Detection by Microwave Spectroscopy of HNO Produced by a Retro-Diels–Alder Reaction

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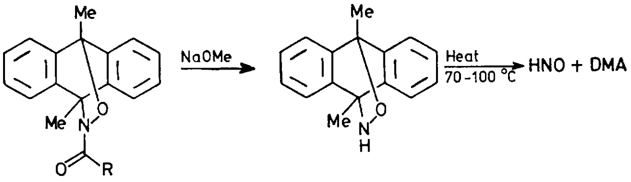
Summary Nitroxyl (nitrosyl hydride), HNO, has been generated by the dissociation of 9,10-dihydro-9,10-epoxyimino-9,10-dimethylanthracene at 70 °C and studied by microwave spectroscopy in the range 18—32 GHz.

Nitroxyl (nitrosyl hydride), HNO, has previously been prepared,[1] for spectroscopic examination, by the direct reaction between nitric oxide and hydrogen atoms or, photochemically, by the reaction of nitric oxide with some suitable hydrogen donor. We report here a new preparation of HNO under mild, non-photochemical conditions.

The cyclo-adducts (**1**; R = Me or Ar) of 9,10-dimethylanthracene (DMA) and *C*-nitrosocarbonyl compounds are readily formed[2] by oxidation of hydroxamic acids in the presence of DMA. They dissociate reversibly under mild conditions. We reasoned that the parent adduct (**2**) might provide a convenient, 'clean' source of HNO. Accordingly, the acetyl derivative[2] (**1**; R = Me) was treated with a tenfold excess of 2M-methanolic sodium methoxide at room temperature overnight. The resulting solution was diluted with ether and washed with water and brine, and then dried. Saturation with hydrogen chloride caused precipitation of 9,10-dihydro-9,10-epoxyimino-9,10-dimethylanthracene (**2**) as the hydrochloride hemihydrate; $\delta[(CD_3)_2SO]$ 7·3—7·7 (m, 8H), 4·2 (br s), 2·38 (s, 3H), and 2·28 (s, 3H). Addition of sodium hydrogen carbonate to an aqueous solution of this salt precipitated the free base (**2**) of sufficient purity† for the following experiments. The structure of (**2**) was confirmed by conversion, with benzoyl chloride in pyridine, into the known[2] benzoyl derivative (**1**; R = Ph).



(1) (2)

The thermal decomposition of the adduct (**2**) was studied initially with a Kofler hot-stage apparatus. Gas evolution

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† Satisfactory microanalytical data for (2) were obtained with a sample crystallised from benzene–light petroleum (b.p. 60—80 °C); crystallisation, however, was wasteful owing to thermal decomposition.

was observed (the sample was covered with a drop of Nujol oil) from *ca.* 75 °C and continued smoothly up to *ca.* 100 °C. Partial melting occurred but the sample resolidified then remelted near 180 °C The residue was shown to be largely DMA. Examination of the decomposition by differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} revealed a strongly exothermic process over the range 85—115 °C and showed an endothermic feature near 186 °C characteristic of DMA itself.

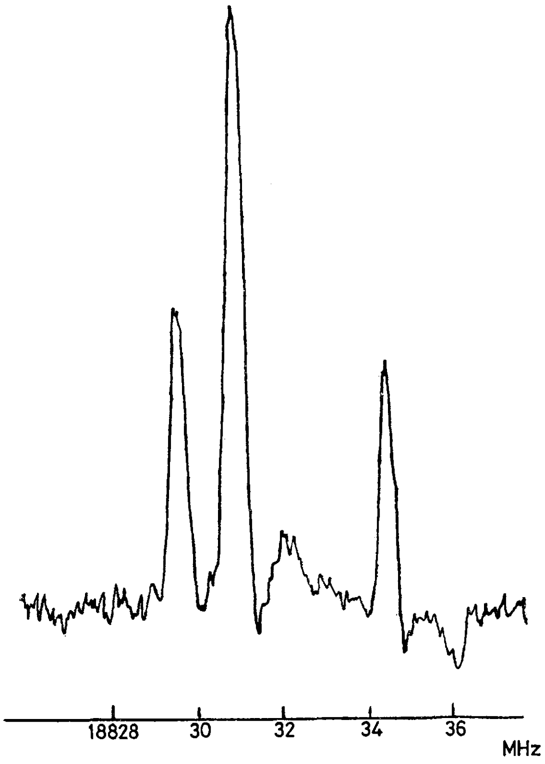

FIGURE. The $3_{13} \leftarrow 3_{12}$ transition of HNO.

We have analysed the gaseous products of this decomposition by microwave spectroscopy. Saito and Takagi[3] have made a detailed microwave study of HNO. From their high frequency data the $J = 3_{12} \leftarrow 3_{13}$ and $4_{13} \leftarrow 4_{14}$ transitions are predicted near 18,832 and 31,383 MHz respectively, each with a characteristic triplet structure due to the ^{14}N quadrupole coupling. These transitions are readily observed (see Figure) when (**2**) is warmed to 70 °C and the evolved gases pumped through a microwave absorption cell at room temperature. The measurements on these transitions are summarised in the Table and there is no doubt that HNO is evolved when (**2**) is thermally decomposed. Water and nitrous oxide are the only other products detected by microwave spectroscopy. The signals from HNO, which was isolated in the copper absorption cell at room temperature, decayed quite rapidly with order *ca.* 3/2, but were still visible for periods of up to 1 min.

TABLE. Line centres and ^{14}N quadrupole coupling parameters for HNO (in MHz)

	Calc.	Obs.	$\chi_{aa} + 2\chi_{bb}$
$3_{12} \leftarrow 3_{13}$	18831·67	18831·73	−10·73
$4_{13} \leftarrow 4_{14}$	31382·96	31383·04	−10·64
		Ref. 3	−10·56

A parallel DSC study of the acetyl derivative (**1**; R = Me) indicated an initial endothermic process (melting) occurring near 130 °C inverting rapidly to an exothermic decomposition over the range 136—141 °C. The gaseous products evolved when (**1**; R = Me) was heated to 130 °C have also been investigated by microwave spectroscopy. We have not yet identified free CH_3CONO in the products, but have detected nitrous oxide, acetic acid, and keten. We also find a stable, quite volatile material, the microwave spectrum of which shows triplets characteristic of a molecule containing two equivalent methyl groups. This substance has not yet been identified.

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[1] M. N. Hughes, *Quart. Rev.*, 1968, **22**, 1; see also citations in ref. 3.

[2] G. W. Kirby and J. G. Sweeny, *J.C.S. Chem. Comm.*, 1973, 704; J. E. T. Corrie, G. W. Kirby, and R. P. Sharma, *ibid.*, 1975, 915; G. W. Kirby, *Chem. Soc. Rev.*, 1977, **6**, 1.

[3] S. Saito and K. Takagi, *J. Mol. Spectroscopy*, 1973, **47**, 99.