α-Chloroacetylenes

John H. Wotiz, Francis Huba, and Robert Vendley

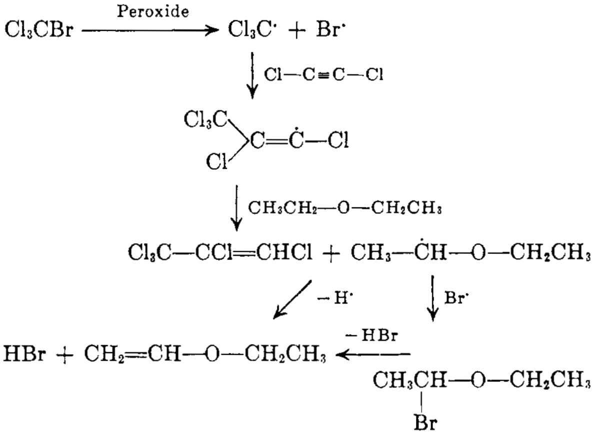
Received July 18, 1960

Dichloroacetylene, Cl—C≡C—Cl, is a toxic gas, explosive and spontaneously flammable when contacted with air. A relatively safe method of preparation was developed by Ott[1], who dehydrochlorinated trichloroethylene with a potassium hydroxide-calcium oxide mixture at 130° in the presence of ether. The solution of dichloroacetylene in ether does not exhibit the explosive or flammable properties of pure dichloroacetylene.

This note deals with preparation of dichloroacetylene and other α-chloroacetylenes prepared by dehydrochlorination reactions, and with the nature of dichloroacetylene-etherate. Following the general procedure of Ott[1], dichloroacetylene-etherate was consistently prepared in 71% yields. On distillation the azeotrope dichloroacetylene-ether, b.p. 32°, was collected. The composition of the azeotrope was previously determined[1] using density measurements, and was now verified with the aid of vapor chromatographic analyses. The pure dichloroacetylene eluted from the chromatographic column was found to detonate. The infrared spectrum of the freshly distilled dichloroacetylene-etherate shows only one strong band at 10.15 μ, which was not found in the spectrum of ether. There was no evidence for a triple bond absorption band in the 4.5 μ region. This is not surprising since it has been demonstrated that an internal triple bond, such as in dialkylacetylenes, is notoriously weak.[2] The infrared spectrum of the dichloroacetylene-etherate stored at −10° for one year did not show any evidence of chemical reaction.

The irradiation (Hg-lamp) of a solution of dichloroacetylene in ether was previously described.[3] Ott isolated two main products, supposedly a 1:1 and a 2:2 adduct, which structure he was not able to establish. In a subsequent publication, Ott[1] referred to $CH_3—CH_2—CCl{=}CCl—O—CH_2—CH_3$, a 1:1 adduct, as the residue from a dichloroacetylene-etherate distillation. However, no proof of structure was offered. In the present study it was found that dichloroacetylene reacts with ether under a variety of conditions, at the reflux temperature, ultraviolet light or sunlight irradiation, or catalyzed by free-radical initiators such as *t*-butyl peroxide and azobisisobutyronitrile. There seemed to be little, if any, difference in the nature of the products. Vapor chromatographic analyses showed the presence of about ten compounds. The two major components were isolated and identified as $CHCl{=}CCl—CH(CH_3)—O—CH_2CH_3$ and $CHCl{=}CCl—CH(CH_3)—O—CH(CH_3)—CCl{=}CHCl$. The identification was made on the basis of elemental analyses, spectroscopic investigation, and by the dehydrochlorination of the 1:1 adduct to $Cl—C{\equiv}C—CH(CH_3)—O—CH_2CH_3$. It is likely that we were dealing with the 1:1 adduct to which Ott assigned an incorrect structure. One of the minor products was $CCl_2{=}CCl—C{\equiv}C—Cl$ for which presence we had only mass spectroscopic analytical evidence. An alternate tetrachlorocyclobutadiene structure was not considered to be likely.

Dichloroacetylene-etherate was also treated with bromotrichloromethane in the presence of *t*-butyl peroxide while ultraviolet light irradiated. The product was 1,1,1,2,3-pentachloropropene, $CCl_3—CCl{=}CHCl$. A possible reaction mechanism is:



On dehydrochlorination, tetrachloropropyne, $Cl_3C—C{\equiv}C—Cl$, was obtained.

The reaction of dichloroacetylene - etherate with an ether solution of thiocyanogen produced 1,4-bis(thiocyano)butene-2 in 80% yield. The origin or mechanism of reaction is not understood.

EXPERIMENTAL

Dichloroacetylene-etherate. A mixture of 328 g. (2.5 moles) of trichloroethylene and 185 g. (2.5 moles) of ether was vaporized by dropping it into a vaporizer immersed in an oil bath kept at 180°. The vapors were swept with nitrogen through 75 inches of Pyrex tubes (1.5 inch diameter) filled with 600 g. of potassium hydroxide–calcium oxide flakes. The flakes were prepared by dipping a cold stainless steel bar into molten potassium hydroxide–calcium oxide (10:1), m.p. about 280°. Large curved thin flakes were preferred to effect a surface reaction and avoid caking. The potassium hydroxide–calcium oxide had to be heated to 120° for the initiation of the exothermic dehydrochlorination. Once the reaction was started, outside heating was stopped and the reaction kept near 130° by adjusting the rate of vaporizing of the trichloroethylene. Usually 250 l. of nitrogen were used and swept through the reactor in 2.5 hr. The product was condensed in a flask cooled in a Dry Ice–acetone mixture. Upon the completion of the dehydrochlorination reaction, the cooling bath was removed and the product distilled through a column filled with granular Drierite. The

---

(1) E. Ott, *Ber.*, **75**, 1517 (1942).

(2) J. H. Wotiz and F. A. Miller, *J. Am. Chem. Soc.*, **71**, 3441 (1949).

(3) E. Ott and K. Packendorff, *Ber.*, **64**, 1324 (1931).

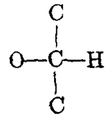
dichloroacetylene-etherate azeotrope distilled at 32° and 387 ml. (d_{20} 0.952) was collected. The azeotrope contained 55.4% dichloroacetylene and 44.6% of ether as determined by vapor chromatographic analysis. There was 0.435 g. of dichloroacetylene per ml. of azeotrope. The yield of dichloroacetylene was 71%.

The reaction of dichloroacetylene with ether. The ultraviolet light irradiation of 550 ml. of dichloroacetylene etherate (azeotrope, contained 1.8 moles of dichloroacetylene) was over a period of 30 hr. The unchanged dichloroacetylene and ether were distilled and recovered, showing that 0.6 mole of dichloroacetylene was consumed. By vacuum distillation of 200 g. of the higher boiling products it was found that it contained 68 g. (34% of the crude mixture) of *α-(1,2-dichlorovinyl)diethyl ether*, $CHCl{=}CCl{-}CH(CH_3){-}O{-}CH_2CH_3$, b.p. 57–58° at 20 mm., n_D^{25} 1.4524.

Anal. Calcd. for $C_6H_{10}OCl_2$: C, 42.6; H, 5.9; Cl, 42.0; mol. wt., 169. Found: C, 42.1; H, 5.8; Cl, 41.8; mol. wt., 170.

The second product (52 g., 26% of the crude mixture) was *α,α'-bis(1,2-dichlorovinyl)diethyl ether*, $CHCl{=}CCl{-}CH(CH_3){-}O{-}CH(CH_3){-}CCl{=}CHCl$, b.p. 104–5° at 6 mm., n_D^{25} 1.5070.

Anal. Calcd. for $C_8H_{10}OCl_4$: C, 36.4; H, 3.7; Cl, 53.8; mol. wt., 264. Found: C, 35.2; H, 3.4; Cl, 53.5; mol. wt., 250. The infrared spectra of the two compounds contained, aside from other characteristic absorption bands, a band near 3.27 μ, characteristic of $H{-}C{=}$, and bands near 3.43 and 7.5 μ, characteristic of a tertiary hydrogen,



$$\begin{array}{c} C \\ | \\ O{-}C{-}H \\ | \\ C \end{array}$$

such as found in isopropyl ethers.

α-Chloroethynyldiethyl ether, $Cl{-}C{\equiv}C{-}CH(CH_3){-}O{-}CH_2CH_3$, was prepared by passing an ether solution of $CHCl{=}CCl{-}CH(CH_3){-}O{-}CH_2CH_3$ through a tube filled with potassium hydroxide–calcium oxide (10:1) kept at 160–180°. There was a 50% recovery of the starting material and the yield of product was 35% (70% conversion), b.p. 53–54° at 55 mm., n_D^{25} 1.4305.

Anal. Calcd. for C_6H_9ClO: C, 54.3; H, 6.7; Cl, 26.9; mol. wt., 132. Found: C, 52.0; H, 6.6; Cl, 27.9; mol. wt., 126. The infrared spectrum showed the triple bond absorption peak of medium intensity at 4.5 μ.

1,1,1,2,3-Pentachloropropene, $Cl_3C{-}CCl{=}CClH$. Dichloroacetylene (166 g., 1.75 moles) in 380 ml. of ether solution was refluxed for 7 hr. with 600 g. (3 moles) of bromotrichloromethane in the presence of 5 ml. of *t*-butyl peroxide, while ultraviolet light irradiated. The reflux temperature rose from 50 to 64° during that time. The reaction mixture was distilled. There was a 29% recovery of dichloroacetylene-etherate, 89% recovery of bromotrichloromethane, and the crude reaction product weighed 302 g. Thus the reaction involved 116 g. (1.22 moles) of dichloroacetylene, 134 g. (0.8 mole) of ether, and 70 g. (0.35 mole) of bromotrichloromethane indicating that some of the dichloroacetylene reacted with ether. During the distillation of the crude reaction product, there was a copious evolution of hydrogen halide. A total of 146 g. (46% yield based on consumed dichloroacetylene) of $CCl_3{-}CCl{=}CHCl$ was collected, b.p. 56° at 6 mm., n_D^{25} 1.5285.

Anal. Calcd. for C_3HCl_5: C, 16.7; H, 0.5; Cl, 82.8; mol. wt., 214. Found: C, 17.0; H, 0.6; Cl, 82.1; mol. wt., 213. The compound was previously prepared[4] by the dehydrochlorination of $Cl_3C{-}CCl_2{-}CH_2Cl$, b. 59–60° at 6 mm., n_D^{20} 1.5286.

Tetrachloropropyne, $Cl_3C{-}C{\equiv}C{-}Cl$. A mixture of 40.4 g of $Cl_3C{-}CCl{=}CHCl$ and 22 g. of ether was swept with preheated nitrogen through a tube filled with potassium hydroxide-calcium oxide (10:1) flakes kept at 140–180°. The condensate contained 4 g. of starting halide and 11 g. (33% yield, redistilled) of $Cl_3C{-}C{\equiv}C{-}Cl$, b.p. 58–60° at 50 mm.; n_D^{20} 1.5100.

Anal. Calcd. for C_3Cl_4: C, 20.2; Cl, 79.8; mol. wt., 178. Found: C, 20.5; Cl, 80.2; mol. wt., 172.

The infrared spectrum shows a strong triple bond band at 4.5 μ.

1,4-Bis(thiocyano)butane-2, $N{\equiv}C{-}S{-}CH_2CH{=}CH{-}CH_2{-}S{-}C{\equiv}N$. Thiocyanogen was prepared from lead thiocyanate in 74% yield as previously described.[5] The addition of dichloroacetylene-etherate (0.1 mole) to thiocyanogen (0.04 mole) in ether produced, after the removal of ether and dichloroacetylene, 5.6 g. (80% yield) of the yellow $NCSCH_2CH{=}CHCH_2SCN$, m.p. 83–84°.

Anal. Calcd. for $C_6H_6N_2S_2$: C, 42.3; H, 3.5; N, 16.5. Found: C, 42.3; H, 3.5; N, 16.8.

This compound was previously described[6] as the product of reaction of 1,4-dibromobuten-2 with NH_4SCN, m.p. 83°. The infrared spectrum of our product confirmed the structure.

Acknowledgment. We wish to acknowledge the assistance of Mr. T. S. Wang of our Spectroscopic Laboratory.

DIAMOND ALKALI CO.
RESEARCH CENTER
PAINESVILLE, OHIO

---

[4] A. N. Nesmeyanov, R. K. Freidlina, and U. I. Firstov, *Izvest. Akad. Nauk. U.S.S.R., Otdel. Khim, Nauk.*, **1951**, 505; *Chem. Abstr.*, **46**, 7034 (1952).

[5] E. Söderback, *Ann.*, **419**, 217 (1919); *Chem. Abstr.*, **14**, 1808 (1920).

[6] J. v. Braun, and G. Lemke, *Ber.*, **55**, 3549 (1922).

Fluorination of Some Nitriles and Ketones with Bromine Trifluoride[1]

TRAVIS E. STEVENS

Received March 25, 1960

In connection with a general investigation of the reaction of bromine trifluoride and organic compounds, the selective fluorination of several substances has been observed. Fluorination of organic compounds by the vigorous fluorinating agent bromine trifluoride previously had been confined to the relatively non-selective fluorination of compounds containing a large percentage of halogen.[2]

The fluorinations reported here were carried out in a solution of hydrogen fluoride or iodine pentafluoride.[3] Some preliminary experiments with

---

[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-5135.

[2] A. A. Banks, H. J. Emeleus, R. N. Hazeldine, and Y. Kerrigan, *J. Chem. Soc.*, 2188 (1948); E. T. McBee, V. V. Lindgren, and W. B. Liggett, *Ind. Eng. Chem.*, **39**, 370 (1947); R. E. Florin, W. J. Pummer, and L. A. Wall, *J. Research Natl. Bur. Standards*, **62**, 107 (1959) [*Chem. Abstr.*, **52**, 19928 (1959)].

[3] The usefulness of anhydrous hydrogen fluoride as a solvent for fluorinations involving halogen fluorides, particularly chlorine trifluoride, has been noted (Gall and Inman, U. S. Pat. **2,702,306**), but no controlled selective fluorination was recorded.