Pyrolysis of Trichloronitrosomethane

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Trichloronitrosomethane, partly in the liquid phase, decomposed at 98° to give nitric oxide, carbon tetrachloride, *N*-(dichloromethylene)trichloromethylamine, trichloronitromethane, nitrosyl chloride, and carbonyl chloride. After 3·5 h, no CCl_3NO could be recovered. Although there was a low yield of less volatile, unidentified materials, the previously reported product, *N*-(dichloromethylene)trichloromethylamine *N*-oxide, could not be positively identified.

TRICHLORONITROSOMETHANE was first pyrolysed by Prandtl and Sennewald[1] during attempted distillation of the neat liquid (normal b.p. 57°); the formation of the products claimed is approximately represented by equation (1). We wished to find a preparative use for solutions of the nitroso-compound,[2] and investigated the decomposition of a 17·2 mole % solution in refluxing chloroform;[3] the previously reported compounds were found, along with some carbonyl chloride and an inseparable fraction of low volatility, which showed a strong i.r. absorption at 1835 cm^{-1} and a highest mass peak corresponding to $C_3Cl_5N_2O^+$ in the mass spectrum.

In a concurrent study, Astley and Sutcliffe[4] pyrolysed neat CCl_3NO at 100° in a sealed tube; they reported no $CCl_3N{:}CCl_2$, but obtained the nitrone $CCl_3N(O){:}CCl_2$ as the major less volatile product. The methyleneamine $CCl_3N{:}CCl_2$ may be supposed to be formed *via* the nitroxide radical $(CCl_3)_2NO\cdot$ [equations (2)—(6)]; this is known to be thermally unstable[5] and at 100° could decompose to the nitrone according to equation (8), or by the elimination of CCl_4 shown by $(CCl_3)_2N-$ compounds[6] [equations (9)—(10)]; this is equivalent to the route suggested by Astley and Sutcliffe. We believe that the nitrone may have been an intermediate in the

$$3CCl_3NO \longrightarrow CCl_3N{:}CCl_2 + CCl_3NO_2 + ClNO \qquad (1)$$

$$CCl_3NO \longrightarrow CCl_3\cdot + \cdot NO \qquad (2)$$

$$CCl_3\cdot + CCl_3NO \longrightarrow (CCl_3)_2NO\cdot \qquad (3)$$

$$(CCl_3)_2NO\cdot + CCl_3NO \longrightarrow CCl_3N(O\cdot)\cdot O\cdot N(CCl_3)_2 \qquad (4)$$

$$CCl_3N(O\cdot)\cdot O\cdot N(CCl_3)_2 \longrightarrow CCl_3NO_2 + \cdot N(CCl_3)_2 \qquad (5)$$

$$\cdot N(CCl_3)_2 \longrightarrow CCl_3N{:}CCl_2 + Cl\cdot \qquad (6)$$

$$Cl\cdot + \cdot NO \longrightarrow ClNO \qquad (7)$$

$$(CCl_3)_2NO\cdot \longrightarrow Cl\cdot + CCl_3N(O){:}CCl_2 \qquad (8)$$

$$(CCl_3)_2NO\cdot \longrightarrow CCl_4 + Cl_2C{:}NO\cdot \qquad (9)$$

$$Cl_2C{:}NO\cdot \longleftrightarrow Cl_2\dot{C}\cdot N{:}O + CCl_3NO \longrightarrow CCl_3N(O){:}CCl_2 + \cdot NO \qquad (10)$$

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

[2] B. W. Tattershall, *J. Chem. Soc.* (*A*), 1970, 3261.

[3] B. W. Tattershall, *J. Chem. Soc.* (*A*), 1970, 3263.

[4] V. Astley and H. Sutcliffe, *J.C.S. Perkin II*, 1972, 197.

[5] H. Sutcliffe and H. W. Wardale, *J. Amer. Chem. Soc.*, 1967, **89**, 5487.

[6] H. Holtschmidt, E. Degener, H.-G. Schmelzer, H. Tamow, and W. Zecher, *Angew. Chem. Internat. Edn.*, 1968, **7**, 858.

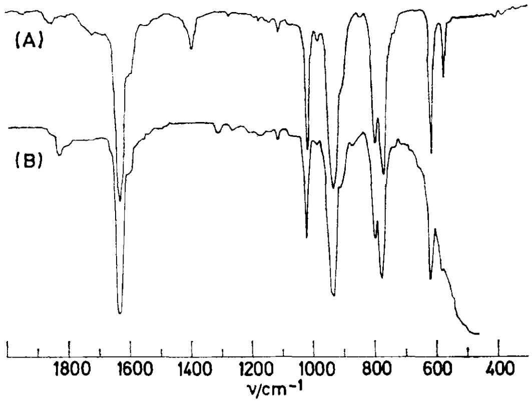
formation of by-products in all the pyrolysis experiments reported, but that it was not an isolable major end-product.

The i.r. spectrum reported[4] for the nitrone was similar to that found by us[3] for $CCl_3N{:}CCl_2$ and subsequently published for the methyleneamine made by a different route.[7] The N–O stretching frequency[4,8] at 1613 cm^{-1} is the only feature which distinguishes the nitrone; this is remarkable in view of the small size of the molecules, and the difference in oxidation state of nitrogen in the two compounds. To check these findings, we have repeated the pyrolysis of CCl_3NO under conditions similar to those described for the formation of the nitrone. We found (Table) similar yields of NO, $COCl_2$, and CCl_4, but a greater yield of ClNO. The i.r. spectrum of a liquid film of the residue after brief removal of volatile components was similar to that given for the nitrone, but evaporation under vacuum (10^{-3} Torr) at 0° for 3 h was sufficient to remove completely a compound absorbing at 1613 cm^{-1}. This was trichloronitromethane: the N–O stretching frequency of liquid CCl_3NO_2 is reported[9] as 1610 cm^{-1}, whereas the absorption is centred[10] at *ca.* 1625 cm^{-1} in the case of gaseous CCl_3NO_2. The remaining residue in our pyrolysis was estimated to be 89% $CCl_3N{:}CCl_2$ by weight. Its i.r. spectrum was similar to that of an authentic spectrum of $CCl_3N{:}CCl_2$ (see Figure). The major peaks in the mass spectrum were those expected for $CCl_3N{:}CCl_2$, and previously reported,[3] although peaks at *m/e* 124 ($C_2Cl_2NO^+$) and 239 ($C_3N_2Cl_5^+$) were also prominent. Samples of the methyleneamine separated by g.l.c. gave satisfactory analytical figures and a mass spectrum free from oxygen-containing fragments. The i.r. spectrum of the purified material was distinguishable from that of the crude residue only by an improved base-line and the absence of a peak at 1835 cm^{-1}. The sum of the yields of $CCl_3N{:}CCl_2$ and of CCl_3NO_2 in our pyrolysis approximated to the sum of the yields reported for $CCl_3N(O){:}CCl_2$ and CCl_3NO_2. Prandtl and Sennewald's results [equation (1)] correspond at least in part to ours, and may be explained in terms of reactions of the nitroxide $(CCl_3)_2NO\cdot$ [equations (4)—(7)].

Estimated yields of products [(moles product) × 100/(moles CCl_3NO taken), with no assumption of reaction stoicheiometries]

	$CCl_3N(O){:}CCl_2$		$CCl_3N{:}CCl_2$	CCl_3NO_2
Present work	†		15·4	10·4
Ref. 4	22·4		†	3·0
	CCl_4	$COCl_2$	ClNO	NO
Present work	37·8	10·6	13·1	42·6
Ref. 4	43·3	8·3	3·0	54·8

† Not found.



I.r. spectra: (A) † of liquid $CCl_3R{:}CCl_2$ (Perkin-Elmer 521 spectrophotometer); (B) of the crude residue from the present pyrolysis of CCl_3NO (Perkin-Elmer 457; shows NaCl window cut-off); spectra reduced to the same scale and redrawn by computer

† Kindly provided by Dr. L. Oehlmann, Farbenfabriken Bayer AG, Leverkusen.

The impurity in our $CCl_3N{:}CCl_2$ could be concentrated by evaporation of the methyleneamine into vacuum at 20°, but was an intractable mixture, probably of several oxygen-containing compounds. By use even of a 3% silicone column ($CCl_3N{:}CCl_2$, b.p. 170°, eluted at 82°), no useful quantity of these could be eluted in temperature programmed g.l.c. The u.v. spectrum of a solution of the mixture in cyclohexane showed a maximum at 211 nm previously attributed to the nitrone,[4,8] but which we have not assigned to any one of the possible components of the mixture. In the i.r. spectrum of the mixture the only peak clearly distinguishable from those of $CCl_3N{:}CCl_2$ was at 1835 cm^{-1}.

EXPERIMENTAL

Handling and spectrometric facilities were as stated previously.[3]

Gas–Liquid Chromatography.—The following apparatus and conditions were employed: stationary phase: 3% MS200/50 on Me_3SiCl-treated 100—120 mesh PhaseSep W; container: 3 m × 3/16 in. (o.d.) (analytical) or 3 m × 5/16 in. (o.d.) (preparative) copper tube, treated with dry Cl_2 after loading; carrier: 30 ml min^{-1} He (analytical) or 120 ml min^{-1} (preparative); temperature: isothermal at 50° until CCl_3NO_2 had been eluted (8 min), then linear programme at 2° min^{-1}; internal standard: *m*-xylene; detector: katharometer at 100°; preparative collection: glass concentric traps at −196°. Under these analytical conditions, the response to CCl_3NO_2 (Eastman Kodak) was linear to within 3% (1—2 mg in sample). Although preparative separations of $CCl_3N{:}CCl_2$ gave samples free from O-containing compounds, the mass spectrum then showed fragments [*m/e* 321 ($C_4N_2Cl_7^+$), 286 ($C_4N_2Cl_6^+$), 251 ($C_4N_2Cl_5^+$), and 190 ($C_3NCl_4^+$)] attributable to dimer formed on the surface of the chlorinated copper outlet tube.

Pyrolysis.—Trichloronitrosomethane (9·41 g, 63·4 mmol) was condensed into a strong glass ampoule (118 ml); the ampoule was sealed and heated at 98° in absence of light for 3·5 h. Gas and liquid phases were then the colour of ClNO. The ampoule was opened to the vacuum system, and volatile materials were transferred to a trap at −196°.

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[7] A. Schmidt, *Chem. Ber.*, 1972, **105**, 3050.

[8] V. Astley and H. Sutcliffe, *Tetrahedron Letters*, 1971, **29**, 2707.

[9] J. Mason, J. Dunderdale, and A. H. Castelli, *J. Chem. Soc.*, 1959, 2014.

[10] J. Mason and J. Dunderdale, *J. Chem. Soc.*, 1956, 759.

The temperature of the ampoule was not allowed to rise above 0°. After 3 h the i.r. spectrum of the residue (1·73 g) was principally that of $CCl_3N{:}CCl_2$, with no band at 1613 cm^{-1} as reported for $CCl_3N(O){:}CCl_2$, and was estimated to contain 89% by weight of $CCl_3N{:}CCl_2$ (1·54 g). Besides $CCl_3N{:}CCl_2$, the mass spectrum of the residue showed oxygen-containing fragments of mass up to *m/e* 368·7722 ($C_4N_2O_3Cl_7^+$). The volatile products were partially separated by vacuum fractionation: $CCl_3N{:}CCl_2$, CCl_3NO_2, and CCl_4 were estimated by g.l.c., further CCl_4 and NO were completely separated and measured directly, and $COCl_2$ and ClNO were estimated by i.r. analysis. The yields are summarised in the Table. Small quantities of CO_2 and N_2O were also detected.

Elemental analyses were carried out by Dr. F. Pascher (Bonn): for $CCl_3N{:}CCl_2$, purified by g.l.c.: Found: C, 11·3; Cl, 81·65; N, 7·25. Calc. for C_2Cl_5N: C, 11·15; Cl, 82·35; N, 6·5% (C_2Cl_5NO requires C, 10·4; Cl, 76·65; N, 6·05%).

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