

8. Rand, R. N. *Clin. Chem. N.Y.* 15 (1969) 839.
9. Dunford, H. B. *Physiol. Vég.* 12 (1974) 13.
10. Maltempo, M. *Personal communication.*
11. Ohlsson, P.-I. and Paul, K.-G. *Unpublished results.*
12. Darbyshire, B. *Cryobiology* 12 (1975) 276.

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Morpholine and Thiophene in Glow Discharge Reactions

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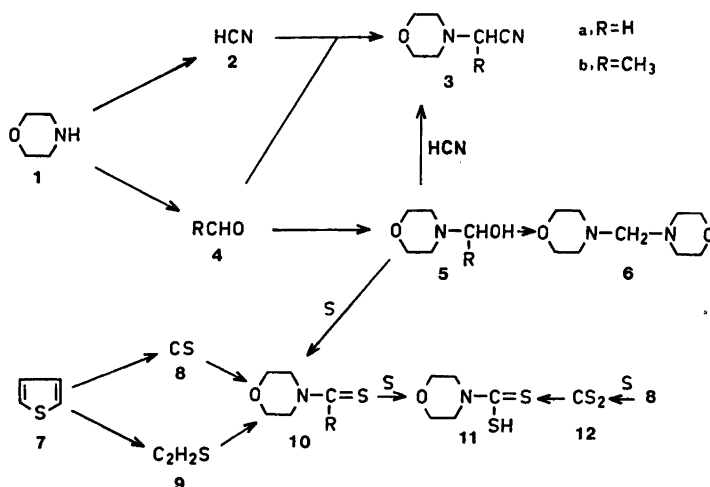
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Organic molecules undergo a number of transformations in high frequency glow discharge reactions.¹ Ring-opening reactions of *N*-heterocyclic compounds often yield products in which the original *N*-heteroatom has become part of a nitrile group.² We have reexamined² the behaviour of morpholine under glow discharge conditions (27 MHz) using the apparatus shown in Fig. 1, and have confirmed morpholinoacetonitrile (*3a*) and dimorpholinomethane (*6*) as

major products. A third product was identified as α -morpholinopropionitrile (*3b*) whereas formation of β -morpholinopropionitrile has previously been reported.² The products obtained in the glow discharge reactions are explained by intermediate formation of formaldehyde, acetaldehyde and HCN which react further with other molecules of morpholine. The respective product paths were readily demonstrated in solution reactions. Formation of the acetonitrile *3a* has previously been explained by dehydrogenation in the plasma zone of β -morpholinoethylamine; the latter was assumed to be an intermediate reaction product.² Such an explanation fails to account for the formation of the propionitrile *3b*.

In the further study morpholine and its reaction products were admixed with the reactive intermediates from plasma reactions of thiophene by feeding morpholine and thiophene together [ratio 5:1 (v/v)] into the glow discharge zone. A solid was identified as the morpholine salt of morpholinocarbodithioic acid (*11*); the other major products were *N*-thioformylmorpholine (*10a*)² and *N*-thioacetylmorpholine (*10b*)⁴ besides the morpholine derivatives *3* and *6*.

The major solid products from thiophene alone were polymeric, whereas the volatile products were identified as S, H₂S and CS. Carbon monosulfide and thioketene may be the initial products in the reactions of thiophene and will react further with morpholine to yield the thioacyl derivatives *10*. Thioketene is highly reactive. It can be formed by pyrolysis of *tert*-butyl ethynyl sulfide but is polymerised above -80 °C.⁵ Photolysis of 1,2,3-thiadiazole has also been shown to yield thioketene and the isomeric ethynylthiol; photodecomposition of thioketene yields carbon mono-



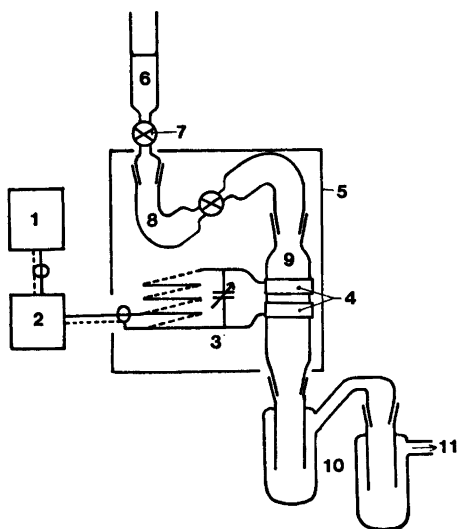


Fig. 1. Apparatus for high frequency glow discharge reactions. For explanations, see text.

sulfide.⁶ The major route to the thioacy derivatives 10, however, probably involves reactions between sulfur radicals formed from thiophene and the intermediate morpholino-adduct 5, since it has been found that sulfur, formaldehyde and primary and secondary amines react under relatively mild conditions to yield thioformamides.⁹ Sulfur is a major product in the plasma reaction of thiophene; in the case of benzo[b]thiophene, phenylacetylene and sulfur were the only products isolated.⁷ Furthermore, sulfur is known to react with thioformamides to yield the corresponding dithioic acid.⁸ By analogy a similar reaction may contribute to the formation of the dithioic acid 11 from 10a although the major route to this compound is probably the reaction between morpholine and CS₂. It is tempting to speculate that CS₂ in part is formed from thiophene-2-thiol after an initial sulfur radical insertion reaction of thiophene.

Experimental. The glass vessels are made of Pyrex glass except for the reaction tube (9) which is of quartz glass (l. 30 cm, i.d. 3.2 cm). The energy for the discharge is provided by a radio frequency generator (1) (Sommerkamp FT DX 505) operated at 27 MHz with a wattmeter (2) (ThruLine model 43) and a tuned circuit. The latter was made from a coil of silver coated 6 mm copper tube (l. 5 cm, d. 5 cm) and a variable capacitor (3) which are coupled to 2 silver bands (4, thick. 1 mm, w. 18 mm) 1 cm apart surrounding the reaction tube (9). The reaction vessels are enclosed in an oven (5) controlled by a thermostat in order to prevent condensation near the plasma

zone, and to secure rapid evaporation of the reactants which are fed slowly into the evaporation tube (8) from the reservoir (6) through a capillary valve (7).

The oven was kept at 70 °C and the oil pump (11) was operated at 0.2 mmHg. The distillation rates of morpholine in two separate experiments were 280 and 490 g/kWh using the effects 78 and 100 W, respectively; the product yields were: 3a, 35 and 30 g/kWh; 3b, 5 and 10; 6, 80 and 70.

In another set of two experiments under the same temperature and pressure conditions a mixture of morpholine and thiophene [5:1 (v/v)] were distilled at the rates 115 and 255 g/kWh with effects of 42 and 51 W, respectively; the product yields were: 10a, 15 and 10 g/kWh; 10b, 1 and 1; 3a, 10 and 5; 3b, 5 and 5; 6, 25 and 15.

The products were collected in the cooling traps (10) and analysed by GC with a Hewlett-Packard 5700A gas chromatograph on an OV-17 glass column (i.d. 2 mm, l. 2.4 m) with the oven programmed at 80–250 °C (4 °C/min) using a flame ionisation detector. Preparative separations were carried out with a Varian 711 gas chromatograph on an OV-17 aluminium column (9 mm, 9 m) with the oven programmed at 50–200 °C (6 °C/min). The identities of the products were established by spectroscopy (MS, NMR) and by comparisons with authentic specimens.

1. Suhr, H. *Fortschr. Chem. Forsch.* 36 (1973) 39.
2. Gorzny, K. and Maahs, G. *Angew. Chem.* 85 (1973) 1054.
3. Maier, L. *Helv. Chim. Acta* 53 (1970) 1216.
4. Reynaud, P., Moreau, R. D. and Samama J. P. *Bull. Soc. Chim. Fr.* (1965) 3623.
5. Howard, E. G. *U.S. Pat.* 3,035,030 (1962).
6. Krantz, A. and Laurenzi, J. *J. Am. Chem. Soc.* 96 (1974) 6768.
7. Fjeldstad, P. E. *Unpublished work.*
8. McMillan, F. H. and King, J. A. *J. Am. Chem. Soc.* 70 (1948) 4143.

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