Attempted Preparation of trans-alpha, alpha'-Dichlorostilbene from Benzene, Chlorine and Calcium Carbide

O. C. DERMER and DONALD V. HERTZLER,

Oklahoma State University, Stillwater

Davidson (1918) reported the remarkable production of *trans*-α, α'-dichlorostilbene (I) (mp 143 C) from a mixture of benzene, calcium carbide, and chlorine. To duplicate this work, chlorine gas was bubbled through a stirred mixture of finely powdered calcium carbide in four times its weight of benzene. No apparent reaction resulted at 0 C nor at 50 C in a two-hour period. No crystals were obtained from either the original mother liquor or the concentrated mother liquor (reduced to one-quarter of the original volume) upon standing for one week in a refrigerator. These results are in contradiction of Davidson's report of an exothermic reaction within 15 minutes accompanied by vigorous evolution of hydrogen chloride and crystallization of I on cooling. Davidson suggested that the reaction first yielded dichloroacetylene, which reacted with benzene to give I, but Riemschneider and Brendel (1961) found that dichloroacetylene does not react with benzene at −5 C to 180 C, and neither they nor earlier workers could obtain dichloroacetylene from calcium carbide and chlorine.

However, it has now been observed that upon addition of a drop of water to the reaction mixture, a gas formed which ignited spontaneously on contact with air. This indicated the production of mono- and/or dichloroacetylene (Huntress, 1948). If the chlorine introduced into the benzene-calcium carbide mixture was first bubbled through water, the temperature of the reaction mixture began to rise within five minutes and vigorous evolution of hydrogen chloride began. White crystals began forming in the reaction flask in one hour. The reaction subsided of its own accord in three hours. From 54 g of calcium carbide in 250 ml of benzene, 30 g of white crystals melting at 158 C were obtained. The infrared spectrum of this solid was identical to that of known benzene hexachloride, which has a melting point of 157-158 C. A similar reaction of ethylene, chlorine, and benzene has been reported to give benzene hexachloride and large quantities of hydrogen chloride gas (Stewart and Hanson, 1931). Alkyl halides have been shown to catalyze the addition of chlorine to benzene in the dark (Orloff and Worrel, 1954).

In summary, Davidson's work could not be duplicated. When wet chlorine gas was bubbled into a stirred suspension of calcium carbide in benzene, benzene hexachloride was formed.

LITERATURE CITED

Davidson, C. 1918. Tolane chlorides from calcium carbide, benzene, and chlorine. J. Am. Chem. Soc. 40: 397.

Huntress, E. H. 1948. Organic Chlorine Compounds. Wiley, p. 552, 930.

Orloff, H. D., and C. J. Worrel. 1954. U. S. Pat. 2,691,051. Chem. Abs. 49: P2015b.

Riemschneider, R., and K. Brendel. 1961. Halogenated acetylenes. Note on preparation and handling of dichloroacetylene. Ann. Chem. 640: 5.

Stewart, T. D., and M. H. Hanson. 1931. The induction of the reaction between chlorine and benzene by ethylene. J. Am. Chem. Soc. 53: 1121.