Synthesis of Substituted Phenyltrichlorocyclopropene Derivatives Using Friedel-Crafts Reaction

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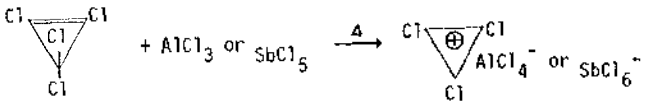
Tetrachlorocyclopropene has been prepared smoothly by the dehydrochlorination of pentachlorocyclopropane which could be obtained easily from sodium trichloroacetate and trichloroethylene in 1,2-dimethoxyethane. By the reaction of aromatic hydrocarbons with tetrachlorocyclopropene and aluminium chloride, new substituted phenyltrichlorocyclopropene derivatives have been prepared. The structures of these compounds were characterized by means of spectroscopic methods.

Introduction

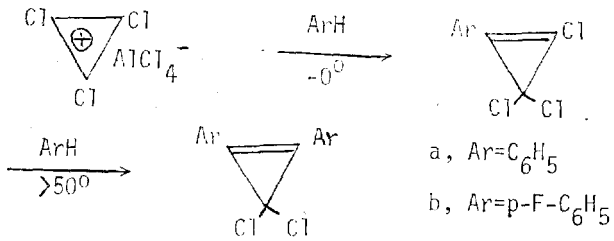
Highly or fully chlorinated organic compounds, which have interesting physical and chemical properties, have long been known and were manufactured on a large scale as solvents, insecticides, and flame retardants. Many of chlorocarbons were highly reactive and gave rise to derivatives with unusual electronic structures. Tetrachlorocyclopropene[1] which was the smallest of these species was used as a versatile precursor for a wide variety of reactions, such as halogen exchange reaction,[2] nucleophilic substitution reaction,[3] Diels-Alder reaction,[4,5] and electrophilic substitution reaction.[6-10]

The reaction of excess tetrachlorocyclopropene with Lewis acids such as aluminium chloride and antimony chloride resulted in the new white powders. The analysis of these salts after removal of excess tetrachlorocyclopropene under vacuum agreed with the structures of trichlorocyclopropenium tetrachloroaluminate and trichlorocyclopropenium hexachloroantimonate.[11]



The structures and chemical bondings of these complexes were fully investigated by the infrared, Raman spectra, normal coordinate analysis using Urey-Bradley force field,[12] and elementaly analysis.[11]

West *et al.*[6,7] found that trichlorocyclopropenium ion reacted smoothl with benzene derivatives to provide either aryltrichlorocyclopropenes or gem-dichlorodiarylcyclopropenes depending on the reaction condition.



Also they[13] obtained triarylcyclopropenium ions and diarlycyclopropenones by the reaction of trichlorocyclopropenium ion with phenol, anisole, 2,6-dimethylphenol, 2,6-diisopropylphenol, and 2,6-di-tert-butylphenol at 30-80 °C. Friedel-Crafts reaction of the trichlorocyclopropenium cation with unsaturated substrates was also studied by other group.[8]

Now we described the synthesis of pentachlorocyclopane by the method which is different from that of Tobey and West.[1] Several changes in the experimental procedure increased the overall yield of pentachlorocyclopropane twice.

Tetrachlorocyclopropene could be easily obtained by the dehydrochlorination of pentachlorocyclopropane using aqueous potassium hydroxide. Gentle warming of a mixture of aluminium chloride and excess tetrachlorocyclopropene initiated an exothermic reaction which resulted in the formation of trichlorocyclopropenium tetrachloroaluminate.

In the present work, we have synthesized several new substituted phenyltrichlorocyclopropene derivatives by the reaction of aromatic hydrocarbons with trichlorocyclopropenium tetrachloroaluminate. Especially *p*-chloro- and *p*-methyl phenyltrichlorocyclopropene which could not be obtained by the previous methods[6,7,14] were prepared by this method.

Results and Discussion

Decarboxylation of sodium trichloroacetate in dry 1,2-dimethoxyethane at 92-94° in the presence of excess trichloroethylene provided pentachlorocyclopropane in 15 % yield in isomerically pure form according to the method of Tobey and West.[1] Such a low yield was due to relatively poor carbene acceptor like trichloroethylene which has three electron withdrawing chlorine atoms. The yield of pentachlorocyclopropane was doubled by employing approximately half of the quantity of glyme previously suggested.[1] This change caused the decomposition of sodium trichloroacetate to proceed more slowly. Although other methods[15-17] of generating dichlorocarbene have been described which led to higher yields of highly halogenated cyclopropanes from relatively poor carbene acceptors like trichloroethylene, simple decarboxylation of sodium trichloroacetate in glyme was found to work adequately. Generally, thermolysis of sodium trichloroacetate in a aprotic solvent produced dichlorocarbene *via* trichlorocarbanion.[18]

The proton nmr spectrum of pentachlorocyclopropane showed a singlet resonance at 4.4 ppm. The proton resonance lay well downfield from the 0.22 ppm resonance position of cyclopropane itself, and a reasonable distance downfield from the 2.98 ppm value for the -CHCl- proton in chlorocyclopropane. It was shown that the value of cyclopropane

ring system increased more and more as hydrogen was replaced by chlorine.

When pentachlorocyclopropane was simply treated with excess strong aqueous potassium hydroxide at 85–95°, a moderately exothermic dehydrochlorination of pentachlorocyclopropane occurred which provided tetrachlorocyclopropene. Tetrachlorocyclopropene showed only one infrared band anywhere near 1600 cm^{-1}, and that was a absorption at 1810 cm^{-1}. The infrared aborsrption band perhaps could be assigned to C=C stretching, although the band lay nearly 200 cm^{-1} above the corresponding frequency of normal chlorinated olefines. The effect of chlorine substitution on open chain olefines was usually to lower the position of C=C stretching. For example; *cis* CHCl=CHCl absorbed at 1655, *trans* CHCl=CHCl at 1595 $CH_2=CCl_2$ at 1600, and CCl=CHCl at 1595 cm^{-1}. This rather large displacement resulted from fact that in the case of cyclopropene it was in correct to consider C=C infrared absorption as being associated with the vibration by itself. As pointed out earlier by Wilcox and Craig,[19] the absorption was due to normal vibrational mode of the entire molecular in which the C=C vibration was strongly coupled to ring and substituent vibrations. As a result the C=C absorption band in cyclopropenes wandered over an exceptionally wide range and depended heavily on the nature of the ring substituents.[19]

The reaction of tetrachlorocyclopropene with aluminium chloride led to the formation of stable salt of the trichlorocyclopropenium tetrachloroaluminate.

A most useful reaction of trichlorocyclopropenium complex was Friedel–Crafts type condensation with aromatic hydrocarbons, leading to substituted phenyltrichlorocyclopropene derivatives. In the reaction of terachlorocyclopropene and aluminium chloride with activated aromatic hydrocarbons such as *tert*-butylbenzene, ethylbenzene, and toluene, they reacted moderately. Also was found that the yield was increased as electron donating properties were stronger. On the other hand, in the reaction of aromatic hydrocarbons containing electron withdrawing groups with trichlorocyclopropenium salt, their tendencies were opposite. Strongly deactivated aromatic compounds such as benzonitrile and trifluoromethylbenzene were unreactive toward trichlorocyclopropenium ion even under the forcing conditions. Anisole and ethoxybenzene reacted very smoothly, but generally gave mixtures of isomers which were difficult to separate. It was likely that the transition state in this reaction involved the reaction of positive charge in the aromatic ring. So its reaction was similiar to Friedel–Crafts type condensation.

It was shown that the absorption frequency of the C=C stretching band of terachlorocyclopropene appeared at 1810 cm^{-1}. In substituted phenyltrichlorocyclopropene derivatives, however, the vibrational mode came to nearly 1600–1620 cm^{-1} which was normal C=C stretching band region. This result supported the absence of strong substituents coupling.

In the case where a single isomer (*p*-*tert*-butylphenyl) or where separation of isomers could be achieved (*p*-tobyl), the substituent was assigned to the *para* position of the aromatic ring. This assignment was based on the AA′ BB′ type spectrum which was observed for the aromatic protons in the nmr.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover melting point apparatus and were uncorrected.

Infrared spectra were recorded on a Perkin-Elmer 267 spectrophotometer on KBr pellet.

^1H NMR spectra were recorded by using a Varian T-60A spectrometer. Chemical shifts were expressed in parts per million(δ) downfield from internal tetramethylsilane in carbon tetrachloride unless otherwise stated. Significant ^1H NMR spectra were tabulated in the order of number of protons and multiplicity (*s*, singlet; *d*, doublet; *t*, *q*, quartet; *m*, multiplet).

Mass spectra were measured on a Hewlett-Packard 5985A mass spectrometer. All the chemicals used were purified immediately prior to use by the known standard methods.[20]

Pentachlorocyclopropane. A slurry of sodium trichloroacetate (350 g, 1.89 mole) in trichloroethylene (1300 g, 14.40 mole) was placed in a 2*l* three neck, round-bottomed flask fit with a heating mantle, powerful teflon-blade stirrer, and condenser vented through a mineral oil bubbler and was mechanically stirred and heat to gentle reflux for 3 hr. at 50–60°C During this period of time approximately 5–10 m*l* water was collected in a Dean–Stark trap. The water trap was removed and 200 m*l* of glyme was added. The mixture was heated to gentle reflux at 92–94° for 5 days. Evolution of carbon dioxide was slow and uniform during this period, as monitored by the bubbler, and the solution began to darken. In addition to carbon dioxide, small amounts of irritating and obnoxious smelling gas were evolved in hood. The final reaction mixture was allowed to cool and settled. The upper oily layer was decanted off and the lower silt layer was drenched with 1 m*l*. of water providing 100 m*l* of a oil which was dried over anhydrous calcium chloride and combined with the decantate. The excess trichloroethylene was removed by fractional vacuum distillation. The fraction boiling between 80 and 85° (31 mm) gave 120 g (30%) of pentachlorocyclopropane. IR (coated on NaCl plate): 3040, 950–890, and 765 cm^{-1} NMR; 4.4 ppm (1H, *s*).

Tetrachlorocyclopropene was prepared as described in the literature.[12] To a solution of 35.5 g of 95% potasium hydroxide in 40 m*l* of water was added 50.0 g (0.23 mole) of pentachlorocyclopropane. The two phase mixture was stirred slowly and heated to 75° and the temperature rose to 88 °C where it was maintained by occasional ice cooling. After 25 min, the mixture was cooled to 50°C and 50 m*l* of ice water followed by 25 m*l* of cold concentrated hydrogen chloride was added. Then the pH of the solution fell below 2 and and emulsion broke. The lower only layer was separated off and dried over anhydrous calcium chloride. Simple distillation of the oil under nitrogen atmosphere provided 24 g (62 %) of clear, colorless compound boiling

at 130–131 °C. IR(coated on NaCl plate); 1810, 1145, 1050, 750, and 610 cm^{-1}. Mass; *m/e* (relative intensity) 178 (100), 140(5), and 76(20).

Phenyltrichlorocyclopropene. Dry benzene (10 m*l*, 0.11 mole) was added to a stirred suspension of trichlorocyclopropenium tetrachloroaluminate prepared from aluminium chloride (4.0 g, 0.03 mole) and tetrachlorocyclopropene (7.0 g, 0.039 mole) at 50 °C. Hydrogen chloride gas was evolved and a homogeneous solution resulted. The dark red reaction mixture was poured into 50 m*l* of ice water and stirred until yellow oil was obtained. Immediate extraction with anhydrous ethyl ether followed by two successive dryings over anhydrous magnessium sulfate gave 4.0 g (46.5 %) of phenyltrichlorocyclopropene, which was recrystallized from *n*-pentane; m.p 37–39 °C, NMR ($CDCl_3$); 7.42 ppm (5H, *m*), IR (KBr); 1830(*s*), 1600(*s*), 1450(*m*), and 790 cm^{-1}(*s*) Mass; *m/e* (relative intensity) 219(3), 206(100), 115(15), 77(10), and 36(2). The following phenyltrichlorocyclopropenes were prepared in the manner outlined above, recrystallized in the solvent indicated.

p-Methylphenyltrichlorocyclopropene (yield 50 %) had m.p 42–43 °C (*n*-hexane) NMR ($CDCl_3$); 7.62 ppm (4H, AA'BB' type pair of doublets) 2.5 ppm (3H, 5) IR (KBr); 1830(*s*), 1620(*s*), 1350(*m*), 1170(*m*), and 810 cm^{-1}(*s*) Mass; *m/e* (relative intensity) 233(90), 218(100), 206(40), 103(20), and 76(5).

p-Ethylphenyltrichlorocyclopropene. (yield 80%) had m.p 44–45 °C (ethyl ether) NMR (CCl_4); 7.64 ppm (47, pair of doublets), 2.80 ppm (2H, *q*), 1.44 ppm (3H, *t*), IR(KBr); 2960(*w*), 1890(*s*), 1620(*s*), 1340(*m*), 1150(*m*), 830 cm^{-1}(*s*) Mass; *m/e* (relative intensity), 247(2), 217(100), 206(40), and 103(20).

p-sec-Propylphenyltrichlorocyclopropene (yield 75 %) had m.p 47–49 °C NMR (CCl_4); 7.47 ppm (4H, pair of doublets) 2.92 ppm (1H, *m*), 1.24 ppm (6H, *d*) IR(KBr); 2940(*m*), 1840(*s*), 1610(*s*), 1400(*m*), 1350(*m*), and 830 cm^{-1}(*s*) Mass; *m/e* (relative intensity) 262(80), 247(100, and 132(7).

p-tert-Butylphenyltrichlorocyclopropene. Following the same procedure, 10.3 g(95 %) of *p-tert*-butylphenyltrichlorocyclopropene was isolated and recrystallized from *n*-pentane m.p; 63– °C NMR($CDCl_3$); 7.76 ppm (4H, pair of doublets) 1.38 ppm (9H, *s*), IR(KBr); 2950(*s*), 1850(*s*), 1620(*s*), 1410(*m*), 1020(*w*), and 830 cm^{-1}(*s*), Mass; *m/e* (relative intensity) 245(5), 115(20), and 103(30).

p-Chlorophenyltrichlorocyclopropene. Trichlorocyclopropenium tetrachloroaluminate was prepared by mixing tetrachlorocyclopropene (8.0 g, 45 mmole) and aluminium chloride (6.0 g, 45 mmole) at 50 °C, To this salt was added 5.3 m*l*(43 mmole) of chlorobenzene and the red reaction mixture was stirred at room temperature for 20 hr. Fractional recrystallization from carbon tetrachloride gave the pure *para* isomer (3.4 g, 34%) m.p; 71–73 °C NMR($CDCl_3$); 7.47 ppm (pair of doublets, IR(KBr); 1850(*s*), 1620(*s*), 1400(*m*), 1340(*m*), 1090(*s*), 840(*m*), and 750 cm^{-1}(*m*), Mass; *m/e* (relative intensity) 251(2), 246(100), 176(57), 123(15), and 75(13).

1,4-Dimethylphenyltrichlorocyclopropene (yield 44 %) had m.p 60–61 °C NMR (CCl_4); 7.58 (1H, *s*), 7. 20 (2H, *s*, 7.20 (2H, *s*), 2.72 (3H, *s*), and 2.72 ppm (3H, *s*) IR (KBr); 2920(*w*), 1820(*s*), 1600(*s*), 1490(*m*), 1320(*m*), and 820(*s*), Mass; *m/e* (relative intensity) 247(2), 233(100), 219(100), 219(50), 204(70), and 103(20).

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