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# A NOVEL PERCHLORINATED NITRONE - α,α-DICHLORO-N-TRICHLOROMETHYL NITRONE

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Stable nitrones are usually substituted in both the α and N positions with alkyl and aryl groups; recently a stable perfluorinated nitrone has been prepared by the reaction of pentafluoronitroacetone with tetrafluorohydrazine.[1] The identification of a stable, fully chlorinated nitrone is now reported.

The thermal decomposition of liquid trichloronitrosomethane at 100°C for 3 hours results, inter alia, in the formation of nitric oxide, phosgene, nitrosyl chloride, carbon tetrachloride and α,α-dichloro-N-trichloromethyl nitrone. The latter compound has been characterised by means of mass spectrometry, infrared spectroscopy, ultraviolet spectroscopy and elemental analysis. The mass spectral data is consistent with the formulation $CCl_3N(O)CCl_2$. The parent ion is detectable but of very low intensity. The intensity patterns are typical of ions containing several chlorine atoms. The main absorption bands in the infrared region 2000 - 700 $cm^{-1}$, together with some assignments are 1639 (N=C), 1613 (N-O), 1016, 931 (C-N), 801 and 777 $cm^{-1}$. The last two absorption bands can probably be attributed to C-Cl bonds. The N-O stretching frequency is high relative to hydrocarbon nitrones,[2] where the N-O stretching frequency is observed in the

region 1200 - 1280 $cm^{-1}$. This shift is not unexpected since, in general, halogenation results in a shift to higher frequencies. The ultraviolet spectrum, measured in cyclohexane, shows a maximum absorption at 210 nm ($\varepsilon_{max}$ = 6,400) which is in the region expected for the nitrone functions.[2] The nitrone is a colourless liquid, b.p. 164°C (isoteniscope) and has a Trouton constant of 16.4.

The formation of α,α-dichloro-N-trichloromethyl nitrone during the thermal decomposition of trichloronitrosomethane probably occurs via dichlorocarbene attack on the nitroso function. Two routes to dichlorocarbene may be envisaged:

$$CCl_3NO \rightarrow :CCl_2 + NOCl$$

or

$$CCl_3NO \rightarrow CCl_3 + NO$$

$$CCl_3\cdot + CCl_3NO \rightarrow CCl_4 + \cdot CCl_2NO$$

$$\cdot CCl_2NO \rightarrow :CCl_2 + NO$$

$$CCl_3NO + :CCl_2 \rightarrow CCl_3N(O)CCl_2$$

Alternatively, attack on the $CCl_2NO$ intermediate by $CCl_3\cdot$ could result in the formation of the nitrone

$$\cdot CCl_2NO \rightarrow CCl_2 = \dot{N} - O \xrightarrow{CCl_3\cdot} CCl_2 = N(O)CCl_3$$

The latter alternative seems least likely since it involves two low concentration species.

Further work is in progress to try and distinguish between these two possibilities.

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