Journal of Organometallic Chemistry, 96 (1975) C1—C3

Preliminary communication

THE CONDENSATION REACTION OF TRICHLOROSILANE WITH ALLYLIC CHLORIDES CATALYZED BY COPPER SALTS IN THE PRESENCE OF A TERTIARY AMINE

N. FURUYA* and T. SUKAWA
Central Research Laboratory, Mitsubishi Metal Corporation, 1-297 Kitabukuro, Omiya, Saitama, 330 (Japan)
(Received May 30th, 1975)

Summary

Trichlorosilane undergoes a smooth reaction at room temperature with allyl chloride, β-methallyl chloride, crotyl chloride, and α-methallyl chloride to give the corresponding allyltrichlorosilanes in excellent yields in the presence of an equimolar amount of a tertiary amine and a catalytic amount of a metal salt such as cuprous chloride.

Allyltrichlorosilane is usually prepared by the high temperature condensation of trichlorosilane with allyl chloride [1]. For a method of silicon—carbon bond formation the tertiary amine-trichlorosilane combination is effective; in particular, various $ArCH_2Cl$ react with $HSiCl_3/R_3N$ to give $ArCH_2SiCl_3$ [2].

In the course of our studies on metal salt-catalyzed hydrosilylation, demonstrated previously by Bluestein to occur in the case of acrylonitrile [3], we have discovered that the reaction of trichlorosilane with allyl chloride gives allyltrichlorosilane at room temperature quite readily, in an excellent yield, in the presence of an equimolar amount of a tertiary amine and a catalytic amount of a metal salt such as cuprous chloride. The following example illustrates the facility with which such reactions proceed.

$$HSiCl_3 + CH_2{=}CHCH_2Cl + R_3N \xrightarrow{CuCl} CH_2{=}CHCH_2SiCl_3 + R_3NHCl \qquad (1)$$

A mixture of trichlorosilane (0.22 mol) and allyl chloride (0.2 mol) was added dropwise (under a nitrogen atmosphere) into a mixture of triethylamine (0.2 mol), cuprous chloride (0.01 mol) and 100 ml of dry ethyl ether. After it had been stirred at room temperature for 4 h, the reaction mixture was filtered to remove white solids (Et_3NHCl). Allyltrichlorosilane (79% yield) was isolated by distillation; b.p. 117 °C (Lit. [4] 117.5 °C); ^1H NMR (CCl_4)

TABLE 1

THE EFFECT OF TYPES OF AMINE IN CuCl-CATALYZED CONDENSATION OF TRICHLOROSILANE WITH ALLYL CHLORIDE IN Et_2O

Amine	Yield (%) [a]		pKa of R_3N^+H [b]
	with catalyst	without catalyst	
Et_3N	83	6 [c]	10.867
$n\text{-}Pr_3N$	90	23 [d]	>10
$n\text{-}Bu_3N$	83	59	>10
Pyridine	—		5.18
$C_6H_5NMe_2$	—		5.15

[a] 4 h at room temperature, average yields determined by GLC. [b] Ref. 7. [c] 23 h of reflux. [d] 18 h of reflux.

δ 2.28 (d, 2H, CH_2Si), 5-6 ppm (m, 3H, CH_2=CH); M^+ *m/e* 174.

Since this procedure appeared to be very useful, we have investigated further the role of the tertiary amines, metal salts and solvents.

Table 1 shows that the yield of allyltrichlorosilane is influenced by the type of amine used. Allyltrichlorosilane can be obtained even without cuprous chloride as a catalyst in the presence of an amine possessing long alkyl chains when such a mixture is heated for a long time. This may be due to the better solubility of a trichlorosilane—tertiary amine complex in the case of an amine with longer alkyl chains. However, the reaction reaches completion almost instantaneously when cuprous chloride is added. The fact that this reaction does not proceed with amines such as pyridine and dimethylaniline indicates the importance of the basicity of amines; apparently p*Ka* of R_3N^+H should be greater than 10.

We have examined various metal salts as possible catalysts for this reaction and have found that other cuprous salts, cupric salts and copper—silicon alloys possess similar catalytic activity. Also, nickel, iron, cobalt, and silver salts exhibit some catalytic activity for this reaction when solvent which dissolves metal salts relatively easily as acetonitrile is used.

Silylations of other allylic chlorides with trichlorosilane have been examined under the same conditions. β-Methallyl chloride gave β-methallyltrichlorosilane in 69% yield; b.p. 136 °C (139.5 °C/746 mmHg [5]); ^{1}H NMR (CCl_4) δ 1.80 (s, 3H, =C(CH_3)), 2.25 (s, 2H, CH_2Si), 4.77 ppm (m, 2H, CH_2=); M^+ *m/e* 188. Both crotyl chloride and α-methallyl chloride gave crotyltrichlorosilane in 85 and 76% yield, respectively; b.p. 142-144 °C (Lit. [6] 143-144 °C); ^{1}H NMR (CCl_4) δ 1.68 (d, 3H, CH_3C=), 2.23 (d, 2H, CH_2Si), 5-6 ppm (m, 2H, CH=CH-); M^+ *m/e* 188.

Acknowledgement

We thank Professor Hideki Sakurai of Tohoku University for continuous helpful discussions.

References

1 E.A. Chernyshev, V.F. Mironov and A.D. Petrov, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, (1960) 2147.
2 R.A. Benkeser, J.M. Gaul, and W.E. Smith, J. Amer. Chem. Soc., 91 (1969) 3666.
3 B.A. Bluestein, J. Amer. Chem. Soc., 83 (1961) 1000.
4 D.T. Hurd, J. Amer. Chem. Soc., 67 (1945) 1813.
5 A.D. Petrov and V.M. Vdovin, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, (1960) 519.
6 S. Munkelt and R. Müller, Chem. Ber., 92 (1959) 1012.
7 R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths Scientific Publications, London, 1955, p. 499.