Unusual Rearrangement of Polychloroalkyl Radicals Involving 1,5-Hydrogen Shift; a Possible Source of Anomalous Structures in Polyvinylidene Chloride

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Summary The addition of 1,1,1,3-tetrachloropropane to vinylidene chloride in the presence of co-ordination catalysts gives the adduct $ClCH_2CH_2CCl_2CH_2CCl_3$ and higher telomers along with an appreciable amount of $CHCl_2CH_2CCl_2CH_2CHCl_2$ formed by 1,5-hydrogen shift in the intermediate radical.

Liquid-phase rearrangement of radicals is mostly known to proceed by conversion of less stable species into more stable ones[1a] with only very few exceptions.[1b,2] During our extensive studies on addition and telomerization reactions of trichloromethyl derivatives and unsaturated compounds in the presence of co-ordination catalysts,[3a] we have observed a novel type of rearrangement which occurs in the addition of 1,1,1,3-tetrachloropropane to $CH_2{=}CCl_2$ at 135–140 °C, with $[Fe(CO)_5]$–$Me_2CHCH_2CH_2OH$ [or $O{=}P(NMe_2)_3$] as initiating system. The reaction procedure is similar to that described in ref. 3b. The usual

$$ClCH_2CH_2CCl_3 + nCH_2{=}CCl_2 \xrightarrow{\text{cat.}} ClCH_2CH_2CCl_2[CH_2CCl_2]_nCl \qquad (1)$$

reaction (1) leads to the adduct $CH_2ClCH_2CCl_2CH_2CCl_3$ (I, $n = 1$) (b.p. 125–126 °C at 1 mmHg)† and higher telomers ($n > 1$). An isomer of adduct (I), $CHCl_2CH_2CCl_2CH_2CHCl_2$ (II)† (b.p. 125–126 °C at 1 mmHg) is also formed. The product ratio of (I) : (II) of 85 : 15 is independent of the co-catalyst used. The isomers were isolated by g.l.c. and structural assignments are based on their ^1H n.m.r. spectra [(I) : δ 3·90 (s) and 2·98 (t) (CH_2), and 3·90 (t, CH_2Cl); (II) : δ 6·32 (t, $CHCl_2$) and 3·40 (d, CH_2)]. An independent synthesis of the latter isomer by the addition of $CCl_3CH_2CHCl_2$ to vinyl chloride under conditions similar to those described in ref. 3c gives a product identical with (II) as shown by the g.l.c. and ^1H n.m.r. data. The overall yield of (I) and (II) is 12—16% (based on $CH_2{=}CCl_2$) and amounts to 35—40% of the total yield of telomers.

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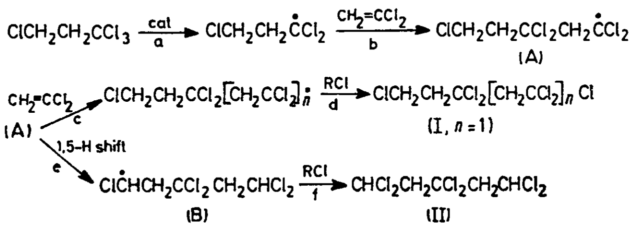
† Satisfactory elemental analyses were obtained.

We suggest that, as shown in the Scheme, the intermediate radical (A) (steps a,b) undergoes, alongside propagation (c) and chain transfer (d) reactions, a 1,5-hydrogen shift (e) to give a more reactive though less stable radical (B) which is converted into (II) (f). The reaction yielding (II) is the first example of a radical rearrangement in telomerization reactions induced by a co-ordination catalyst that does not occur in the presence of peroxide initiating agents. Earlier, a similar rearrangement was suggested for the $Cl[CH_2]_3CH(CCl_3)\dot{C}Cl_2$ radical in the addition of CCl_4 to 1,1,5-trichloropent-1-ene.[2]



Scheme. RCl denotes a chlorine-donating agent; *i.e.* CCl_3CH_2-CH_2Cl in combination with a co-ordination catalyst.

The radical $ClCH_2CH_2CCl_2CH_2\dot{C}H_2$ (C) that occurs in the telomerization of ethylene with 1,1,1,3-tetrachloropropane[3d] is less stable and more reactive than (A). It shows no marked tendency for the 1,5-hydrogen shift and is converted into the adduct $ClCH_2CH_2CCl_2CH_2CH_2Cl$ (III). The expected rearrangement product, $CHCl_2CH_2CCl_2CH_2CH_3$ (IV)† (b.p. 84 °C at 1 mmHg), was shown by g.l.c. to be present in negligible amounts, the ratio of (III) to (IV) being 99 : 1. Compound (IV) was prepared independently by the addition of $MeCH_2CCl_3$ to vinyl chloride under conditions similar to those described in ref. 3c; δ 6·12 (t, $CHCl_2$), 3·22 (d) and 2·40 (q) (CH_2), and 1·18 (t, Me).

We believe that a 1,5-hydrogen shift may play a significant role in the processes that involve the formation of intermediate radicals of the type $RCH_2(CX_2)_3\dot{C}Cl_2$ of low reactivity. This rearrangement may be a possible source of anomalous structures in polyvinylidene chloride.

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[1] R. Kh. Freidlina in 'Advances in Free-Radical Chemistry,' ed. G. H. Williams, Academic Press, New York, 1965; (a) p. 234; (b) p. 248.

[2] N. V. Kruglova, Sh. A. Karapet'yan, and R. Kh. Freidlina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1975, 1569.

[3] R. Kh. Freidlina, and E. C. Chukovskaya, *Synthesis*, 1974, (a) p. 477; (b); p. 485; (c) p. 483; (d) p. 478.