Coupling of Compounds containing an Allylic Trichloromethyl Group. 3,3,4,4-Tetrachlorohexa-1,5-diene

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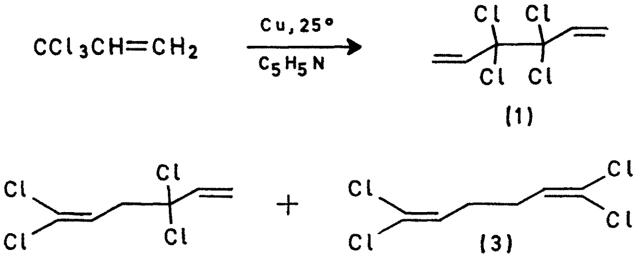
Summary In accord with reactivity predictions for unsymmetrical allyl radicals, the coupling of 3,3,3-trichloropropene using Cu powder results in a mixture of hexa-1,5-dienes, the major component being 1,1,6,6-tetrachlorohexa-1,5-diene.

IT has been reported that treatment of 3,3,3-trichloropropene with powdered copper in pyridine gives a single isomeric product, 3,3,4,4-tetrachlorohexa-1,5-diene, (**1**)[1] in 57% yield. No mention was made of isomers (**2**) and (**3**). This result is unexpected if the reaction proceeds *via* a coupling of 1,1-dichloroallyl radicals (**4**). Kinetic considerations predict a reaction mechanism involving coupling at the more reactive C-3;[2,3] thermodynamic considerations also favour the formation of product (**3**).

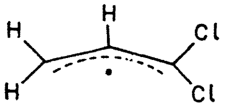


(1)

(2)

(3)

We attempted to reproduce the results described above, but obtained only a mixture of (**1**), (**2**), and (**3**) in the ratio of 4 : 25 : 71 (approximated by n.m.r. integrations). The total yield was 71%. The n.m.r. spectrum of the major constituent (**3**) clearly distinguished it from (**1**). It showed a doublet at δ2·37 (*J* 7 Hz) and a triplet at δ5·92 p.p.m. (*J* 7 Hz) with the relative intensities being 2 : 1. There was evidence of virtual coupling in the spectrum which caused the multiplets to be somewhat more complex than would be expected for a first-order system. The lack of a significant yield of (**1**) was verified by its synthesis as shown in the Scheme.



(4)

$$\begin{tikzcd}
CCl_3CH_2CH_2Br \arrow[r, "H_2/PtO\ (18\ lb/in^2)", "EtOH,\ NH_3"'] & (BrCH_2CH_2CCl_2)_2 \arrow[d, "65°"] \\
(1) & \arrow[l, "KOH", "MeOH/Pr^nOH"']
\end{tikzcd}$$

SCHEME

1,1,1-Trichloro-3-bromopropane[4] could be coupled under hydrogenolysis conditions[5] to produce 1,6-dibromo-3,3,4,4-tetrachlorohexane in 8% yield. The n.m.r. spectrum of this compound was very similar to that of the starting material with a pair of equal intensity, unsymmetrical triplets, showing secondary splitting, at δ3·10 and 3·73 p.p.m. (*J* 7 Hz). This intermediate was dehydrobrominated at 65° for 4 h to produce (**1**) in 55% yield. The n.m.r. spectrum left no doubt of the structure assignment, with two doublets appearing at δ5·50 (*J* 10 Hz, 2H) and 5·84 (*J* 16 Hz, 2H) and a doublet of doublets centred at 6·44 p.p.m. (*J* 10 and 16 Hz, 2H). This spectrum was remarkably

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similar to that of 3,3,3-trichloropropene which showed a pair of doublets at δ5·32 (*J* 10 Hz, 1H) and 5·79 (*J* 16 Hz, 1H), and a doublet of doublets centred at 6·48 p.p.m. (*J* 10 and 16 Hz, 1H). Both these spectra are typical of monosubstituted vinyl systems.

The coupling results are completely consistent with the intermediacy of free 1,1-dichloroallyl radicals and again reveal that the lack of regiospecificity in such reactions is *not* uncommon, a fact which makes such reactions of only limited synthetic value.

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