THE INTERACTION OF DIHYDROFURYLSILANES WITH DICHLOROCARBENE UNDER PHASE-TRANSFER CONDITIONS

E. LUKEVICS*, V.N. GEVORGYAN, Y.S. GOLDBERG, A.P. GAUKHMAN, M.P. GAVARS, J.J. POPELIS and M.V. SHYMANSKA

Institute of Organic Synthesis, Latvian SSR Academy of Sciences, 21 Aizkraukles St., Riga (U.S.S.R.)

Summary

Dichlorocarbene generated in a two-phase catalytic system reacts with 3-trimethylsilyl-2,5-dihydrofuran to give both possible products of mono-insertion into the C–H bond in positions 2 and 5 of the ring, together with a C=C bond adduct. Reaction of 2-trimethylsilyl-4,5-dihydrofuran with dichlorocarbene leads to 2,3-dichloro-2-trimethylsilyl-5,6-dihydro-2*H*-pyran, which is formed via isomerization of the primary bicyclic adduct.

The reaction of 2,3- and 2,5-dihydrofurans with dihalocarbenes under conditions of phase-transfer catalysis (PTC) is generally used to obtain various derivatives of these heterocycles [1,2]. The reaction of silicon-containing dihydrofurans with dihalocarbenes has not been studied before. In the present paper the reactions of 3-trimethylsilyl-2,5-dihydrofuran (I) and 2-trimethylsilyl-4,5-dihydrofuran (II) with dichlorocarbene under PTC conditions were investigated.

Dichlorocarbene was generated using four known variants of a two-phase procedure: (1) treatment of chloroform with 50% aqueous NaOH in the presence of tributylbenzylammonium chloride (TBBA) as a catalyst [3] (Method A); (2) treatment of $CHCl_3$ with solid NaOH powder in the presence of TBBA [4] (Method B); (3) by Method B in the absence of catalyst, but under ultrasonic irradiation of the reaction mixture [5] (Method C); (4) thermal decomposition of sodium trichloroacetate in chloroform in the presence of trioctylmethylammonium chloride as a catalyst [6] (Method D).

In all cases the reaction of I with dichlorocarbene yields both possible products of :CCl_2 mono-insertion into the C–H bond, i.e. 2-dichloromethyl- and 5-dichloromethyl-3-trimethylsilyl-2,5-dihydrofuran (III and IV, respectively), and a C=C bond adduct, 1-trimethylsilyl-6,6-dichloro-3-oxabicyclo[3.1.0]hexane (V), in a total yield of 60–80% (Tables 1 and 2).
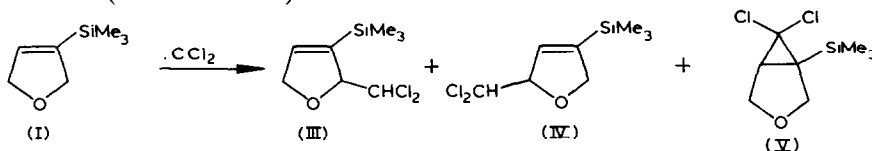
TABLE 1

INTERACTION OF 3-TRIMETHYLSILYL-2,5-DIHYDROFURAN WITH DICHLOROCARBENE UNDER PHASE-TRANSFER CONDITIONS

Dichlorocarbene generation method	Temperature (°C)	Reaction time (h)	Yield of products (%) (by GLC)		
			III	IV	V
A	25	1	23	17	44
B	25	5	20	23	32
C	40–45	8	21	31	32
D	60	55	16	26	16

The ratio of insertion and addition product depends on the $:CCl_2$ generation method applied. Predominant formation of the bicyclic adduct V is provided by using Method A where the reaction also proceeds rapidly at room temperature. When the time and temperature of the process are increased, the distribution pattern of the insertion and addition products approaches a statistical value of one.

A comparison of the different variants of the two-phase methods of $:CCl_2$ generation (Table 1) shows that for preparative purposes Methods A, B and C, which use NaOH as the deprotonation agent, are preferable. On the one hand, this result is somewhat unexpected because of the high sensitivity of trialkylsilyl-dihydrofurans to bases. On the other hand, this is in agreement with the data of refs. 7 and 8 that OH^- ions are extracted into the non-polar medium by salts of the $(alkyl)_4 N^+$ $(haloid)^-$ type to an insignificant degree, even with a great excess of sodium hydroxide.

The reaction of I with alkali, which may take place at the interphase, probably proceeds much slower than the homogeneous reaction of I with $:CCl_2$, thus accounting for the high overall selectivity of the process.

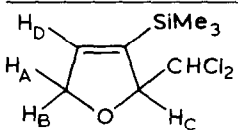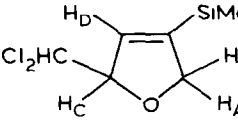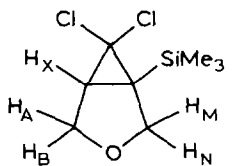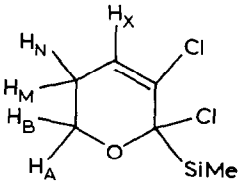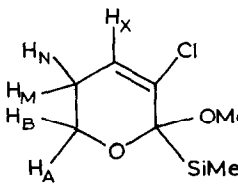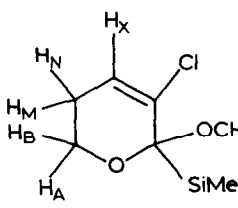It must be noted that Method C using ultrasound "instead of" catalyst presents, in our opinion, many advantages. The authors of this method [5] obtained satisfactory results in reactions of some alkenes with $:CCl_2$ when operating with small amounts of substrates (< 5 mmol), with simultaneous vigorous stirring of the reaction mixture. This was believed to be due to the low power (35 W) of the ultrasonic irradiation. In fact, our experiments show that Method C may also be successfully applied when working with larger amounts of alkene (10 mmol), without mechanical stirring, under ultrasonic irradiation of 100 W power.

The neutral trichloroacetic Method D, which, as expected, proved to be the most suitable procedure for alkali-sensitive substrates, was less effective in the given case, probably due to the instability of I and the products of its reaction with $:CCl_2$ during prolonged heating.

The pattern of 2-trimethylsilyl-4,5-dihydrofuran (II) transformations in the reaction with $:CCl_2$ is significantly different from that observed for I.
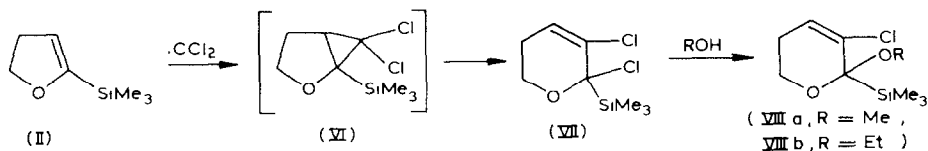
In the reaction of II with dichlorocarbene (Method B) using commercially available chloroform containing ~ 1% ethanol, only one product, 2-trimethylsilyl-2-

TABLE 2. ^{1}H NMR (90 MHz, CDCl$_3$) AND MASS SPECTRAL (70 eV) DATA OF PRODUCTS OBTAINED FROM THE REACTION BETWEEN DIHYDROFURYLSILANES AND DICHLORO-CARBENE UNDER PHASE-TRANSFER CONDITIONS

Compound	δ (ppm)	m/z (rel. intensity, %) [a,b]
	0.23 (s,9H,SiMe$_3$), 4.73 (m,2H,H$_A$ + H$_B$), 5.31 (m,1H,H$_C$), 5.80 (d,1H,CHCl$_2$, J 3.6 Hz), 6.37 (m,1H,H$_D$)	141 (M^+ – CHCl$_2$,32), 93(23), 73(100)
	0.19 (s,9H,SiMe$_3$), 4.85 (m,2H,H$_A$ + H$_B$), 5.12 (m,1H,H$_C$), 5.65 (d,1H,CHCl$_2$, J 4.8 Hz), 5.96 (m,1H,H$_D$)	189 (M^+ – Cl,0.8), 141 (M^+ – CHCl$_2$, 13), 93(10), 81(13), 74(13), 73(100)
	0.23 (s,9H,SiMe$_3$), 2.33 (dd,1H,H$_X$), 4.02–4.04 (2d,2H,H$_M$ + H$_N$, J_{MN} 10.7 Hz), 4.00–4.10 (dd + dd, 2H,H$_A$ + H$_B$)	209 (M^+ – Me,0.5), 189 (M^+ – Cl,25), 115(10), 95(11), 93(30), 81(16), 74(11), 73(100), 53(10)
	0.24 (s,9H,SiMe$_3$),188 (M^+ –HCl,11), 2.20–2.46 (m,2H, H$_M$ + H$_N$), 3.97–4.17 (m,2H,H$_A$ + H$_B$), 4.51 (m,1H,H$_X$)	173(4), 153(6), 95(16), 93(40), 80(19), 73(100), 52(10)
	0.17 (s,9H,SiMe$_3$), 2.04–2.36 (m,2H, H$_M$ + H$_N$), 3.38 (s,3H,OMe), 3.67– 3.84 (m,2H,H$_A$ + H$_B$), 6.09 (q,1H,H$_X$)	220 (M^+,1.4), 205 (M^+ – Me,28), 189 (M^+ – OMe,11), 185 (M^+ – Cl,86), 147(12), 95(13), 93(24), 89(58), 82(14), 81(22), 75(11), 74(11), 73(100), 59(24), 54(16), 53(34)
	0.17 (s,9H,SiMe$_3$), 1.99 (t,3H,OCH$_2$CH_3), 2.13–2.40 (m,2H,H$_M$ + H$_N$), 3.68–3.88 (m,2H,H$_A$ + H$_n$), 4.06 (q,2H,OCH_2CH$_3$), 6.06 (q,1H,H$_X$)	234 (M^+,36), 199 (M^+ – Cl,26), 189 (M^+ – OEt,52), 171(15), 161(14), 159(20), 155(64), 127(18) 125(12), 123(14), 103(10), 95(48), 93(100), 79(12), 75(32), 73(73), 54(11), 53(17)

^{a} The peaks of characteristic ions and ions of $\geqslant 10\%$ intensity are given. ^{b} The chlorine-containing ion peaks are given for the ^{35}Cl isotope.

ethoxy-3-chloro-5,6-dihydro-2*H*-pyran (VIIIb), was isolated from the reaction mixture in a 66% yield, b.p. 60°C/1 mmHg (Table 2).

Similarly, VIIIa was prepared using methanol containing CHCl$_3$ (yield 60%, b.p. 56°C/1 mmHg). The formation of compounds VIIIa and VIIIb indicates that the reaction of II proceeds, as in the case of unsubstituted 2,3-dihydrofuran [1], through a bicyclic adduct (VI) which readily isomerizes with ring expansion to afford 2,3-dichloro-2-trimethylsilyl-5,6-dihydro-2*H*-pyran (VII).

In fact, when the reaction of II with :CCl$_2$ was carried out in ethanol-free chloroform, compound VII (Table 2) was isolated in small amounts by high-vacuum distillation (10^{-3} mmHg, bath temperature 25°C). The latter was quantitatively converted into VIIIb after the addition of methanol. Preliminary experiments have shown that the intermediate VII is very unstable and undergoes various transformations depending on the method of :CCl$_2$ generation and the reaction conditions (temperature, ratio of reagents, and sequence of their addition, etc.). A detailed account of these transformations will be presented in our next paper.

References

1 E.V. Dehmlow and K. Franke, Liebigs Ann. Chem., (1979) 1456.
2 H. Maskill, J. Chem. Soc. Perkin Trans. 2, (1975) 197.
3 M. Makosza and M. Wawrzyniewicz, Tetrahedron Lett., (1969) 4659.
4 S. Julia and A. Ginebreda, Synthesis, (1977) 682.
5 S.L. Regen and A. Singh, J. Org. Chem., 47 (1982) 1587.
6 E.V. Dehmlow, Tetrahedron Lett., (1976) 91.
7 E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, Verlag Chemie, Weinheim, 1980.
8 E.V. Dehmlow and M. Lissel, Liebigs Ann. Chem., (1981) 28.