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CHEMISTRY OF DI- AND TETRAHYDROPYRANS.

REPORT 7. REACTIONS OF DIHALOCARBENES WITH 2-METHYL-5,6-DIHYDRO-2H-PYRAN

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Unsaturated simple ethers, especially vinyl, easily form adducts with dihalocarbenes (DHC) [1]. In the case of some allyl ethers, particularly 2,5-dihydrofuran (I) [2-4] and allyl ethyl ether [4], along with addition insertion into the C-H α -bond is observed. We showed earlier that the reaction of 2-methyl-5,6-dihydro-2H-pyran (II) with CCl₂ is even more complex. Three products are formed: cis- and trans-7,7-dichloro-2-methyl-3-oxabicyclo{4.1.0}-heptane (III) and 2-dichloromethyl-2-methyl-5,6-dihydro-2H-pyran (IV) in the ratio 1:5.7:3.3.



One can assume that the mobility of the α -H atom is caused by the simultaneous influence of the allyl double bond and the lone electron pair of the heteroatom. Yet in the reaction of DHC with the analogs of (II) - 5,6-dihydro-2H-pyran [2], benzopyran [6], and even its isomer 4-methyl-5,6-dihydro-2H-pyran [7]), only cyclopropane derivatives are formed. It is reasonable to assume the existence of competition between addition and insertion, which can be controlled together with the olefin structure by the reaction conditions [1].

During generation of CCl_2 in the systems CCl_3COOEt -MeONa and CCl_3COONa -dioxane the ratio of insertion and addition products of (I) is 1:2 [3] and 1:1.1 [2]. However (II) under these conditions does not react with CCl_2 . Products are formed in 16% total yield upon heating CCl_3COONa in $CHCl_3$ with a phase transfer catalyst, but in its absence the reaction does not occur. The yield of (III) and (IV) also does not exceed 2% for CCl_2 formation in the $CHCl_3$ -t-BuOK system and addition of a phase transfer catalyst has practically no effect on the reaction with (II). It is important to note the absence of any noticeable influence on the isomer composition of (III). The most successful system was $CHCl_3$ -alkali. The results of the experiments under various conditions are shown in Table 1.

The influence of temperature is noticeable from -14 to $+20^{\circ}$ C; with further heating to 50°C the yield of products changes insignificantly. Better results in the experiments with +- 50% KOH were obtained using Bu₄NI and crown ether (31-27%). It is interesting that with NaOH

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Alkali	Catalyst	Т,℃	Catalyst amount, mole %	Yield of products (III) and (IV), %
50% KOH	$\begin{array}{c} \overset{+}{\operatorname{Et_3NCH_2PhCl}}\\ \text{The same}\\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$	$ \begin{array}{r} 20 \\ -14 \\ -19 \\ 50 \end{array} $	5,4 5,4 5,4 5,4 5,4	$ \begin{array}{c c} 15,0\\ 2,0\\ 5,0\\ 21,0 \end{array} $
50%	Bu4 ^N I Dibenzo-18-crown-6 The same	20 20 20	5,0 1,0 1,0	$\begin{array}{c} 31,0 \\ 26,5 \\ 9,7 \end{array}$
NaOH	El ₁ NCH ₂ PhCl- The same » Katamin-AB The same » »	20 20 20 20 20 20 20 20 20 20	$\left \begin{array}{c} 1,3\\2,7\\5,4\\10,8\\0,5\\1,0\\2,0\\3,0\end{array}\right $	$\begin{array}{c} 35.6\\ 39.0\\ 29.0\\ 40.0\\ 24.0\\ 44.0\\ 36.4\\ 24.5\end{array}$
	$\begin{array}{c c} & Bu_4 \overset{+}{NI} \\ & Et_3 \overset{+}{NC}_{16} H_{33} Br \\ Dibenzo-18-crown-6 \\ Katamin AB (15-Crown-6) \\ Dicyclohexy1-18- \\ crown-6 \end{array}$	20 20 20 20 20 20	3,0 1,0 5,0 5,0 1,1	33,0 26,5 20,0 23,0 31,7
Solid NaOH	$\rm Et_3NCH_2PhCl^-$	20	1,0	50,0

TABLE 1. Reaction of 2-Methyl-5,6-dihydro-2H-pyran with Dichlorocarbene Generated from CHCl₃ using Phase Transfer Catalysis

the reaction proceeds even without a phase transfer catalyst, but with low yield (10%). Catalyst concentration has significant influence on the product yield and its optimal amount depends on its nature. The highest yield of (III) and (IV) (44%) was obtained with the use of 1% katamin AB. The crown ether ring size has practically no effect on the results, but even

with Et₃NCH₂PhCl⁻, not the most effective catalyst, the yield increases to 50% upon going from aqueous solution to solid NaOH. In all cases the ratio of isomers (III) and (IV) remains constant.

Unlike with CCl₂, reaction of (II) with CBr₂ proceeds satisfactorily in the CHBr₃-t-BuOK system (36%). Three products are also formed: cis- and trans-7,7-dibromo-2-methyl-3-oxabi-cyclo[4.1.0]heptane (V) and 2-dibromomethyl-2-methyl-5,6-dihydro-2H-pyran (VI) in the ratio 0.9:5.3:3.8. The ratios of addition to insertion products do not depend on the investigated parameters, at least in the range we used.

In order to explain the possible paths of isomer formation, the products were separated by a chemical method and reacted with CCl₂. It turned out that (III) and (IV) do not inter-

(III) + (IV) or $\xrightarrow{Br_2} (III)$ or	$(V) + 0 \longrightarrow Br \xrightarrow{MgI_2} (IV) \text{ or } ($	(VI)
(V) + (VI)	Me CX ₂ H	

convert. This excludes their sequential formation. Simultaneous formation could occur in two ways — coordination of CCl₂ by the heteroatom or by direct attack on the double bond. In [8] the first route was ruled out for reaction of CCl₂ with a series of cyclic allylalcohols. Hence CCl₂ ought to give adduct (IV) also by attack of the double bond, yet this assumption was not confirmed experimentally. Therefore, reaction of (II) with CCl₂ starts with coordination by the heteroatom followed by simultaneous formation of (III) and (IV). This explains the lack of dependence of the isomer ratio on the method of carbene generation. The two α substituents in (IV) shield the heteroatom enough to prevent further reaction with CCl₂.

EXPERIMENTAL

Reaction of 2-methyl-5,6-dihydro-2H-pyran (II) with CCl₂. a) To a mixture of 11.1 ml (0.1 mole) of (II) and 11.2 g (0.1 mole) of t-BuOK with stirring for 3 h, 16.0 ml (0.2 mole) of CHCl₃ was added dropwise and the mixture stood for 12 h. The mixture was diluted with a two-fold volume of water. The organic layer was separated, dried with MgSO₄, and distilled. There was isolated 0.35 g (20%) of a mixture of (III) and (IV) (GLC, 3000 × 3 mm, 20% PEGA on Chromosorb, H₂ flow: 60 ml/min, 130°C) with b.p. 70°C (14 mm).

The reaction was carried out analogously in the presence of 0.2 g (1 mole %) of Et_3 -+ NCH₂PhCl⁻. The yield of (III) and (IV) was 2.2%.

b) To a mixture of catalyst (see Table 1), 0.1 mole of (II), and 0.3 mole alkali (50% solution), 0.15 mole of CHCl₃ was added dropwise over 2 hr with stirring. After 3 h at \sim 20°C the mixture was extracted with ether, dried with MgSO₄, and distilled (see Table 1).

c) Reaction of (II) with CCl_3COONa with phase transfer catalysis was carried out by the method of [9] and with CCl_3COOEt by the method of [6].

d) Reaction of (II) with CHCl₃ in the presence of solid alkali and 1 mole % of Et₃NCH₂-- PhCl⁻ [10] resulted in (III) and (IV) with 49% yield.

Reaction of (II) with CBr₂ by the method of [11] gave (V) and (VI) with 36% yield and b.p. 111°C (5 mm).

Separation of the Products of Addition and Insertion. a) To a solution of 14.0 g (0.09 mole) Br₂ in 30 ml CCl₄ at 0-5°C, 38.6 g (0.21 mole) of the (III) and (IV) mixture in 30 ml CCl₄ was added dropwise. The mixture was stirred for 3 h, then washed with NaHCO₃ solution and dried with MgSO₄. Upon distillation there was obtained 23.3 g (90%) of a mixture of isomers (III) with b.p. 81°C (5 mm), $n_D^{2°}$ 1.5080.

PMR spectrum (CCl₄, δ , ppm): 1.35 d (3H, CH₃), 1.60-2.20 m (4H, CH₂, 2CH), 2.90-3.65 m (3H, CH₂O, CHO). The residue from distillation was purified on a column with Al₂O₃ (400 × 7 mm, eluent CCl₄). There was isolated 23.6 g (98%) of 3,4-dibromo-2-dichloromethyl-2-methyl-tetrahydropyran with m.p. 49°C. PMR spectrum (CCl₄, δ , ppm): 1.95 s (3H, CH₃), 2.00-2.70 m (2H, CH₂), 3.80-4.10 m (2H, CH₂O), 4.40 m (1H, CHBr), 4.86 m (1H, CHBr), 5.80 s (1H, CHCl₂).

Analogously the mixture of isomers (VI), (63%) was isolated, with b.p. $112^{\circ}C$ (5 mm), $n_D^{2^{\circ}}$ 1.5532, and also 3,4-dibromo-2-dibromomethyl-2-methyltetrahydropyran (62%) with m.p. 109°C.

b) Debromination of 3,4-dibromo-2-dichloromethyl-2-methyltetrahydropyran was carried out by the method of [12]. The yield of (IV) was 43%, b.p. 55°C (1 mm), n_D^{20} 1.4988. PMR spectrum (CCl₄, δ , ppm): 1.35 s (3H, CH₃), 1.90-2.25 m (2H, CH₂), 3.75 m (2H, CH₂O), 5.65 s (1H, CHCl₂), 5.85 m (2H, CH=CH).

<u>Reaction of (III) and (IV) with CCl₂.</u> Compound (III) and (IV) were separately reacted with CCl₂ by the method of [10]. In both cases there was obtained 95% of starting material.

CONCLUSIONS

Formation of the addition and insertion products upon reaction of 2-methyl-5,6-dihydro-2H-pyran with dihalocarbenes proceeds through a common intermediate which is the result of coordination of the carbene by the heteroatom. This explains the independence of the ratio of addition and insertion products on the reaction conditions and method of generation of the carbenes.

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