Pyrolysis of Phenylalkylsulphonyl Azides and 2-Phenethyl Azidoformate. Selectivity of Sulphonylnitrenes and Contrast between Sulphonyl- and Carbonyl-nitrenes

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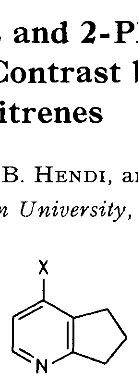
Summary Flash vacuum pyrolysis and solution thermolysis of $\mathrm{Ph[CH_2]_nSO_2N_3}$ indicate that intramolecular addition to the phenyl group is preferred in solution, provided that up to an eight-membered sultam ring is formed, otherwise side-chain insertion results, while in the gas phase the latter process is favoured when $n = 4,5$, but not 3; some 5,6,7,8-tetrahydroquinoline is obtained when $n = 3$ at 990 °C, but 2-phenethyl azidoformate gave monomeric tetrahydro-1,3-oxazino[3,4-*a*]azepin-2-one and 4-phenyloxazolidinone, but no dihydrocyclopenta[*b*]pyridine, even at 900 °C.



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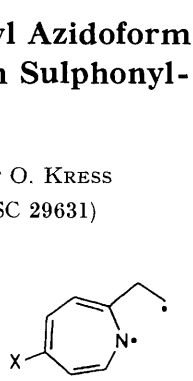

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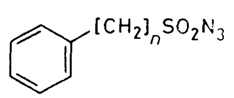
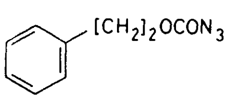


(3) n = 3

(4) n = 4

(5) n = 5



(6)

The flash vacuum pyrolysis (FVP) of 2-phenethylsulphonyl azides[1] led to the formation of remarkable ring-transformation products; 6,7-dihydro-5*H*-cyclopenta[*b*]pyridines (**1**) could be isolated in good yields. One possible mechanism suggested for the formation of (**1**) involved the intermediacy of a diradical (**2**). We now report the extension of these studies to 3-phenyl-1-propane-, (**3**), 4-phenylbutane-, (**4**) and 5-phenyl-pentane-sulphonyl azides (**5**) and an attempt to generate (**2**: X = H) *via* the pyrolysis of 2-phenethyl azidoformate (**6**).

Decomposition of (**3**) in Freon 113 at 135 °C for 36 h gave 2,7,8,9-tetrahydrobenzo[1,2-*c*]thiazepine 1,1-dioxide (**7**), m.p. 172—173 °C (44%),† together with 3-phenyl-1-propanesulphonamide, m.p. 59—61 °C (2·3%) (identical to the known compound),[2] and recovered azide (37·3%). Authentic (**7**) was synthesised (28·1%) by catalytic reduction (10% Pd–C, 50 lb in^{-2} $\mathrm{H_2}$, 10% aq. NaOH) of 3-(*o*-nitrophenyl)-1-propanesulphonyl chloride. FVP of (**3**) at 360 °C/0·25 mm gave (**7**) (27%), primary amide (1·1%), 1,2,3,4-tetrahydroquinoline (**8**) (5·3%),‡§ and allylbenzene (3·7%).‡ At 650 °C/0·5 mm FVP gave (**7**) (7·5%), (**8**) (60·3%), and allylbenzene (trace). FVP of (**3**) at 990 °C/0·05 mm ($\mathrm{N_2}$

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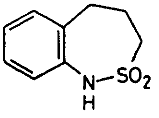
† All new compounds gave correct microanalytical and spectral (i.r., n.m.r., and mass) data.

‡ Identical with an authentic sample (Aldrich).

§ FVP of (**7**) at 360 °C/0·005 mm also gives (**8**). At 650 °C/0·005 mm an 86·9% yield is obtained.

carrier gas 1·5 ml/min) gave azide (**3**) (0·8%), (**7**) (0·4%), (**8**) (72·4%), and allylbenzene (11·9%). In addition, two new products were obtained: 5,6,7,8-tetrahydroquinoline (**9**) (6·2%), b.p. 110 °C/13 mm, identical to a sample prepared by the reduction of quinoline in CF_3CO_2H in the presence of PtO_2,[3] and phenethyl cyanide (**10**) (3·2%).[‡][¶] The formation of (**7**) and (**8**) has some precedent.[1] Compound (**9**) probably arises by a mechanism similar to that which leads to dihydrocyclopentapyridines in the 2-phenethyl cases.[1] Clearly, the latter ring transformation occurs much more readily than that leading to (**9**).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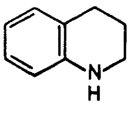
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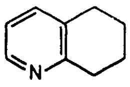
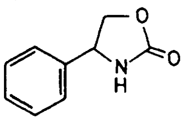

(9)

$PhCH_2CH_2CN$

(10)

On the basis of length of the side chain alone, it might be expected that thermolysis of the azidoformate (**6**) might lead to products similar to those obtained from (**3**). It was also hoped, as noted above, to generate diradical (**2**) from the corresponding *N*-acylazepine. Neither of these expectations was fulfilled. It has recently been shown[4] that pyrolysis of benzyl azidoformates at 300—350 °C/0·1 mm gives oxazolo[3,4-*a*]azepin-2-ones which spontaneously dimerise.[5] FVP of (**6**) at 650 °C/0·025 mm gave a mixture of (**11**) (40%), identical with an authentic sample,[6] and (**12**), m.p. 115—117 °C (26%).† No dimer of (**12**) was observed, nor was any (**1**; X = H) formed. Indeed, (**12**) appears to be very stable thermally and was recovered unchanged on FVP at 650 °C/0·025 mm. At 900 °C/0·025 mm some (**12**) (18%) was still recovered, together with a gum (i.r. spectrum still shows the presence of a carbonyl group), but no (**1**) [**]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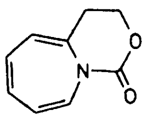
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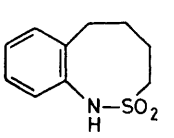
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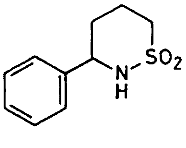
Thus, unlike the corresponding sulphonylnitrene which adds intramolecularly to an aromatic double bond and then gives the *N*-sulphonylaniline under thermodynamic-control conditions,[7] and does not give 5-membered sultams by C–H insertion, alkoxycarbonylnitrenes give azepines both inter-[8] and intra-molecularly and insert intramolecularly into the aliphatic side chain to form a 5-membered ring.

Thermolysis of (**4**) in Freon 113 at 154 °C for 36 h gave the 8-membered sultam (**13**) (30·3%), m.p. 160—162 °C,† together with 4-phenyl-1-butanesulphonamide (2·6%),[2] and recovered azide (8%). In contrast, FVP of (**4**) at 710 °C/0·025 mm did not give any (**13**). Instead, a 6-membered sultam (**14**) (17%), m.p. 117—118 °C, resulting from side-chain C–H insertion, was isolated, together with 4-phenyl-*trans*-1-butenesulphonamide (**15**) (7·5%), m.p. 132 °C, and some 4-phenylbut-1-ene (3·3%), identical to an authentic sample.[9] No precedent could be found for the formation of an α,β-unsaturated sulphonamide from a sulphonylnitrene $RCH_2CH_2SO_2N$, though the simultaneous abstraction of two neighbouring hydrogen atoms from an aromatic side-chain by an *ortho*-carbene[10] or -nitrene[11] has been suggested.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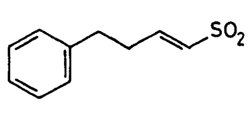
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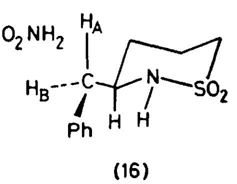
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Thermolysis of (**5**) in Freon 113 at 154 °C for 36 h gave 3-benzyl-2,3,4,5,6-pentahydro-1,2-thiazine 1,1-dioxide (**16**) (26%), m.p. 133—134 °C,† together with the hydrogen-abstraction product (1·4%), m.p. 79·5—81 °C,[2] and recovered azide (13·6%). FVP at 710 °C/0·025 mm also gave (**16**) (20·3%) and primary amide (1·3%). No other sultam was detected. The n.m.r. spectrum of (**16**) was extremely complex, even at 200 MHz, but the structure was established unambiguously by 400 MHz n.m.r. spectroscopy.

It would appear, therefore, that an arylalkylsulphonylnitrene in solution will preferentially add intramolecularly to an aromatic double bond rather than insert into an aliphatic side chain as long as a sultam of maximum ring size eight can be formed. A 9-membered ring is not formed, however, and the nitrene inserts selectively into the aliphatic chain to form a 6-membered ring. In the gas phase, formation of the thiazine dioxide is the preferred mode of intramolecular attack.

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[¶] Similarly, phenylacetonitrile (66·6%) was obtained together with other products, in the FVP of *trans*-β-styrenesulphonyl azide at 690 °C/1·5 mm.

[**] In a recent review, O. Meth-Cohn reports the observation that (**6**) gives (**11**) at 300 °C (*Heterocycles*, 1980, **14**, 1497).

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