

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

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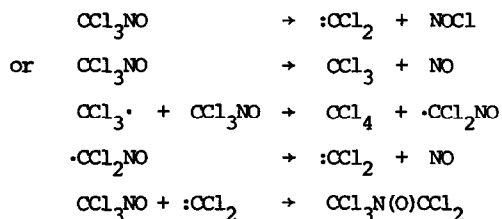
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Stable nitrones are usually substituted in both the α and N positions with alkyl and aryl groups; recently a stable perfluorinated nitrone has been prepared by the reaction of pentafluoronitroacetone with tetrafluorohydrazine.¹ The identification of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

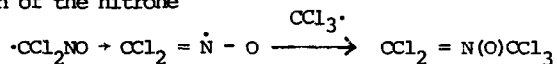
The thermal decomposition of liquid trichloronitrosomethane at 100°C for 3 hours results, inter alia, in the formation of nitric oxide, phosgene, nitrosyl chloride, carbon tetrachloride and α,α -dichloro-N-trichloromethyl nitrone. The latter compound has been characterised by means of mass spectrometry, infrared spectroscopy, ultraviolet spectroscopy and elemental analysis. The mass spectral data is consistent with the formulation $\text{CCl}_3\text{N}(\text{O})\text{CCl}_2$. 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 $1200 - 1280 \text{ cm}^{-1}$. 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 ($\epsilon_{\text{max}} = 6,400$) which is in the region expected for the nitron functions.² The nitron 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 nitron during the thermal decomposition of trichloronitrosomethane probably occurs via dichlorocarbene attack on the nitroso function. Two routes to dichlorocarbene may be envisaged:



Alternatively, attack on the CCl_2NO intermediate by $\text{CCl}_3\cdot$ could result in the formation of the nitron



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.

REFERENCES.

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