REACTIONS OF $CHCl_3$ AND CCl_4 WITH 1-HEPTENE, INITIATED BY IRON, MOLYBDENUM, AND MANGANESE CARBONYLS AND THE $Mo(N_2)_2(dppe)_2$* COMPLEX

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The addition of CCl_4 and $CHCl_3$ to 1-alkenes in the presence of metal carbonyls (MC) and their complexes is a convenient way of synthesizing the 1,1,1,3-tetrachloro- and 1,1,3-trichloroalkanes. As initiators of these reactions, for which the radical mechanism is proposed, were used $Fe(CO)_5$ [1,2], $Fe_2(CO)_9$ [3], $Mo_2(CO)_6 \cdot (\eta\text{-}Cp)_2$ [4,5], and $Mn_2(CO)_{10}$ [6]. In addition, the various MC were used to initiate the reduction by isopropanol of CCl_4 and $CHCl_3$ [7], and long-chain gem-trichloroalkanes [8]. In the latter case, the reaction is accompanied by rearrangement of the intermediate dichloromethyl radical with the 1,5- and 1,6-migration of hydrogen.

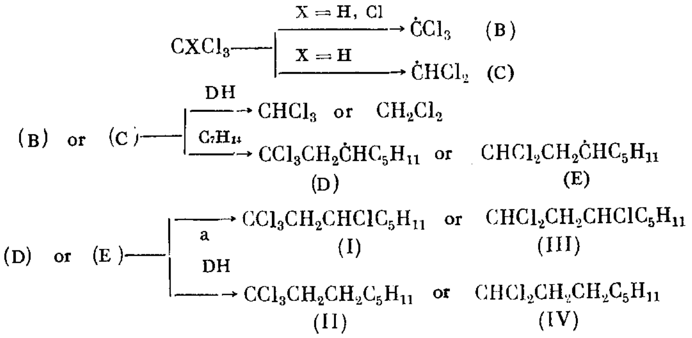
The intermediate radical-adduct $RCCl_2CH_2\dot{C}HC_4H_9$(A), which is formed by the reaction of $RCCl_3$ with 1-hexene in isopropanol when initiated by an MC, is stabilized by the cleavage of either chlorine or hydrogen. The ratio of the obtained adducts (A^{Cl}) and (A^{H}) depends on the nature of the MC [9].

In order to study the effect of the solvent and the nature of the MC on reactions of this type, we studied the reaction of CCl_4 and $CHCl_3$ with 1-heptene in either isopropanol or CH_3CN as the medium, and using as the initiators $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$ and the $Mo(N_2)_2(dppe)_2$ complex (Table 1).

An increase in the relative amount of (A^H) and a reduction of the starting CCl_3X (X = H, Cl) could be expected in isopropanol when compared with CH_3CN.

In the studied reactions the formation of the adducts, and specifically polychloroalkanes (I)-(IV), is described by Scheme 1 (DH and DCl = hydrogen and chlorine donors)

Scheme 1



The obtained chloroalkanes (I) and (II) contain a CCl_3 group and in isopropanol can be reduced with rearrangement to the intermediate radical [10]. On the example of polychloroalkane (I), the reaction is described by scheme 2. Chloroalkane (II) can behave in a similar manner (see Scheme 2 on following page).

As a result, polychloroalkane (III) can be formed either by the cleavage of chlorine by the (E) radical (see Scheme 1) or by the reduction of polychloroalkane (I) (see scheme 2).

$CHCl_3$ is not reduced and does not add to 1-heptene in isopropanol when the reaction is initiated by $Fe(CO)_5$ at 120°C. These reactions begin to go only at 130-140° to give adducts (II) and (III) in a 1:4 ratio [1].

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*dppe = $Ph_2PCH_2CH_2PPh_2$.

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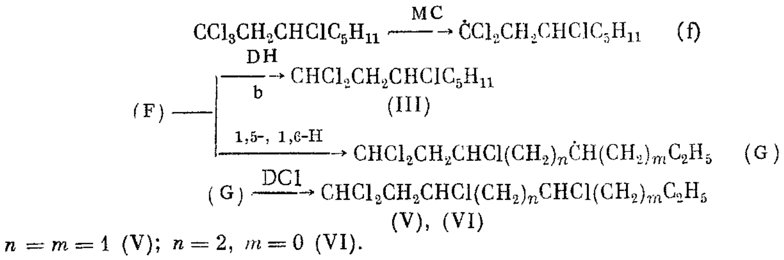
Scheme 2



$$CCl_3CH_2CHClC_5H_{11} \xrightarrow{MC} \dot{C}Cl_2CH_2CHClC_5H_{11} \quad (f)$$

$$(F) - \left| \begin{array}{l} \xrightarrow[b]{DH} \underset{(III)}{CHCl_2CH_2CHClC_5H_{11}} \\ \xrightarrow{1{,}5\text{-},\ 1{,}6\text{-}H} CHCl_2CH_2CHCl(CH_2)_n\dot{C}H(CH_2)_mC_2H_5 \quad (G) \end{array} \right.$$

$$(G) \xrightarrow{DCl} \underset{(V),\ (VI)}{CHCl_2CH_2CHCl(CH_2)_nCHCl(CH_2)_mC_2H_5}$$

$n = m = 1$ (V); $n = 2$, $m = 0$ (VI).

With $Mn_2(CO)_{10}$, adducts (II) and (IV) are formed in the same reaction due to cleavage of the C—H bond of chloroform (cf. [6]) and the subsequent reduction of adduct (II) to (IV); this process could have interest as a one-step route for the synthesis of compounds of type $RCHCl_2$ directly from $CHCl_3$ and an α-olefin. However, the $CHCl_3$ conversion is very low. Here the reduction of $CHCl_3$, which proceeds easily in the absence of an alkene [7], does not go in the presence of 1-heptene (see Table 1, Expt. 2). A similar inhibiting effect of an α-olefin on the reduction of 1,1,1,3-tetrachloropropane by isopropanol, with initiation by $Mn_2(CO)_{10}$, was observed previously [9].

In contrast, for the reaction of $CHCl_3$ with 1-heptene, initiated by $Mo(CO)_6$ in isopropanol, the reduction of $CHCl_3$ to CH_2Cl_2 plays an important role. Adducts (III) and (IV) are also formed (Expt. 3). As a result, similar to $Fe(CO)_5$, $Mo(CO)_6$ initiates the addition of $CHCl_3$ to α-olefins predominantly at the C—Cl bond, while $Mn_2(CO)_{10}$ initiates addition predominantly at the C—H bond.

With all of the studied MC, the reaction of CCl_4 with 1-heptene in isopropanol proceeds with a complete conversion of the starting CCl_4. However, the main direction is the reduction of CCl_4 to $CHCl_3$, and to a mixture of $CHCl_3$ and CH_2Cl_2 when using $Mo(CO)_6$ (experiments 4-6). Adduct (I) is also formed, but in the presence of $Mo(CO)_6$ and $Mn_2(CO)_{10}$ it is reduced to (III).

The reduction of (I) to (III) is accompanied by rearrangement with a 1,5- and 1,6-migration of hydrogen and the formation of (V) and (VI). The presence of (V) and (VI) in the reaction products of experiments 4-6 indicates that chloroalkane (III) can also be obtained by the reduction of (I), together with the addition of the formed $CHCl_3$.

To eliminate the transformations of the addenda and adducts, caused by their reaction with isopropanol, the reaction was also run in CH_3CN as the medium. Here a decrease in the total conversion of CCl_3X was observed in all cases. Thus, with either $Mo(CO)_6$ or $Mo(N_2)_2 \cdot (dppe)_2$ the $CHCl_3$ conversion was ~20%, and with CCl_4 it was ~60%. We identified 55-70% of the CCl_3X transformation products in the reaction mixtures. Judging by the structure of these products, when initiation is by Mo complexes, the adducts of $CHCl_3$ with 1-heptene are formed with cleavage of the C—Cl bond in $CHCl_3$ (experiments 10 and 11), while CCl_4 gives main-

TABLE 1. Addition of CCl_3X (5 mmoles) to 1-Heptene (2.5 mmoles) with Initiation by Metal Carbonyls (0.25 mmole), 3 h

Expt. no.	Initiator	T., °C	Additive (40 mmoles)	CCl_3X	CCl_3X conversion, %	Yield of products, in % of reacted CCl_3X*					
						$CHCl_3$	CH_2Cl_2	(I)	(II)	(III)	(IV)
1	$Fe(CO)_5$	120	*i*-PrOH	$CHCl_3$	0	—	—	—	—	—	—
2	$Mn_2(CO)_{10}$	120	*i*-PrOH	$CHCl_3$	8	—	—	—	5	1	40
3	$Mo(CO)_6$	140	*i*-PrOH	$CHCl_3$	56	—	46	1	—	44	7
4	$Fe(CO)_5$	120	*i*-PrOH	CCl_4	100	57	—	35	2	3	1
5	$Mn_2(CO)_{10}$	120	*i*-PrOH	CCl_4	100	67	2	5	11	8	4
6	$Mo(CO)_6$	140	*i*-PrOH	CCl_4	100	62	16	3	—	10	4
7	$Mo(CO)_6$ †	140	CH_3CN	CCl_4	56	5	—	46	2	—	—
8	$Mo(N_2)_2$ (dppe)$_2$	140	CH_3CN	CCl_4	52	15	—	58	1	—	—
9	$Mn_2(CO)_{10}$	120	CH_3CN	CCl_4	67	25	—	32	1	—	—
10	$Mo(CO)_6$	140	CH_3CN	$CHCl_3$	25	—	—	—	—	49	6
11	$Mo(N_2)_2$ (dppe)$_2$	140	CH_3CN	$CHCl_3$	19	—	—	—	—	53	3

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*In experiments 4-6 we also obtained (V) and (VI) in 2-4% yield.

†Experiment 7 was run on a preparative scale (see Experimental section). It was shown that the reaction is accompanied by some tarring of the products.

ly adduct (I) (experiments 7 and 8). With $Mn_2(CO)_{10}$ the reduction of CCl_4 to $CHCl_3$ proceeds noticeably even in CH_3CN, where, in addition, adduct (I) is formed (experiment 9).

As a result, a comparison of the reaction of CCl_4 and $CHCl_3$ with 1-heptene, with initiation by various MC, disclosed that, depending on the nature of the MC, these reactions lead to different products.

EXPERIMENTAL

The experiments, listed in Table 1, were run in rotated sealed glass ampuls. The yields of the products were determined by GLC using an internal standard (IS). The GLC analysis was run on an LKhM-8MD chromatograph equipped with a katharometer. The columns were: A) 3 m × 3 mm, 15% Silicone E-301; B) 2 m × 3 mm, 15% Silicone E-301; C) 1 m × 3 mm, 7% FS-1265 the solid support was Chromaton N-AW-HMDS (0.16-0.20 mm), and the carrier gas was helium. To determine the yields of $CHCl_3$ and CH_2Cl_2 we used column A, an analysis temperature of 45°, and either CCl_4 or 1,2-dichloroethane (for the experiments with incomplete CCl_4 conversion) as the IS. Polychloroalkanes (I)-(VI) were identified by GLC on the basis of their retention times coinciding with those of samples, obtained by an independent route, on phases with a different polarity (columns B and C). See [10] for the preparation of (I), (III), (V), and (VI), and [11] for (II) and (IV). For a quantitative determination of the yields of (I)-(VI) we used column B, an analysis temperature of 160°, and 1,1,1-trichlorononane as the IS.

Addition of CCl_4 to 1-Heptene. A mixture of 9 g of CCl_4 (60 mmoles), 2.94 g of 1-heptene (30 mmoles), 17.8 g of MeCN (480 mmoles), and 0.79 g of $Mo(CO)_6$ (3 mmoles) was heated for 3 h at 140° in rotated sealed glass ampuls. The following fractions were obtained by fractional distillation: 1) 68-71°, 2.4 g; 2) 72-79°, 3.9 g; 3) 80-81°, 15.6 g; 4) 93-98° (3 mm), 4.7 g. Residue (hard tar) 3.1 g. Based on the GLC analysis data, fractions 1-3 contain CCl_4 (28 mmoles) and CH_3CN (475 mmoles), and fraction 4 contains 1,1,1,3-tetrachlorooctane (17.4 mmoles) and 1,1,1-trichlorooctane (2 mmoles). The CCl_4 conversion was 53%. The yield of the adduct was 54% (based on reacted CCl_4).

CONCLUSIONS

1. $Mo(CO)_6$ and $Mo(N_2)_2 \cdot (dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) initiate the addition of $CHCl_3$ and CCl_4 to α-olefins in either i-PrOH or MeCN as the medium, and here $CHCl_3$ reacts with cleavage of the C—Cl bond.

2. $Mn_2(CO)_{10}$ does not initiate the reduction of $CHCl_3$ by i-PrOH in the presence of 1-heptene.

LITERATURE CITED

1. R. Kh. Freidlina, E. Ts. Chukovskaya, and B. A. Énglin, Dokl. Akad. Nauk SSSR, 159, 1346 (1964).
2. N. A. Rybakova, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 249 (1979).
3. J. Elzinga and H. Hogeveen, J. Org. Chem., 45, 3957 (1980).
4. R. Davis and J. E. Groves, J. Organometal. Chem., 215, C23 (1981).
5. T. Susuki and J. Tsuji, J. Org. Chem., 35, 2982 (1970).
6. A. B. Terent'ev, M. A. Moskalenko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1406 (1980).
7. E. Ts. Chukovskaya, M. A. Rozhkova, N. A. Kuz'mina, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 354 (1982).
8. N. A. Kuz'mina, N. P. Zhiryukhina, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2090 (1981).
9. E. Ts. Chukovskaya, N. A. Kuz'mina, M. A. Rozhkova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1345 (1982).
10. N. A. Rybakova, L. N. Kiseleva, and I. V. Laputina, Izv. Akad. Nauk SSSR, Ser. Khim., 863 (1983).
11. E. Ts. Chukovskaya, A. A. Kamyshova, and R. Kh. Freidlina, Zh. Org. Khim., 3, 1358 (1968).