αα-Dichloro-*N*-(dichloromethyl)nitrone Radical, a Novel Free Radical

By V. ASTLEY and H. SUTCLIFFE*

(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT)

Summary Attack on αα-dichloro-(*N*-trichloromethyl)-nitrone by chlorine atoms or phenyl radicals results in chlorine abstraction and the formation of the radical $\cdot CCl_2–\overset{+}{N}(\overset{-}{O})CCl_2$.

THE recent report of a ready synthesis of αα-dichloro-(*N*-trichloromethyl)nitrone[1] (I) has made available a possible route to the radical bis(trichloromethyl)nitroxide, namely by addition of a chlorine atom to the CCl_2 group of the nitrone. The observation that radical attack on the nitrone function gives rise to the formation of nitroxide and tri-substituted hydroxylamines lends further support to this idea.[2] Surprisingly, the addition of chlorine atoms or phenyl radicals does not occur. Instead, chlorine abstraction takes place giving rise to the new radical species the αα-dichloro-(*N*-dichloromethyl)nitrone radical.

Chlorine was bubbled through compound (I) contained in a 3 mm silica tube, and the resulting solution examined by e.s.r. spectroscopy. All the features of the spectrum may be interpreted in terms of the radical $\cdot CCl_2–\overset{+}{N}(\overset{-}{O})=CCl_2$ (II). Interaction of the unpaired electron with the ^{14}N nucleus gives rise to the main triplet with a splitting of 7·4 ± 0·1 gauss. Each component of this triplet is split into a series of hyperfine lines with a coupling constant of 1·25 ± 0·05 gauss. Some overlapping of these lines occurs in the centre of the spectrum, but examination of the amplified wings of the spectrum reveals all the expected hyperfine structure for (II). The intensity ratio of the third, fourth, fifth, and sixth lines is 7 : 15 : 28 : 41 : 45, which suggests that there are thirteen hyperfine lines in each component of the main triplet. Such a pattern can arise by the interaction of an unpaired electron with four equivalent chlorine nuclei, and has a theoretical intensity ratio of 1 : 4 : 10 : 20 : 31 : 38 : 42 : 38 . . . *etc.* Irradiation of the solution of chlorine in (I) with light of wavelength >400 nm eliminates the signal from the radical. When the source of light is removed, the signal returns immediately and builds up to a maximum in 40 min. The radical is also produced, although in much lower concentration, when (I) is warmed with benzoyl peroxide.

The formation of the radical (II) is thought to occur by chlorine atom abstraction from the CCl_3 group of the nitrone (I):

$$Cl\cdot + CCl_3\overset{+}{N}(\overset{-}{O})CCl_2 \rightarrow \cdot CCl_2–\overset{+}{N}(\overset{-}{O})=CCl_2 + Cl_2$$

$$Ph\cdot + CCl_3\overset{+}{N}(\overset{-}{O})CCl_2 \rightarrow \cdot CCl_2–\overset{+}{N}(\overset{-}{O})=CCl_2 + PhCl$$

The radical (II) has some structural similarities to both iminoxy and nitroxide radicals but the value for a_N is quite different. For iminoxy radicals $a_N \approx 30$ gauss and the odd electron is contained in an orbital which is derived from a *p*-orbital on oxygen and a non-bonding sp^2-orbital on nitrogen; nearly 50% of the spin density is associated with the nitrogen nucleus.[3] In the present case $a_N = 7·4$ gauss, thus more extensive delocalisation of the unpaired electron is expected. Each of the two carbon and nitrogen atoms in addition to forming σ-bonds has available a *p*-orbital and an electron. A linear combination of these three *p*-orbitals will result in three molecular orbitals which are expected to be bonding, nonbonding, and antibonding, respectively. Two electrons are contained in the bonding molecular orbital and the unpaired electron in the nonbonding orbital. Thus, the bonding system is similar to that described for a π-allyl radical.[4] The unpaired electron is therefore delocalised over the nitrogen and the two carbon nuclei in a π-type molecular orbital with some additional delocalisation onto the four chlorine nuclei. In the case of the two nitroxides $(CF_3)_2NO$[5] and $(CCl_3)_2NO$[6] where such extensive delocalisation cannot be envisaged the a_N values are larger, namely 9·3 and 11·8 gauss.

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