



The sulphonylhydrazide (II) may be tautomeric and, in the enol form (III), decompose to the carboxylic acid (IV), and then form the acid chloride (V). This, with excess of hydrazide (I), can give the dihydrazide (VI).

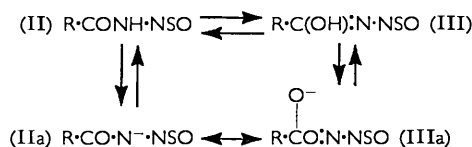
The possibility of the enol (III) being attacked by thionyl chloride to give a chloro-sulphonylhydrazide (VII), which then decomposes to the acid chloride (V), we consider to be generally unlikely, since octanoic acid was isolated quantitatively from octanohydrazide. Moreover, during the reactions an initial copious evolution of nitrogen and hydrogen chloride is followed by a slower release of hydrogen chloride, the opposite of which would be expected if the sequence (III)  $\rightarrow$  (VII)  $\rightarrow$  (V) operated. It is, however, possible that this route may operate with aromatic sulphonylhydrazides in which the enol form (IIIb) is the favoured tautomer.

That some relationship exists between the decomposition temperature of a sulphonylhydrazide (*i.e.*, the lowest temperature at which decomposition is observed on a Kofler hot-stage apparatus), its rate of reaction with thionyl chloride, and its rate of hydrolysis is shown in Table 2.

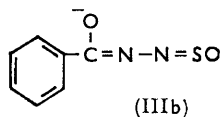
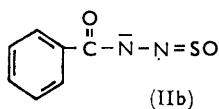
TABLE 2  
Reactions of sulphonylhydrazides

Sulphonylhydrazide	Approx. decomposition	Approx. time (days) for	Approx. time for
	temperature (II) $\rightarrow$ (IV)	complete formation of acid chloride (II) $\rightarrow$ (V)	hydrolysis (II) $\rightarrow$ (I)
Benzo .....	65°	1	$\frac{1}{2}$ hr.
Aceto .....	70	—	Very rapid
Hexano .....	85	1	$\frac{1}{2}$ hr.
<i>p</i> -Toluo .....	100	1	$\frac{1}{2}$ hr.
Octano .....	110	3	3—4 hr.
Phenylaceto .....	130	>3	Not hydrolysed
1-Naphthylaceto .....	158	>3	20% in 24 hr.

Tautomerism and ionisation of sulphonylhydrazides can in general give rise to the following relationships:



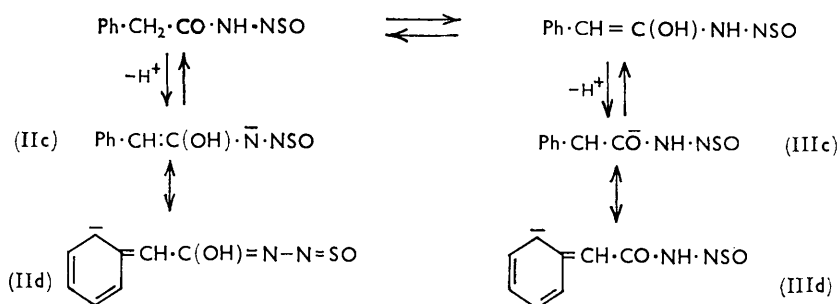
In the aliphatic series the inductive effect (+I) of the group R will render the carbonyl oxygen atom more negative, and will favour the anion (IIIa), and hence the formation of the carboxylic acid (IV). Thus sulphonylacetohydrazide is readily decomposed, but the effect is offset when the sulphonylhydrazide group is part of a long hydrocarbon chain, and sulphonyloctanohydrazide is more stable. This behaviour is comparable with that of the aliphatic azides,  $\text{R}\cdot\text{CON}_3$ ,<sup>3</sup> in which the lower members decompose more readily than the higher. With aromatic sulphonylhydrazides the anion (IIIb) will be favoured since it is more highly conjugated than (IIb), and sulphonylbenzohydrazide is readily converted into the acid. Sulphonyl-*p*-toluohydrazide is more stable. A similar stabilising effect has been noted for all *para*-substituted benzazides.<sup>4</sup>



<sup>3</sup> P. A. S. Smith, *Org. Reactions*, 1964, **3**, 366.

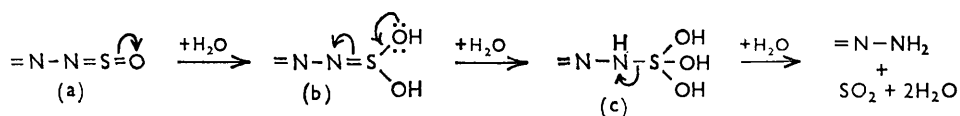
<sup>4</sup> Y. Yukawa and Y. Tsuno, *J. Amer. Chem. Soc.*, 1957, **79**, 5531.

With *N'*-sulphonylarylaceto-hydrazides an additional type of tautomerism and ionisation is possible, *e.g.*:



The ion (IIc) has contributory structures such as (IIId) which are more conjugated than (IIIId), derived from the ion (IIIc). This greater possibility of charge delocalisation gives *N'*-sulphonylarylaceto-hydrazides greater thermal stability than the benzo-compound. However, in the presence of pyridine, which favours ionisation, *N'*-sulphonylphenylaceto-hydrazide is readily decomposed to phenylacetic acid. It is noteworthy that phenylacetyl azide,  $\text{PhCH}_2\cdot\text{CON}_3$ , is stable to heat.<sup>5</sup>

We suggest that hydrolysis of sulphonylhydrazides occurs in the following way:



The rate of hydrolysis will depend on the extent of polarisation of the S-N bond (b). This polarisation will occur most readily in the aromatic sulphonylhydrazide anion (IIIb) where the negative charge is localised on the carbonyl oxygen atom, and *N'*-sulphonylbenzo-hydrazide is very readily hydrolysed. Conversely, an *N'*-sulphonylarylaceto-hydrazide anion will carry a proportion of the negative charge on the nitrogen atom (IIc), and this will oppose the polarisation of the S-N bond, so that these compounds are far more resistant to hydrolysis. In alkaline solution all sulphonylhydrazides, except the insoluble octano-compound, are rapidly hydrolysed.

Acid chlorides have been prepared from hydrazides by Carpino<sup>6</sup> using hydrogen chloride and chlorine, by reaction with sulphur monochloride,<sup>7</sup> and in the present work using thionyl chloride. The latter method gives very high yields of the acid chloride, possibly rather better than those obtained by Carpino, but the yields from the sulphur monochloride process are significantly lower. Production of the acid chloride using thionyl chloride is considerably slower than with hydrogen chloride and chlorine.

Benzohydrazide and thionyl chloride gave only a moderate amount of dibenzohydrazide in contrast with the excellent yield using sulphur monochloride. The product can originate in two ways, (i), by the condensation of sulphonylbenzohydrazide with benzoic acid obtained from its decomposition (equations 1 and 2), and (ii), by reaction of the hydrazide with the acid chloride (V) + (I)  $\longrightarrow$  (VI; R = Ph). The latter reaction is the limiting factor, since most of the benzohydrazide reacts immediately with thionyl chloride to give the sulphonyl derivative

<sup>5</sup> T. Curtius and E. Boetzclen, *J. prakt. Chem.*, 1901, **64** (2), 314.

<sup>6</sup> L. A. Carpino, *J. Amer. Chem. Soc.*, 1957, **79**, 96.

<sup>7</sup> P. Hope and L. A. Wiles, *J.*, 1964, 5837.



gave *sulphonylbenzohydrazide* (7.4 g., 81%), m. p. 82° (decomp.),  $\nu_{\max}$ . 1720 (-CO), 1470 and 1290 (-NH/-CN coupling bands), and 1090  $\text{cm}^{-1}$  (*sym* -NSO) (Found: C, 47.1; H, 3.5; N, 15.1; S, 16.9.  $\text{C}_7\text{H}_6\text{N}_2\text{OS}$  requires C, 46.2; H, 3.3; N, 15.4; S, 17.6%). Repetition of the experiment at 20° using 3 moles of thionyl chloride to 1 mole of benzohydrazide gave benzohydrazide hydrochloride (2 moles) but only 10% yield of sulphonylbenzohydrazide. The compound decomposed on heating to give a mixture of dibenzohydrazide (m. p. and mixed m. p. 239°), benzoic acid, and sulphur. It was readily hydrolysed in cold water.

*Sulphonyl-p-toluohydrazide*.—*p*-Toluohydrazide (7.5 g.) and thionyl chloride (14.5 ml.) were boiled under reflux in chloroform (100 ml.; 2 hr.). Extraction with light petroleum gave *sulphonyl-p-toluohydrazide* (2.2 g., 83.5%), m. p. 105° (decomp.),  $\nu_{\max}$ . 3125 (-NH), 1670 (-CO), 1460 and 1270 (-NH/-CN coupling bands), 1210w (*asym* -NSO), and 1100  $\text{cm}^{-1}$  (*sym* -NSO) (Found: C, 49.8; H, 4.3; N, 14.2; S, 15.9.  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{S}$  requires C, 49.0; H, 4.1; N, 14.3; S, 16.3%). It was rapidly hydrolysed by cold water to *p*-toluohydrazide, m. p. and mixed m. p. 117°.

*Formation of Acid Chlorides*.—(a) *From sulphonylhydrazides*. The sulphonyl hydrazide (1 g.) was boiled under reflux with thionyl chloride (2 ml.) in chloroform (25 ml.) until hydrogen chloride, nitrogen, and sulphur dioxide ceased to be evolved. The solution was evaporated and the acid chloride distilled. The reactions with sulphonyloctanohydrazide, and sulphonylphenylacetohydrazide were stopped after 24 hr., and the intermediate carboxylic acid was separated by distillation:

Sulphonyl- hydrazide	Hexano-	Octano-	Octano-	Phenylaceto-	Benzo-	<i>p</i> -Toluo-
Reaction time (days) .....	1	1	3	1	1	1
Product .....	-COCl (79%)	-CO <sub>2</sub> H (49%)	-COCl (80%)	-CO <sub>2</sub> H (30%) -COCl (13%)	-COCl (77%)	-COCl (52%)

(b) *From hydrazides*. The hydrazide (0.05 mole) and thionyl chloride (0.2 mole) were boiled under reflux in chloroform (100 ml.) until hydrogen chloride, nitrogen, and sulphur dioxide ceased to be evolved. The solution was evaporated, the acid chloride distilled, and characterised as the amide. The use of varying proportions of benzohydrazide and thionyl chloride gave a maximum yield of benzoyl chloride (76%) with a molar ratio of 1 : 4.

Hydrazide	Hexano-	Octano-	Phenylaceto-	Benzo-	<i>p</i> -Toluo-	<i>p</i> -Toluene- sulphono-
Reaction time (days) .....	1	3	3	1	1	1
Yield (%) ...	73	83	83	76	95	68

*Formation of Octanoic Acid from Octanohydrazide*.—Octanohydrazide (7.9 g.) and thionyl chloride (14.5 ml.) were boiled under reflux in chloroform (100 ml.; 12 hr.). On distillation there was a sudden evolution of gas, probably from the decomposition of sulphonyloctanohydrazide, and octanoic acid (7.2 g., 100%) was obtained (Found: *Equiv.* 148. Calc. for  $\text{C}_8\text{H}_{16}\text{O}_2$  *Equiv.*, 144).

*Formation of Benzoic Acid from Benzohydrazide*.—Benzohydrazide (3.4 g.) and thionyl chloride (7.8 ml.) were boiled under reflux in chloroform (50 ml.; 4 hr.). Benzoic acid (0.3 g., 10%), benzoyl chloride (0.2 g., 6%), and dibenzohydrazide (0.3 g., 10%; m. p. and mixed m. p. 239°) were isolated.

*Formation of Dibenzohydrazide from Benzohydrazide*.—Benzohydrazide (3.4 g.) and thionyl chloride (8.2 ml., 1.05 mole) were boiled under reflux in benzene (50 ml., 24 hr.) until hydrogen chloride ceased to be evolved. On cooling, dibenzohydrazide (46.7%; m. p. and mixed m. p. 243°) crystallised.

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