Sulphur Dioxide Mediated Conversion of Strained Furazan *N*-Oxides into Di-isocyanates

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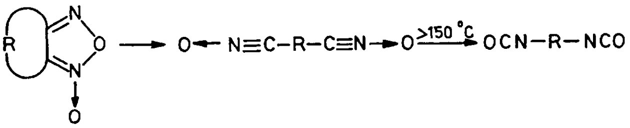
Summary Thermolysis of strained furazan *N*-oxides of the norbornane series results in fragmentation of the oxadiazole ring, the isolated products being di-isocyanates when the reactions are carried out in the presence of sulphur dioxide, while in its absence unstrained polymeric furoxans are formed.

Furazan *N*-oxides (furoxans) with the heterocycle fused to a second ring (i.e. **1**) have been shown[1,2] to fragment on heating to give bis-nitrile oxides, which may be trapped as 1,3-dipolar cycloadducts, or (Scheme) rearrange to di-isocyanates. The decomposition temperature is critically dependent on the substituents at the 3 and 4 positions of the oxadiazole ring, decamethylenefuroxan (**1**, R = $[CH_2]_{10}$) requiring[1] temperatures > 200 °C while the more strained compound (**2**) is cleaved[2] at *ca.* 100 °C.† So far the synthetic utility of the reaction as a route to di-isocyanates has been restricted to those bicyclic furoxans, such as decamethylenefuroxan, which require elevated temperatures (>150 °C) at which the nitrile oxide to isocyanate rearrangement takes place readily.[3] We now report that by inclusion of sulphur dioxide in the reaction medium the previously unattainable conversion of strained furoxans of the norbornane series into the corresponding di-isocyanates (*e.g.* **3** into **4**) is realised.



(1)

Scheme

A solution of (**3**)‡ in toluene (0·14M) saturated with sulphur dioxide was heated under reflux for 30 min. After cooling and removal of the SO_2 with a stream of dry nitrogen,

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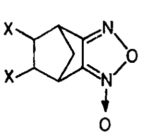
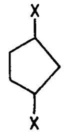
† *Hazard Warning:* Some strained furoxans have been found to decompose explosively if heated neat at temperatures as low as 80 °C. We strongly recommend they be handled in solution.

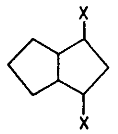
‡ Prepared (ref. 4) from norbornene by treatment with N_2O_3 and subsequent isomerisation and dehydration *via* reaction with chlorosulphonic acid.



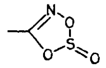
(2) XX -$[CH_2]_3$-
(3) X = H



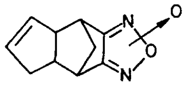
(4) X = NCO
(5) X = NHCONHPh



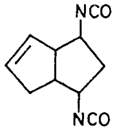
(6) X = NCO
(7) X = CNO
(8) X =



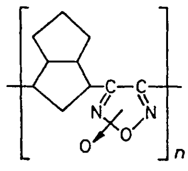
(9) X = CONHOH



(10)



(11)



(12)

the solvent was evaporated off under reduced pressure to leave a yellow oil, which afforded 1,3-di-isocyanatocyclopentane (**4**, 72%) on vacuum distillation. Treatment of the product with excess of aniline yielded the bis-urea adduct (**5**). Similarly, (**2**) and the furoxan (**10**) prepared from dicyclopentadiene[5] were converted into the di-isocyanates (**6**) (55%) and (**11**) (78%), respectively. Addition of aniline again produced the corresponding bis-phenyl ureas in high yield.

The essential role of the sulphur dioxide was demonstrated by studying the thermolysis of (**2**) in its absence. No isocyanate was detected (i.r. 2250—2270 cm^{-1}) in the product. Instead, removal of the solvent left a white amorphous solid, believed, on the basis of its i.r. spectrum, to be the polymeric furoxan (**12**) formed by polymerisation of the bis-nitrile oxide (**7**), the intense broad absorption at 1590—1600 cm^{-1} being typical of an unstrained aliphatic furoxan.§

While the mechanism of the isocyanate-forming reaction has yet to be established, the known ability of sulphur dioxide to react with nitrile oxides to yield dioxazathiole cycloadducts[6] and the latter's ready thermolysis to isocyanate and SO_2, suggested the bis-dioxazathiole (**8**) as a likely intermediate. Persuasive evidence for the presence of (**8**) was provided by following the course of the reaction of (**2**) and SO_2 in toluene at room temperature by i.r. spectroscopy. A peak characteristic[6] of dioxazathioles appeared at 1245 cm^{-1}, its intensity subsequently decreasing as the final isocyanate product absorption at 2260 cm^{-1} reached its maximum. Furthermore, the deep purple colour formed on shaking the reaction mixture (after removal of SO_2) with aqueous $FeCl_3$ is consistent with hydrolysis[6] of (**8**) to the bis-hydroxamic acid (**9**), and formation of its Fe^{3+} complex.[7] On the other hand, it was also observed that the presence of sulphur dioxide caused a marked increase in the rate of consumption of the furoxans compared with the uncatalysed reactions,¶ making the straightforward fragmentation of (**2**) to the bis-nitrile oxide (**7**) improbable and suggesting direct interaction between the furoxan and SO_2.

Notwithstanding the mechanistic uncertainties, this furoxan–sulphur dioxide reaction provides a new, phosgene-free, route to aliphatic diisocyanates currently inaccessible and some of which (*e.g.* **11**) are both potentially cheap and suitable for polyurethane formation.

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§ For example, dibutylfuroxan (ref. 4) absorbs at 1605 cm^{-1}. In contrast, the corresponding peak for strained furoxans such as (**2**) is at *ca.* 1670 cm^{-1} (ref. 2).

¶ For example, the pseudo-first-order rate constant for the disappearance of (**10**) in mesitylene in the presence of excess of SO_2 at 80 °C is 169 times that for the reaction in the absence of SO_2 (ref. 4).

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