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.

1T 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).

$$CCl_3CH=CH_2 \xrightarrow{Cu,25^{\circ}} \xrightarrow{C_5H_5N} \xrightarrow{Cl} \xrightarrow{Cl} \xrightarrow{Cl} Cl$$
(1)

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 $\delta 2:37$ (J 7 Hz) and a triplet at $\delta 5:92$ 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.

$$\begin{array}{c|c} \text{CCl}_3\text{CH}_2\text{CH}_2\text{Br} & \xrightarrow{\text{H}_2/\text{PtO} \ (18 \text{ lb/in}^2)} \text{ (BrCH}_2\text{CH}_2\text{CCl}_2)_2 \\ \hline & \text{EtOH, NH}_3 & & 65^{\circ} \\ \hline & \text{(1)} & \xleftarrow{\text{KOH}} & & \\ & \text{SCHEME} & & \\ \end{array}$$

1,1,1-Trichloro-3-bromopropane⁴ could be coupled under hydrogenolysis conditions⁵ 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 $\delta 3.10$ 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 $\delta 5.50$ (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 $\delta 5.32$ (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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