th*, 1934.]