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PHENYLNITRENE FROM PHENYLSULPHINYLAMINE
CORRELATION OF THERMOLYSIS WITH ELECTRON IMPACT

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Abstract High temperature gas-phase pyrolysis of phenylsulphinylamine (I) gives the same types of products as inferred from mass spectral fragmentation; 1-cyanocyclopentadiene (III), aniline, benzonitrile, thiophene, 2- and 3-cyanothiophene and a compound to which is assigned the structure 2-cyanothiacyclohexa-2,4-diene (XII). These products correspond formally to elimination of SO, NSO, CO and O. Formation of 1-cyanocyclopentadiene is ascribed to the generation of phenylnitrene by SO loss, and the possible use of this reaction to determine the spin state of the nitrene is discussed. Azobenzene was not isolated.

INTRODUCTION

IN THE course of investigations of the gas phase transformations of phenylnitrene (II),[1] we became interested in possible precursors other than phenyl azide. Phenyl isocyanate, isosteric with phenyl azide, gave an abundant $C_6H_5N^{+\cdot}$ fragment in the mass spectrum,[2] but proved to be too stable to pyrolysis even at 1000° (it gave 1% benzene and cyanic acid instead).[1a] The structurally similar molecule phenylsulphinylamine (ϕ-NSO, I) was another possibility which seemed to offer additional features. Although the leaving group (SO) is not a stable entity, its existence in the gas phase is well established and, moreover, it is a ground state triplet.[3] This opened the possibility that pyrolysis might give rise to triplet phenylnitrene directly—a process not possible by pyrolysis of phenyl azide, due to the needs of spin conservation. Such a cleavage could not be regarded as any more than a possibility, since neither the phenylnitrene nor the SO would be generated at the ground vibrational level.

The mass spectrum[4,5] of ϕNSO (I) shows as the base peak an ion due to loss of CO from $M^{+\cdot}$, rationalised as a seven-membered ring structure $C_5H_5NS^{+\cdot}$, since it undergoes further fragmentation by loss of HCN (giving thiophene), CS (giving pyrrole) and NS.[4] The interest in ϕNSO as a source of phenylnitrene (II) was stimulated by the observation that its second major fragmentation is due to loss of SO from the molecular ion to give $C_6H_5N^{+\cdot}$. Subsequent fragmentation of this ion (including metastables) was similar to that of phenylnitrene from phenyl azide[1a] and phenyl isocyanate,[2] indicating[6] the same structure for the ion in these cases.†

PYROLYSIS

Pyrolysis of Ph–NSO at temperatures up to 800° gave largely unchanged starting material plus an increasing yield of aniline (10% at 800°). The condensable gas was

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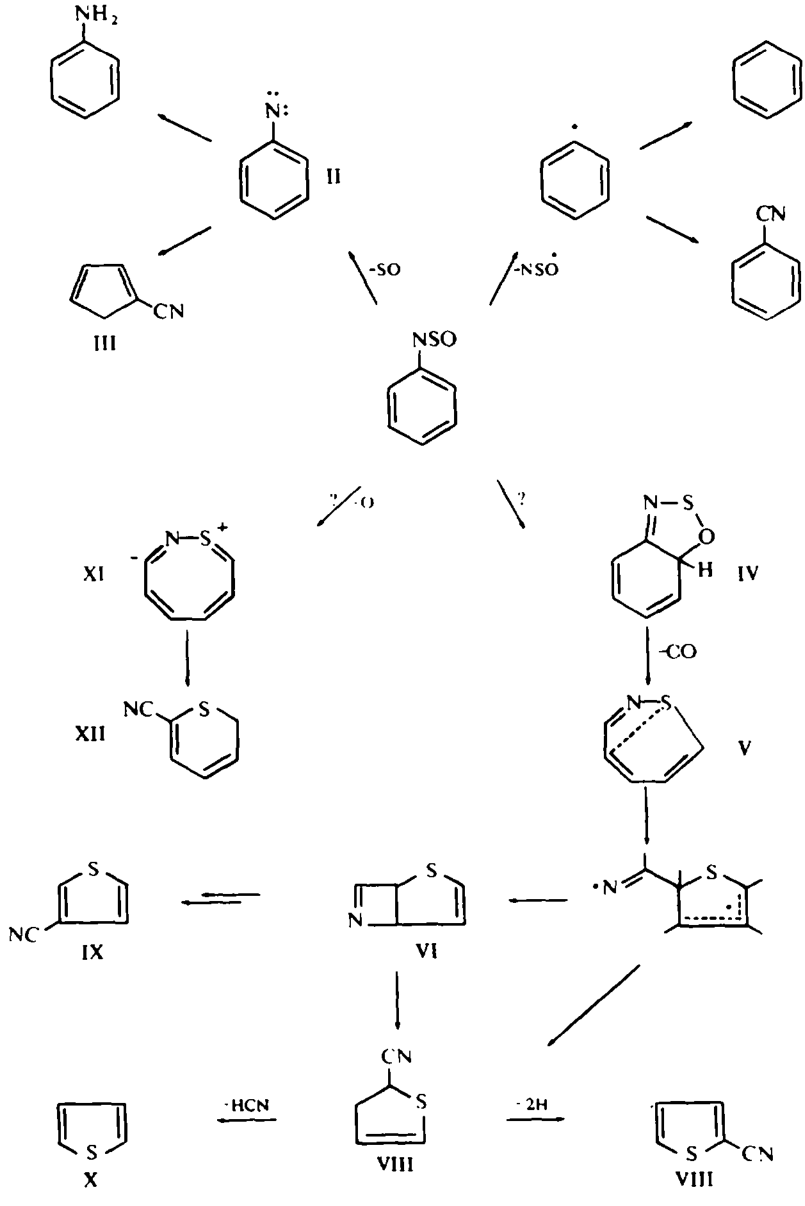
[†] Full mass spectra of nitrene precursors, together with a discussion of the ion structures, will be published in a forthcoming paper. The mass spectrum of I is listed in the Experimental; peak intensities differ from those recorded[4,5] due to different instrumentation.

analysed by mass spectrometry and found—on the basis of sulphur isotope peaks, to consist of H_2S and SO_2. CO was probably present, but coincides with N_2. The result corresponds to formation of phenylnitrene and SO; the former giving aniline, the latter decomposing to SO_2 and S.[3] It is possible, however, that some or all aniline and SO_2 resulted from hydrolysis (although water was rigorously excluded) or in some other way not involving nitrene formation. Under identical conditions, phenyl azide gave both aniline and azobenzene;[1a] the latter has not been found in pyrolysis of Ph–NSO, but it was reported formed in the presence of a copper catalyst.[7]

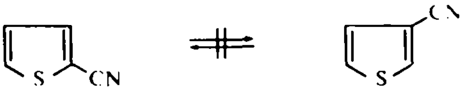
SCHEME 1



At 1000° most of the fragmentations inferred from the mass spectrum took place, as indicated in Scheme I. The products were analysed and isolated by GLC. 1-Cyanocyclopentadiene[8] III (4%) is presumably the result of ring contraction in "hot" phenylnitrene.[1] Only a trace of aniline was found. Benzonitrile (5·1%) and benzene (0·05%) are supposedly formed from phenyl radicals. 2- and 3-Cyanothiophenes VIII and IX (3% each) correspond to loss of CO from Ph–NSO, followed by loss of 2H. It should be noted that the mass spectrum of Ph–NSO indicates loss of H (m*) from $(M—CO)^+$, formally giving protonated cyanothiophene. This is analogous to the behaviour of methylcyanocyclopentadienes[9] which lose 2H on pyrolysis and 1H by mass spectrometry, and to 1,3,5-trimethylpyrazole[1b] which loses 2H to yield 4,6-dimethylpyrimidine by pyrolysis and 1H by mass spectrometry.

Thiophene X (0·3%) corresponds to loss of CO + HCN as in the mass spectrum. It is possible that the thiophenes arise by isomerisation of a 7-membered ring V (*cf* ref. 4) which in turn could arise from IV, formed in a reaction similar to the photochemical conversion of phenyl azide to benzotriazole.[10]

The formation of 3-cyanothiophene (IX) is difficult to rationalise. Contrary to the behaviour of cyanocyclopentadienes and cyanopyrroles the cyanothiophenes do not interconvert thermally, even at 1000°:[9]



VIII IX

A conjugated nitrile C_6H_5NS was detected in small yield (2%) and is believed, on spectroscopic grounds, to be 2-cyano-thiacyclohexa-2,4-diene (XII). One of the possible ways it could be formed is *via* XI in a valence isomerisation similar to the formation of benzonitrile from azocine.[11] Loss of oxygen from Ph–NSO is understandable when the molecule is looked upon as a sulphoxide.[12] Pyridine N-oxide analogously loses oxygen both photolytically[13] and thermally.[14]

DISCUSSION

The main piece of evidence in favour of fragmentation of Ph–NSO into phenylnitrene and SO is the isolation of the known ring-contraction product III from the pyrolysis at 1000°.[1, 15] The absence of azobenzene, the typical reaction product of phenylnitrene, does not exclude the possibility of nitrene formation, for azobenzene is usually absent from phenyl azide pyrolysis above 800°, where it decomposes into multiple products, *inter alia* bezene, biphenyl, diphenylamine, benzonitrile, and a trace of cyanocyclopentadiene (III);[16] and below 800° in the present reaction there is probably no nitrene formation at all: the aniline may result entirely from hydrolysis and/or hydrogen capture prior to fragmentation.*

It is important to note that the yield of aniline decreases sharply between 800° (10%) and 1000° (trace), as the yield of conversion of Ph–NSO increases. The probability for a nitrene to capture hydrogen would increase under these conditions,

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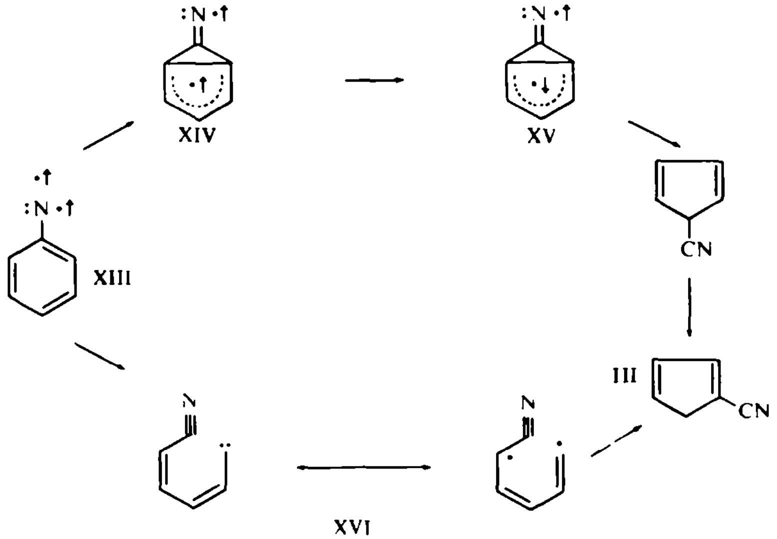
* The mass spectrum of Ph-NSO obtained with a carefully evacuated glass inlet system usually exhibits peaks due to hydrolysis. These are absent when direct inlet is used. The more hygroscopic 2-sulphinylaminopyridine hydrolyses completely in a glass inlet system; on direct inlet it gives a spectrum indicating the same types of reactions as for Ph-NSO[14].

but the probability of Ph–NSO surviving long enough to react with water present in the apparatus or formed in the reaction decreases. If, on the other hand, aniline is indeed derived from phenylnitrene at all temperatures, it raises the interesting possibility that only triplet nitrene is formed, from which aniline is derived,[17] and that azobenzene should be absent because it is only formed from singlet nitrene. While the spin state of the azobenzene-forming nitrene is by no means known with certainty, indications are that it is a triplet.[18,10]

The formation of benzene and benzonitrile at 1000° has a parallel in the violent pyrolysis of phenyl azide,[1b,15] in which case they may be derived from phenyl radicals formed either by pyrolytic cleavage of azobenzene[15] (*vide supra*) or by loss of azide radicals from PhN_3.[1b] In the pyrolysis of Ph–NSO, the phenyl radicals may also be derived from the non-observed azobenzene, or by loss of NSO in a reaction similar to the cleavage of phenyl isocyanate to benzene and cyanic acid—a reaction which quite certainly cannot involve azobenzene.[14]

The spin state of the nitrene which undergoes ring contraction to cyanocyclopentadiene (III) is though to be singlet.[1] If the reaction is concerted, an excited cyanocyclopentadiene must be formed unless the reacting nitrene is a singlet. However, there are several non-concerted ways in which a triplet nitrene (XIII) could react (Scheme 2). If the previously postulated[1,15] intermediate (or transition state) XV is realistic, it may be formed initially in the triplet state (XIV) because the 2,6-overlap in the triplet nitrene (p_l, p_0 configuration) appears larger than in the singlet (p_l^2 configuration).[19] Subsequent spin demotion would lead ultimately to III. The reason why III is formed only under conditions of high temperature[1,15] (where the chance of trapping the singlet nitrene is highest) may then be purely that the reaction requires a high activation energy.

Scheme 2



Another non-concerted pathway which may involve either singlets or triplets is *via* ring opening (XVI). Such a mechanism has been considered a possibility in other, related nitrenes.[20]

The fact that both phenylnitrene and SO have triplet ground states provides a possibility of forming them both in this state at 1000°. The first excited singlet SO is only *ca* 23 kcal/mole above the ground state triplet,[21] however, and thus could well be formed in the present reaction. In the thermolysis of thiiran 1-oxide[21,22] it appears as if SO is formed in the triplet state, even though this is a spin-forbidden process. Otherwise, there must be a very efficient mechanism of spin inversion in originally formed singlet SO.[21] It may prove possible to detect the sulphur monoxide supposedly formed from phenylsulphinylamine, and determine its spin, either spectroscopically[21] or chemically.[22] If so, it will allow conclusions as to (i) whether phenylnitrene is formed both below and above 800°, and (ii) its probable spin.[25]

EXPERIMENTAL

The pyrolysis technique has been described.[23,9] A packed quartz tube was used throughout. The pyrolysates were analysed by GLC on a 5′ × 1/6 in column of 5% Carbowax 20M on Aeropak at 100°; carrier gas He at 60 ml/min (F and M instrument with thermal conductivity detection). Mass spectra were recorded on an AEI MS 10C2 (low resolution) or MS 902 (high resolution) instrument.

Mass spectrum of phenylsulphinylamine* (I) (all glass heated inlet at 100°, 70 eV; MS 902). [Ion] relative abundance:

[M^+]100, [M—16]1, [M—17]1, [M—CO = C_5H_5NS]19, [M—CHO = C_5H_4NS]10, [M—33]1, [M—SO = C_6H_5N]19, [M—CO—HCN = C_4H_4S]16, [C_4H_5N]15, [M—CNOS = C_5H_5]7, [M—CHNOS = C_5H_4]11, [M—CH_2NOS = C_5H_3]14, [$(M—CO)^{2+}$]2, [*m/e* 52]5, [*m/e* 51]11, [*m/e* 50]5.

Pyrolysis of phenylsulphinylamine (I)

(a) The condensable gas from pyrolysis of I at 600–800°/10^{-3}–10^{-2} mm was collected in a tap-vessel in liquid N_2 and found by mass spectrometry to consist of mainly SO_2 (*m/e* 64 and 48; isotope peaks), H_2S (*m/e* 34; isotope peaks), and probably CO and/or N_2 (*m/e* 28).

(b) Compound I (1·00 g) was distilled at 20° through the pyrolysis tube at 800°/0·001–0·005 mm in 25 min. The ether-soluble liquid product (77% w/w recovered) consisted of starting material (60%) and aniline (10%).

(c) Compound I (1·00 g) was pyrolysed at 1000°/0·05–0·10 mm in 30 min. After removing the condensable gases by distillation there was left 0·190 g liquid ether-soluble product. The following compounds were estimated and isolated by GLC: benzene (0·05%), thiophene (0·3%), 1-cyanocyclopentadiene[8] (4·0%), benzonitrile (5·1%), 2-cyanothiophene (3%) 3-cyanothiophene (3%), a compound assigned structure XII (2%), and aniline (trace).

2- and 3-Cyanothiophene (VIII and IX) were identified by comparison of their UV[24] and IR spectra with authentic data (IR: ν_{max} 2225 and 2232 cm^{-1}, resp.), and by high resolution mass measurement (measured mass: 108·9982; calc. for C_4H_4S: 108·9986).

The compound assigned the structure XII, 2-cyano-thiacyclohexa-2,4-diene, eluted from the gas chromatograph between 2-cyanothiophene and 3-cyanothiophene (measured mass: 123·0139; calc. for C_6H_5NS: 123·0143). IR: ν_{max} 2213 cm^{-1} (conj. nitrile).

Three other products with the formulae C_8H_7N, $C_{10}H_8$, and $C_6H_4N_2S$ were also detected by high resolution mass spectrometry.

No-reaction pyrolysis of 2-cyanothiophene (VIII). (0·50 g) distilled unchanged through the pyrolysis tube at 1000° in 2½ h. The pressure, recorded after the traps, was 10^{-3} mm. Failure to achieve a higher pressure, even with faster distillation, was due to efficient trapping, and lack of decomposition.

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* The compositions of those ions for which chemical formulae are given were determined by high resolution measurements, but only the major component in multiplets is mentioned here. *cf* also refs 4, 5.

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