

Trichloronitrosomethane. Part II. Thermal Decomposition, and an Improved Synthesis, of Trichloronitrosomethane

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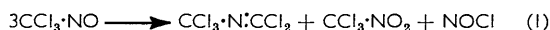
Trichloronitrosomethane decomposes within 3 hours at 100 °C to give nitrogen, nitric oxide, nitrosyl chloride, carbon tetrachloride, *N*-(dichloromethylene)trichloromethylamine *N*-oxide, and phosgene. The dichloronitrosomethyl radical is postulated as a reaction intermediate and a simple MO picture of bonding in that radical is outlined.

EARLY syntheses of trichloronitrosomethane, carried out at relatively high temperatures, gave a wet, impure product.^{1,2} More recently, a low-temperature synthesis has been developed which gives a dry purer product.³ This latter method has now been modified so as to avoid the use of a sealed reaction vessel and at the same time to remove sulphur dioxide, an inhibitor to the formation of trichloronitrosomethane, from the reaction zone.

When gaseous nitrosyl chloride is passed through a cooled bed of sodium trichloromethanesulphinate, a reaction occurs as witnessed by the appearance of a blue colour. The progress of the reaction is easily observed by the movement of the coloured reaction zone through the bed of reactant. Purification of the product is simplified since the sulphur dioxide and excess of nitrosyl chloride are vented and the trichloronitrosomethane is collected in a cooled trap.

Recently a synthesis from chloroform has been reported but as yet no satisfactory method of separating trichloronitrosomethane from unchanged chloroform has been devised.⁴

Prandtl and Sennewald¹ reported the formation of the compounds $\text{CCl}_3\text{N}:\text{CCl}_2$, $\text{CCl}_3\cdot\text{NO}_2$, NOCl , together with smaller amounts of nitric oxide and hexachloroethane during the thermolysis of trichloronitrosomethane. This reaction was carried out under reflux in an atmosphere of carbon dioxide using an oil-bath at 120 °C. The main thermal decomposition was represented by equation (1). During the course of the



present work Tattershall reported confirmation of

† In previous work, this compound has been named $\alpha\alpha$ -dichloro-*N*-trichloromethyl nitrene.

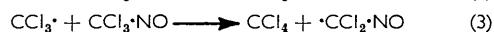
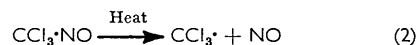
¹ W. Prandtl and K. Sennewald, *Ber.*, 1929, **62**, 1754.

² W. Prandtl and W. Dollfus, *Ber.*, 1932, **65**, 754.

this mode of decomposition but no experimental details were quoted.⁵

In the present work a careful examination of the thermal decomposition at 100 °C has been made. The main products are nitric oxide, carbon tetrachloride, and *N*-(dichloromethylene)trichloromethylamine *N*-oxide,⁶ † together with smaller amounts of nitrosyl chloride, nitrogen, phosgene, and chloropicrin (trichloronitromethane). An unidentified compound (A) having a pink colour has also been noted. The yields of these compounds are given in the Table. Compound (A) is found in the carbon tetrachloride fraction; its pink colour fades on exposure to light and nitrogen gas is evolved. The carbon tetrachloride solution of (A) shows weak absorption in its visible spectrum at 265—290 nm and absorption bands at 5.7 and 9.5 μm in the i.r. region which are not attributable to either carbon tetrachloride or chloropicrin. The ease of breakdown to elemental nitrogen suggests two possibilities for (A), namely CCl_2N_2 or $\text{CCl}_3\cdot\text{N}:\text{N}\cdot\text{CCl}_3$, but no positive confirmation has yet been obtained.

The high yield of carbon tetrachloride and nitric oxide is attributed to initial cleavage of the C-N bond in trichloronitrosomethane followed by chlorine abstraction by $\text{CCl}_3\cdot$ from a molecule of $\text{CCl}_3\cdot\text{NO}$ [equations (2) and (3)].



It is interesting at this stage to consider the bonding

³ Part I, H. Sutcliffe, *J. Org. Chem.*, 1965, **30**, 3221.

⁴ B. W. Tattershall, *J. Chem. Soc. (A)*, 1970, 3261.

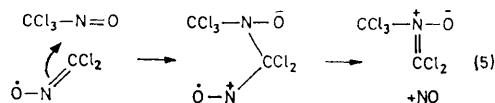
⁵ B. W. Tattershall, *J. Chem. Soc. (A)*, 1970, 3263.

⁶ V. Astley and H. Sutcliffe, *Tetrahedron Letters*, 1971, **29**, 2707.

of the $\cdot\text{CCl}_2\text{NO}$ radical since this will influence its stability and reactivity.

The carbon atom will form three σ -bonds to chlorine and nitrogen leaving an orbital which is essentially p in character. The nitrogen atom in addition to having a lone pair of electrons will form σ -bonds to oxygen and carbon and will have a p -orbital available for further bonding. Similarly, the oxygen atom will have a σ -bond

equation (5). The latter mechanism is similar to that



proposed by Baldwin *et al.* for the reaction of diazomethane with nitroso-compounds.⁹ The alternative

Product distribution

Experiment	Products	NO	CCl_4 *	$\text{CCl}_3\text{N}(\text{O})\text{CCl}_2$	CCl_3NO_2	COCl_2	NOCl	SO_2	(A)	CCl_4 †	N_2
1	23.3 g	1.16	10.03	5.3	0.66	1.45	3.69	2.73	N.E.		0.0
	157 mmol	38.8	66	23.2	4.0	14.9	56.3	42.6			
	Yield (%)	24.7	42	14.8	2.6						
2	9.65 g	1.53	4.67	3.0	0.3	0.49	0.15	0.0	N.E.		0.0
	65 mmol	35.0	30.7	13.0	1.85	5.0	30.7	0.0			
	Yield (%)	54	47.2	20	2.8	7.7	3.5	0.0			
3	15.8 g	1.745	7.1	5.5	0.5	0.86	0.207	0.0	1.7 ‡	5.4 †	0.02
	106.4 mmol	58.3	46	23.8	3.2	8.8	3.2	0.0	6.5 ‡	35.1 †	0.725
	Yield (%)	54.8	43.3	22.4	3.0	8.3	3.0	0.0	6.1	33 †	0.68

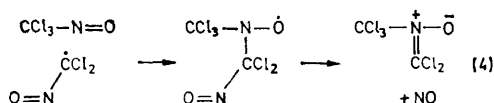
* Not corrected for (A). † Corrected for (A). ‡ Estimated assuming (A) is $\text{CCl}_3\text{N}_2\text{CCl}_3$. N.E. = Not estimated.

to nitrogen, two lone pairs of electrons and a p -orbital. The structure C-N-O is expected to be bent at nitrogen since the molecule from which it is derived is also bent at this point. Taking a linear combination of the three p -orbitals will give three molecular orbitals. One of these resulting orbitals, the bonding orbital, will extend over all three atoms and contain two electrons. The other two molecular orbitals may be of a non-bonding or antibonding character and one of these will contain the unpaired electron. The situation is thus not unlike that of a π -allyl ligand, and the orbital shapes may be expected to be similar.⁷ Some additional delocalisation of the unpaired electron onto the two chlorine atoms may also be expected, analogous to that observed in the case of bis(trichloromethyl)nitroxide.⁸ The overall effect will be a stabilisation of the $\cdot\text{CCl}_2\text{NO}$ radical relative to one in which no delocalisation can occur. This concept may also be expressed in resonance terms, thus



The possibility that this radical is of the iminoxyl type cannot be excluded, but in the absence of e.s.r. data no firm conclusion can be reached.

The formation of *N*-(dichloromethylene)trichloromethylamine *N*-oxide is considered to arise by attack of the dichloronitrosomethyl radical on trichloronitrosomethane followed by elimination of nitric oxide. Two alternative mechanisms may be envisaged; either equation (4) since the nitrogen atom of the nitroso-

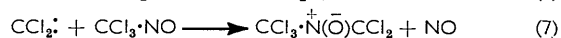


function is known to be susceptible to radical attack, or

⁷ G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 2, Methuen, 1948, p. 45.

⁸ H. Sutcliffe and H. Wardale, *J. Amer. Chem. Soc.*, 1967, **89**, 5487.

dichlorocarbene route [equations (6) and (7)] is not pre-

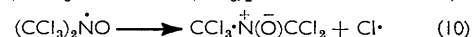


ferred in view of the expected stabilisation of the dichloronitrosomethyl radical.

The overall reaction giving rise to the main reaction products may be represented by equation (8).



Another possible mode of formation of *N*-(dichloromethylene)trichloromethylamine *N*-oxide is *via* the intermediate formation of bis(trichloromethyl) nitroxide followed by the expulsion of a chlorine atom [equations (9) and (10)]. This is not favoured since the chlorine



atom would react with nitric oxide to give nitrosyl chloride in a yield compatible with that of the nitrone. Only a low yield of nitrosyl chloride is observed, therefore at best this reaction makes only a minor contribution to the overall reaction scheme.

The reaction sequence summarised by equation (8) is not the complete picture since the molar ratio of the three main products is not exactly 1 : 1 : 2. Taking a corrected value for the yield of carbon tetrachloride and assuming the NOCl is derived from the NO, then

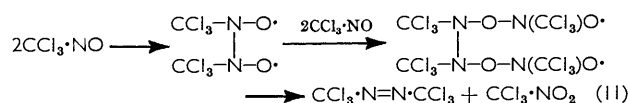
$$\text{CCl}_4 : \text{CCl}_3\cdot\text{N}(\text{O})\text{CCl}_2 : \text{NO} = 1.1 : 0.8 : 2.0.$$

Thus there is a greater yield of carbon tetrachloride than predicted but a reduced yield of the *N*-oxide. This could be due to other reactions of the radical $\cdot\text{CCl}_2\text{NO}$ especially in the later stages of the reaction when the concentration of $\text{CCl}_3\cdot\text{NO}$ is considerably reduced, and the chance of reaction (4) or (5) taking place is also

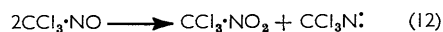
⁹ J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc. (C)*, 1969, 1073.

reduced. Furthermore, chlorine abstraction by $\text{CCl}_3\cdot$ may take place by species other than $\text{CCl}_3\cdot\text{NO}$, notably $\text{CCl}_3\cdot\ddot{\text{N}}(\ddot{\text{O}})\text{CCl}_2$, thus increasing the yield of carbon tetrachloride at the expense of that of the nitron. It is noteworthy that the total molar yield of CCl_4 and $\text{CCl}_3\cdot\ddot{\text{N}}(\ddot{\text{O}})\text{CCl}_2$ approximately equals that of nitric oxide.

The formation of chloropicrin may be attributed to a reaction analogous to that postulated for the thermal decomposition of trifluoronitrosomethane¹⁰ [equation (11)] or to a disproportionation reaction [equations



(12) and (13)]. Neither of these products has as yet



been identified but the unknown compound (A) may be one of them.

Further decomposition of chloropicrin satisfactorily accounts for the formation of phosgene and nitrosyl chloride.¹²

In one thermal decomposition experiment sulphur dioxide was observed among the reaction products. This is attributed to the presence of the unstable compound $\text{CCl}_3\cdot\text{SO}_2\cdot\text{NO}$ present in the trichloronitrosomethane. This compound has been suggested previously as a possible intermediate during the synthesis of trichloronitrosomethane.³ The compound $\text{CCl}_3\cdot\text{SO}_2\cdot\text{NO}$ breaks down into $\text{CCl}_3\cdot\text{NO}$ and SO_2 when stored at 0 °C for 12 h which enables purification of trichloronitrosomethane to be carried out.

EXPERIMENTAL

Trichloronitrosomethane was prepared by the method previously described³ and also by the method described below. The product was purified by trap-to-trap fractionation *in vacuo*.

I.r. spectra were measured on a Perkin-Elmer model 221 spectrophotometer, mass spectra on an A.E.I. model MS12, and u.v. spectra on a Perkin-Elmer model 137 spectrophotometer. G.l.c. analysis was carried out with a 5-m × 3-mm i.d. column packed with 20% dinonylphthalate on Celite using helium as the carrier gas.

Nitrosyl chloride was prepared by the method of Morton and Wilcox.¹²

Preparation of Trichloronitrosomethane.—Sodium trichloromethanesulphinate (36.7 g, 0.178 mol) prepared from trichloromethanesulphonyl chloride by the procedure of Prandtl and Sennewald,¹ was loosely packed into the centre tube of a conventional water condenser. This was mounted in a sloping position with the lower end attached to a trap cooled to 0 °C and the upper end attached to the nitrosyl chloride generator. Cooling water was passed through the jacket of the condenser and nitrosyl chloride passed slowly through the sodium trichloro-

methanesulphinate. Reaction began as soon as the gaseous nitrosyl chloride contacted the sodium salt and the blue-green reaction zone passed slowly through the bed of sodium trichloromethanesulphinate. At the end of the reaction the tube was flushed with nitrogen to ensure complete transfer of the product into the cooled trap. The impure product (18.0 g.) was transferred to a vacuum line and purified by trap-to-trap fractionation *in vacuo* to give pure trichloronitrosomethane (15.5 g, 0.105 mol) in 60% yield.

Thermal Decomposition of Trichloronitrosomethane.—Trichloronitrosomethane (26.1 g, 0.176 mol) was sealed *in vacuo* in a heavy walled glass Carius' tube and heated to 100 °C for 3½ h; at the end of this time the blue colour of the nitroso-compound had completely faded. The tube was cooled and the volatile products were removed to leave a colourless involatile oil together with traces of a white solid.

The volatile products were fractionated *in vacuo* through traps cooled to -46, -63, -96, -131, and -196 °C. Each fraction was analysed by molecular-weight measurement, i.r. spectroscopy, g.l.c., and, in some cases, mass spectrometry. The products and yields are given in the Table.

The mass spectrum of the involatile oil indicates the presence of the following fragments: Cl, CCl, CCl₂, CCl₃, CNCl, COCl, C₂NCl, CNCl₂, C₂NCl₃, C₂NOCl, C₂NOCl₃, C₂NCl₂, C₂NCl₄, C₂NOCl₄, and is consistent with the formulation of the nitron $\text{CCl}_3\cdot\ddot{\text{N}}(\ddot{\text{O}})\text{CCl}_2$. The i.r. spectrum was measured in the liquid phase, in the region 2000—700 cm⁻¹ and shows the following main absorption bands: 1639, 1613, 1016, 931, 801, and 777 cm⁻¹. The u.v. spectrum shows an absorption maximum at 210 nm with ϵ_{max} 6,400 (Found: C, 10.8; H, 0.2; N, 6.3. C₂Cl₅NO requires C, 10.4; H, 0.0; N, 6.1%.)

The variation of vapour pressure with temperature was measured in the range 20—150 °C using an isoteniscope, the results were treated by a computerised least-squares plot to give equation (14). The correlation is -0.996

$$\log_{10}(p/\text{mmHg}) = 6.473 - 1566/T \quad (14)$$

indicating a very good fit of the data to a straight line. The calculated latent heat of vaporisation is 7140 cal mol⁻¹, the calculated boiling point of the liquid is 163 °C and the Trouton constant 16.4 cal deg⁻¹ mol⁻¹.

The thermal decomposition was repeated using trichloronitrosomethane which had been stored at 0 °C for 12 h prior to final purification to allow the postulated intermediate, $\text{CCl}_3\cdot\text{SO}_2\cdot\text{NO}$, time to break down into $\text{CCl}_3\cdot\text{NO}$ and SO_2 . The results are given in the Table, and show that this technique is effective in removing sulphur dioxide.

During the course of these two experiments a pink colour was noticed in those fractions containing carbon tetrachloride. This colour faded on exposure to light with the formation of a small amount of non-condensable gas. A third experiment was carried out with the object of identifying the cause of this pink colour.

Trichloronitrosomethane (15.8 g) was heated in a sealed Carius' tube at 100—110 °C for 3 h. On freezing the contents of the tube and opening *in vacuo* a small amount of nitrogen (0.02 g) was found. The volatile products

¹¹ P. G. Ashmore and R. G. W. Norrish, *Proc. Roy. Soc.*, 1950, **A204**, 34.

¹² J. R. Morton and H. Wilcox, *Inorg. Synth.*, 1953, **4**, 48.

¹⁰ R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, *J. Chem. Soc.*, 1965, 7209.

were fractionated and analysed as described above, with some additional treatment as described below.

Fraction condensing at -96 °C. This was of a pink colour although i.r. and g.l.c., and measurements indicated carbon tetrachloride and chloropicrin, both of which are colourless. Measurement of the u.v. and visible spectra showed maxima at 520 and 265—290 nm. The i.r. spectrum also showed two absorption bands at 5.7 and 9.5

μm which could not be attributed to either carbon tetrachloride or chloropicrin. The pink colour of the sample faded on exposure to light. A sample (0.1 g) of the fraction was sealed *in vacuo* and exposed to daylight until the pink colour had faded. On freezing the sample 2.2 ml of nitrogen was removed by Toepler pump.

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