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CHLORINATION OF METHYLTRICHLOROSILANE IN A BARRIER DISCHARGE

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Thus far, chlorination of alkylchlorosilanes has been carried out in a liquid phase in the presence of different radical initiators and also photochemically in the gas phase [1]. For the case of methyltrichlorosilane (I) we showed, for the first time, the possibility of gas-phase chlorination of alkylchlorosilanes by chlorine in a barrier discharge.

The process was carried out in an ozonizer-type reactor described previously [2]. The reactor was fed from a high-voltage transformer with 50-Hz alternating current. The voltage on the electrodes was 10 kV, and the current density and the power with respect to a unit of area of the barrier were 0.00011 A/cm<sup>2</sup> and 1.1 W/cm<sup>2</sup>, respectively.

The unit consisted of a still connected to a fractionating column, a feeder, an evaporator, a reactor, a condenser, and a liquid seal.

The vapors of (I) from the still entered the feeder via the fractionating column, and part of (I) was returned to the column as reflux. From the feeder, (I) was fed into the evaporator heated to  $80^{\circ}$ C, into which dry  $Cl_2$  was also fed via a rheometer. The mixture of (I) and  $Cl_2$  entered the reactor, whose discharge space was thermostated at  $80^{\circ}$ C. The reaction products from the reactor were fed to the condenser, from which the liquid condensate entered back into the still via the seal, and the gaseous reaction products entered an entrainment separator cooled by liquid N<sub>2</sub>. The mixture of the reaction products was fractionated and analyzed by GLC and proton NMR.

As a result of the studied reaction, we obtained not only the expected chloromethyltrichlorosilane, but also a series of products of both direct and destructive chlorination of (I).

# EXPERIMENTAL

The proton NMR spectra were recorded on a Tesla BS-487B instrument (80 MHz,  $CC1_4$  solvent, and TMS internal standard).

GLC analysis was carried out with an LKhM-72 instrument with an I-02 integrator, the detector was a katharometer with temperature programming from 50 to  $150^{\circ}C$  (4 deg/min), the columns were 3 m × 3 mm with 10% PMS on Hesasorb AW-HMDS (0.15-0.25 mm), and the carrier gas was He. When (I) was fed into the reactor at a rate of 2.5 moles/h and  $Cl_2$  at 0.05 mole/

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h, from 149.5 g (1 mole) of (I) we obtained in 17 h 163.1 g of a complex mixture of liquid products in the still and 38.2 g of a condensate in the entrainment separator; 105.8 g (0.708 mole) of the starting (I) did not enter into reaction (29.2% conversion).

After fractionation of the reaction products, we isolated and identified 35.4 g of  $ClCH_2SiCl_3$  [65.7% yield based on reacted (I)], 5 g of  $Cl_2CHSiCl_3$ , 3.9 g of  $Cl_3CSiCl_3$ , 6.3 g of  $SiCl_4$ , 0.7 g of  $CH_3Cl_1$ , 0.5 g of  $CH_2Cl_2$ , 0.5 g of  $CHCl_3$ , 1.1 g of  $CCl_4$ , and 3.9 g of the undistilled still residue. The condensate in the cooled entrainment separator consisted of unreacted  $Cl_2$ , HCl, and  $CH_3Cl_1$ .

#### CONCLUSION

1. The possibility of gas-phase chlorination of alkylsilanes in a barrier discharge was shown for the first time.

2. The composition of products of direct and destructive chlorination of methylchlorosilane was ascertained.

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## FUNCTIONALLY DISUBSTITUTED $\sigma$ - AND $\pi$ -2-FERROCENYLALLYL

IRON COMPLEXES

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The first known example of a  $\sigma$ -allyl complex of cyclopentadientylcarbonyliron containing two functional groups on the terminal C atom of the allyl ligand was 3,3-dicyano-2-ferrocenylallyl(cyclopentadienyl)dicarbonyliron (I), which was prepared by us via the reaction of the organometallic carbonium ion salt (II) with malononitrile [1].

$$[Cp(CO)_2 FeCH_2C(Fc)OC_2H_5]^+ BF_4^- \xrightarrow{CH_3(CN)_2} Cp(CO)_2 FeCH_2C(Fc) = C(CN)_2$$
(II)
$$Fc = C_5H_4 FeC_5H_5.$$
(I)

Compound (I) is a high-melting solid which is stable in air, in contrast to other known  $\sigma$ -allyl complexes of the type Cp(CO)<sub>2</sub>FeAll containing alkyl, aryl, or functional groups on the allyl ligand, which tend to be low-melting or oily solids; many of these latter derivatives have not been characterized by elemental analysis due to their instability [2-4]. In the present paper we report the synthesis of a new functionally disubstituted  $\sigma$ -2-ferrocenyl-allyl iron complex, namely, 3-cyano-3-ethoxycarbonyl-2-ferrocenylallyl(cyclopentadienyl)dicarbonyliron (III), and its rearrangement to give a  $\pi$ -allyl complex.

Complex (III) was obtained in a manner analogous to (I) from the salt (II) and ethyl cyanoacetate and was characterized by PMR and IR spectroscopy.

(II) 
$$\xrightarrow{CH_2(CN)COOC_2H_5} Cp(CO)_2FeCH_2C(Fc) \approx C(CN)COOC_2H_5$$
(III)

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