Complex C.I.D.N.P. Effects in the Rearrangement of *O*-Sulphinylated Oximes

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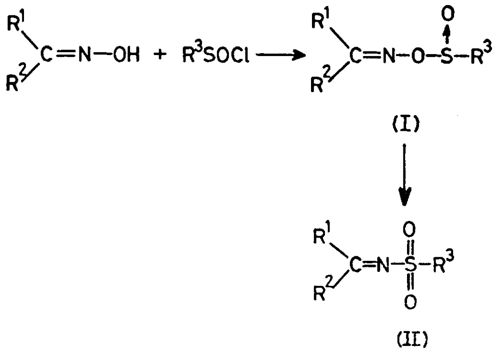
Summary Enhanced polarisations of several nuclei suggest that the thermal rearrangement of $R^1R^2C{=}N{-}OS(O)R^3$ to sulphonyl imine proceeds partly by a recombination of geminate radical pairs and partly by the scavenging of escaped radicals.

Oximes react rapidly[1] with sulphinyl chlorides at low temperatures (*ca.* −30 °C) in the presence of base to give the corresponding *O*-sulphinylated oximes (I), which rearrange at temperatures above 0 °C to the *N*-sulphonyl imines (II) in high yield. Strong e.s.r. signals are observed for both iminyl[1] and sulphonyl[2] radicals, and in C.I.D.N.P. experiments polarisations of the iminyl, aromatic C(1) (R^1 = Ph), and methyl (R^3) carbon atoms are produced. Application of the Kaptein–Closs equation[3] to the data (Table) for the compounds with $R^1 = R^2$ = Ph, R^3 = Me and R^1 = Ph, $R^2 = Me_2N$, R^3 = Me with g(iminyl)[1] = 2·0028 $A_{C(1)}$ +ve, $A_{C=N}$ −ve, and g(sulphonyl)[2] = 2·005, leads to a positive value of ϵ showing that part, at least, of the rearrangement proceeds by combination of geminate radical pairs. With this value of ϵ, analysis of the polarisation of the carbon in the methanesulphonyl group gives a positive value for the carbon hyperfine splitting constant A_C.


(I)

(II)

† The *syn* forms of all the aldoximes were used in the preparation of (I, R^1 = Ar, R^2 = H).

Aldoximes† react under similar conditions to give a quantitative yield of a mixture of rearranged product (II) ($R^1 = Ar$, $R^2 = H$) (*syn* form) and nitrile (III). These are formed in a complex process as shown by a consideration of the C.I.D.N.P. data (Table).

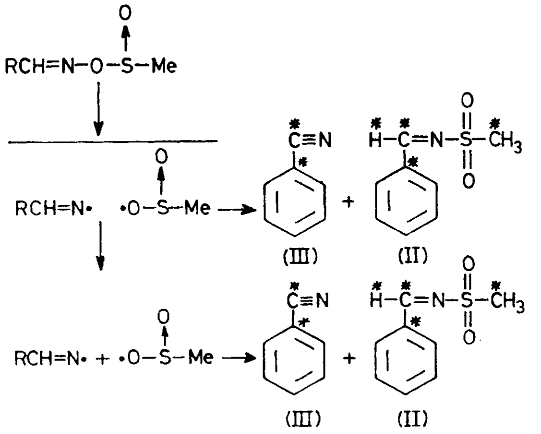
Table. C.I.D.N.P. effects for the product $R^1R^2C=N-SO_2Me$ in $CDCl_3$ at 40 °C.

Substituent		Nucleus			
R^1	R^2	C(CN)	C(1)	Me	H(D)
Ph	Ph	E	A	E	
Me_2N	Ph	E	A	E	
Ph	H		E	A	A
p-Me·C_6H_4	H	EA(E)[a]	E	A	A
p-MeO·C_6H_4	H	EA(E)[a]	E		A
Ph	D	E[b]	A	E	A[c]
p-Me·C_6H_4	D	E[b]	A	E	A[c]

[a] Proton coupled spectra. [b] Deuterium coupled. [c] Deuterio compound.

The most significant features of the results may be summarised as follows: (i) Polarisations due to the iminyl carbon and formyl hydrogen atoms originate from a geminate pair recombination process. However the observed polarisations of the C(1) atom of the phenyl ring (both in coupled and decoupled spectra) and of the carbon atom of the methanesulphonyl group in (II) arise from a radical scavenging process. (ii) When the hydrogen atom of the iminyl group is substituted by deuterium, all the polarisations including that of the deuteron originate from recombination of geminate radical pairs.

If a diffusion model[3] of the kind developed by Kaptein, Closs, and others is assumed, the C.I.D.N.P. effects for the various nuclei can be analysed. In the Scheme the polarised nuclei are starred.

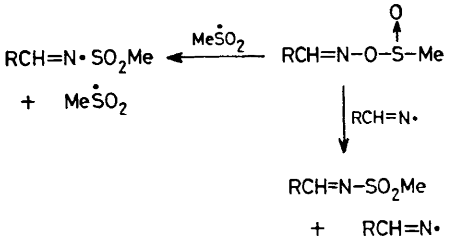


Scheme

Polarisations of the C(1) atom of the phenyl ring are particularly strong owing to hyperconjugation in the iminyl radical.[4] These polarisations show that ε is positive for the nitrile and negative for the sulphonyl imine. Using the derived (positive) hyperfine splitting constant for the methanesulphonyl carbon atom and its observed polarisation, ε, is again negative. However the polarisations of the iminyl carbon atom and of the formyl hydrogen atom lead to a positive value of ε. This is the first time that opposite signs for ε from C.I.D.N.P. observations on two nuclei in the same fragment have been derived.

The C.I.D.N.P. of the nuclei of (II) and (III) from diffusive encounter of radicals (F-pairs)[3] will be opposite to that of (II) and (III) formed by geminate combination of radical pairs. The product ratio (II:III) from diffusive encounter of radicals and from in cage geminate recombination should be identical. Thus the net polarisations of all the nuclei should lead to the same prediction of the origin of the products.

Since this is not observed, it is clear that part of (II) must be formed in an alternative out of cage process, such that the out of cage product ratio (II:III) is larger than the ratio (II:III) derived from the geminate radical pair. One such process is the scavenging of the escaped radicals by starting material (I).‡



Unpolarised radicals so produced can either repeat this process (to give unpolarised products) or can combine in a termination process to give polarisations in the product appropriate for F-pair precursors.[3]

The radical scavenging process should have a rate constant similar to that for nuclear spin relaxation in radicals ($T_1 = 10^{-3}$ to 10^{-5} s), and some of the nuclei will lose their abnormal spin populations before reaction. This leads to the observation of differential C.I.D.N.P. effects within the same radical fragment. In particular the nuclear spin relaxation of the iminyl and C(1) aromatic carbon atoms must be considerably different.

Substitution of the formyl hydrogen atom of (I) by deuterium reduces the yield of nitrile from 34 to 18% and the observed polarisations of all nuclei of (II) are indicative of its formation by geminate recombination of the radical pair. Since this isotopic substitution has a negligible effect on the rate of formation of (II) by any of the mechanisms proposed, the change of the sign of the polarisation of the C(1) carbon nucleus reflects a change in the product ratio (II:III) arising from the geminate radical pair. According to this explanation product (II) is formed in such a proportion within the cage that the C.I.D.N.P.

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‡ Crossover experiments have detected scavenging processes of this kind for similar rearrangements involving the iminyl radical (R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Perkin II*, 1974, 869).

due to this process outweighs the C.I.D.N.P. due to (II) formed by out of cage processes.

Added in proof: The product compositions from *syn* and *anti* anisaldoximes are identical within experimental error.

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[4] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 4115; M. C. R. Symons, *Tetrahedron*, 1973, **29**, 615; R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1974, 488.