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APPLICATIONS OF PHASE TRANSFER CATALYSIS, VII[1]
THE FIRST CASE OF DOUBLE CH-INSERTION OF DICHLOROCARBENE

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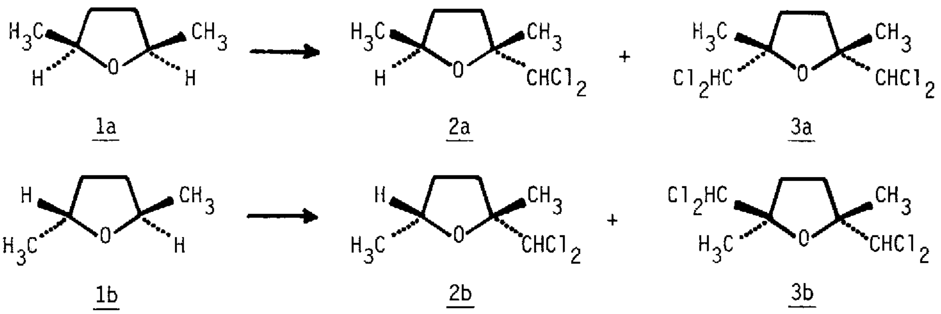
Summary: The first case of a bis-CH-insertion of dichlorocarbene into the 1,3-standing CH-bonds in position 2 and 5 of 2,5-dimethyltetrahydrofuran is described.

Since the early work of Makosza[2] the generation of dihalogenocarbenes in two phase systems from haloforms and concentrated aqueous sodium hydroxide in the presence of phase transfer catalysts like quaternary ammonium salts or crown ethers has found wide application[3]. The great advantage of this system is a carbene activity for many days resulting from a subtle equilibrium at the interface and in the organic phase[4] which is displaced very much to the left side and is able to release CX_2 in the presence of an appropriate substrate. Thus even compounds with relatively low reactivity afford dihalogenocarbene reaction products in fair to good yields. In the case of dichlorocarbene this led to the possibility of multiple addition to compounds with two or more olefinic double bonds, like 1,3-butadiene[5], 1,3-cyclopentadiene[5], 1,3,5-cycloheptatriene[6], 1,3,5,7-cyclooctatetraene[6], trans,trans,cis-1,5,9-cyclododecatriene[7] or cis,cis-1,5-cyclooctadiene[8]. Reactions with two CCl_2 were also found with some substrates having a double bond and a carbene-reactive CH-bond like 2,5-dihydrofuran[9] (there is a competition in the first step between addition and insertion, only the insertion product gives the bis-adduct) or 2-(3-cyclohexenyl)-1,3-dioxolan[10] (here the first step is the cyclopropanisation followed to some extent by insertion into the C(2)H-bond of the dioxolan system). Some selective CH-insertion reactions were performed with good yields, e.g. into the bridgehead position of adamantane[11] or the C(2)H-bond of 1,3-dioxolans[12]. Double insertion of CCl_2 into two CH-bonds of the same molecule was hitherto unknown.

Here we report on the reaction of 2,5-dimethyltetrahydrofuran (1) with excess CCl_2 under two phase conditions, which was carried out in the course of investigations concerning structure and reactivity in reactions of electrophilic carbenes[10]. We used commercially available 1 (mixture of the cis- and trans-isomers 1a and 1b) and obtained four compounds[13]:


1a 2a 3a
1b 2b 3b

the two mono-insertion products 2a and 2b (yield: 47%, bp. 60-65°C/10 torr) and the two bis-insertion products 3a and 3b (yield: 40%, bp. 130-133°C/10 torr). The ^{1}H-nmr spectrum ($CDCl_3$) for 3a/b showed no more O-CH-protons, singletts for the methyl groups (δ=1.50, 6H), multipletts for the $C(3)H_2$ and $C(4)H_2$ (1.78-2.67, 4H) and two $CHCl_2$-protons (5.60 and 5.70, 2s, 2H). 3a and 3b were separated and characterized by glc/ms-coupling[14]; both mass spectra were consistent with the proposed structure 3 and had the characteristic peaks M-CH_3 (249/251/253/255 with Cl_4-distribution) and M-$CHCl_2$ (181/183/185/187 with Cl_2-distribution).

The remarkable reactivity of 1 which gives rise to the first example for a double insertion of CCl_2 into 1,3-standing CH-bonds may be explained by two facts: the outstanding situation of the five-membered ring[15] and the activating effect of the methyl groups[16]. Analogous open chain ethers like diisopropylether (46 % mono-insertion into α-CH[10]) or distorted tetrahydrofurans like 9-oxabicyclo[4.2.1]nonan (only 15% mono-insertion into bridgehead-CH[10]) do not reveal comparable reactivity. The necessity of the second methyl group is demonstrated by the reaction of 2-methyltetrahydrofuran which affords only the products of insertion into the C(2)H- or the C(5)H-bonds (93%, ratio 90 : 10) and no bis-dichloromethyl compound[10]. The more detailed results of our investigations esp. concerning the difference in reactivity of 1a and 1b and an extensive study on the question of a bis-insertion of CCl_2 into CH-bonds of 1,3-dioxolans[17] will be given in the full paper.

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17) We did not observe double insertion of CCl_2 in position 2 and 4 of one dioxolan ring, but in both C(2)H-bonds of bis-dioxolans derived from succinic and glutaric dialdehyds.

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