Intramolecular Aromatic Cyclisation of a Sulphonyl Carbene

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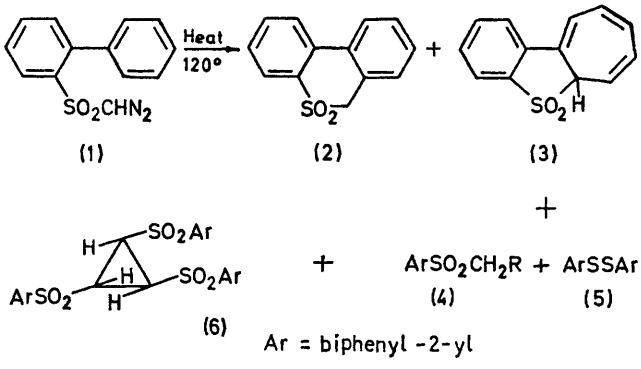
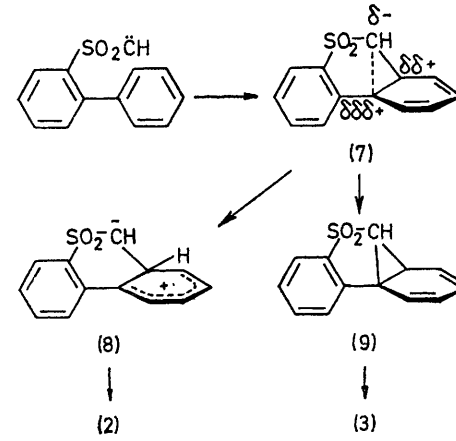
Summary Thermal decomposition of (1) gives both six- and seven-membered cyclised products, the ratio of which depends on the solvent polarity, and products probably resulting from radical reactions.

THERE are few examples recorded of intramolecular attack of a carbene on an aromatic nucleus.[1,2] We have shown[3] that intermolecular aromatic substitution by a sulphonyl carbene takes place in low yield. Whereas intermolecular aromatic substitution of benzene by phenylnitrene does not occur,[4] intramolecular substitution of biphenyl-2-ylnitrene proceeds in high yield.[5] Since there is precedent for intramolecular cyclisations of sulphonyl azides[6] we have investigated the decomposition of biphenyl-2-sulphonyldiazomethane (1) and report the nature of the cyclisation products and the influence of solvent on their ratio.

The diazo-compound (1) was prepared in 28% overall yield from 2-aminobiphenyl *via* the sulphinic acid, aminomethylurethan, and its *N*-nitroso-derivative. Thermolysis of (1) gave a mixture of products, including (2), (3), (5), and (6), most of which may arise from a sulphonyl carbene intermediate. The structures of the products were established unambiguously by n.m.r., i.r., and mass spectroscopy

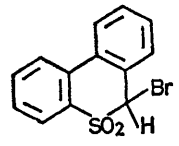




Solvent and conditions (120 °C)	% Yields of products (2)	(3)	(5)	(6)	Other	(3/2)
Cyclohexane, 3 h	8·0	22·5	4·5	17·0	(4) (7·6%)	2·8
Cyclohexene, 2 h	7·6	22·0		6·3	Mixture of addition and insertion products (10·4%)	2·9
Benzene, 4 h	16·2	25·5	2·8	3·6		1·6
CH_2Br_2, 1 h[a]	23·2	25·5		10·4		1·1
CH_2Br_2, 1 h[b]	7·0	10·0	4·0	4·8	Mixture of brominated products[c]	1·4
EtOH, 1 h	12·9	15·1		11·8	$ArSO_2SAr$ (3·5%)	1·2
Pyridine, 1 h	8·2	14·5			$ArSO_2SAr$ (4·8%)[d]	1·7
Benzene, tetracyanoethylene, 1 h	5·8	7·6			$ArSO_2CH_2OSO_2Ar$ (5·1%)	1·3

[a] 0·32M-Solution of (1) in CH_2Br_2. [b] 0·16M-Solution of (1). [c] N.m.r. and mass spectroscopy on the isolated and resolved by-products suggests that they are $ArSO_2CH{=}CHBr$ (2%) and (**10**) (1·5%). [d] The ylide $ArSO_2\bar{C}H\overset{+}{N}C_5H_5$ was also isolated (10·4%) and characterised by n.m.r. and mass spectrometry but was too unstable to permit microanalysis.

and microanalysis. The cycloheptatrienyl sulphone (3) was stable, did not form a (4 + 2)-adduct with tetracyanoethylene, and could not be rearranged thermally to the aromatic six-membered isomer (2). Indeed, (3) was recovered unchanged following g.l.c. at 300° for 1 h. The yields of products are summarised in the Table, as is the effect of change of solvent and of addends upon both yields and nature of the products.



(10)

It can be seen that, in general, the ratio of (3)/(2) decreases with increasing solvent polarity, which is consistent with a transition state (7) in which bond formation between the carbene and the two ring carbon atoms has proceeded to different extents; the more polar solvents will favour the greater separation of charges leading to the σ-complex (8) and hence onto (2), while the less polar ones favour formation of the norcaradiene intermediate (9) which undergoes electrocyclic ring-opening to (3). No seven-membered cyclisation product has been isolated from the decomposition of biphenyl-2-sulphonyl azide at 120°.[6]

The formation of the disulphide (5), of $ArSO_2SAr$, and $ArSO_2CH_2SO_3Ar$ in some of these reactions suggests the intervention of radical intermediates. Radical cleavage of (1) could lead to $ArSO_2\cdot$ which could be reduced to $ArS\cdot$; this could dimerise to (5) or couple with $ArSO_2\cdot$. Alternatively, the latter could abstract oxygen to give $ArSO_3\cdot$, which could couple with $ArSO_2CH_2\cdot$ to give the observed sulphone sulphonate ester, as previously suggested.[3] More likely, $ArSO_3\cdot$ could abstract hydrogen to give the sulphonic acid which, with undecomposed diazomethane, could lead to $ArSO_3CH_2SO_2Ar$. The function of the TCNE (last reaction in the Table) is not clear but it must suppress completely the formation of $ArS\cdot$.

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