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RADICAL REACTIONS IN THE COORDINATION SPHERE II.[1)]
STEREOSELECTIVE ADDITION OF CARBON TETRACHLORIDE TO CYCLOHEXENE CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II).

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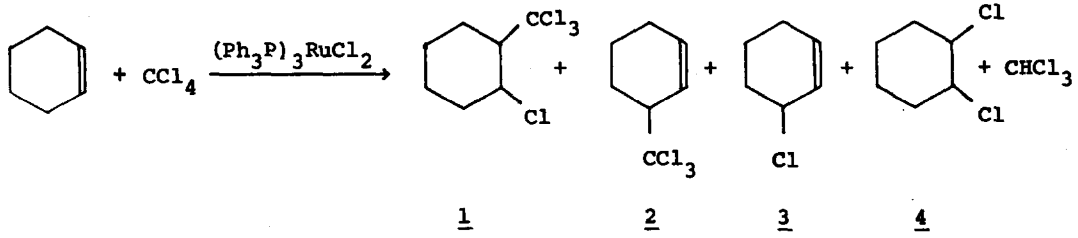
Although synthetic application of free-radical addition of polyhaloalkanes across the double bonds of olefins has reached considerable success,[2)] carbon tetrachloride was reported to react with cyclohexene by peroxide initiation to give the expected adduct only in low yield. For instance, Israelashvili and Shabatay have obtained a complex mixture of the products from cyclohexene, carbon tetrachloride and benzoyl peroxide from which an approximately 10% yield of the adduct was isolated.[3)] Further, no data are available on the stereochemistry of this addition reaction and our investigation has shown that there was obtained a 53:47 mixture of the trans and cis adduct when a 3:1 mixture of carbon tetrachloride and cyclohexene was heated in the presence of benzoyl peroxide at 80°C.[4)]

In the present communication, we wish to report a highly stereoselective addition of carbon tetrachloride to cyclohexene catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) that produced chiefly trans-1-trichloromethyl-2-chlorocyclohexane in good yield.

In a typical experiment, a mixture of 1.65g (20.1 mmol) of cyclohexene, 9.24g (60.1 mmol) of carbon tetrachloride and 0.18g (0.16 mmol) of the ruthenium complex was heated in a sealed tube at 80°C for 30 hours. GLC analysis of the resulting mixture disclosed that 95% of the olefin was consumed and that 77% yield (based on the olefin consumption) of 1-trichloromethyl-2-chlorocyclohexane 1 was produced as a 96:4 mixture of the trans and cis isomer. The geometrical isomerism was established by 100 MHz-NMR measurements including the decoupling experiments.[5)]

^1H NMR of trans 1 (in CCl_4): δ 1.37-2.53 (8H, multiplet, CH_2), 2.84 (1H, multiplet, H^mCCCl_3) and 4.51 (1H, multiplet, H^nCCl); J_{mn} 5.0 Hz. Cis 1 : δ 1.35-2.34 (8H, mutiplet, CH_2), 2.60 (1H, mutiplet, H^mCCCl_3) and 4.89 (1H, multiplet, H^nCCl); J_{mn} 2.5 Hz.[6)]

The reaction was accompanied by the formation of 3-trichloromethyl-1-cyclohexene 2 (trace), 3-chloro-1-cyclohexene 3 (trace), 1,2-dichlorocyclohexane 4 (6% yield) and chloroform (25% yield), but these by-products were easily separable from 1 by distillation. Thus, distillation of the reaction mixture gave pure 1 in 63% yield.



Although the illustrated reaction was carried out using 3:1 ratio of the halide and the olefin, we found that almost the same results could be obtained with a 1:1 mixture of the reactants. Thus, the present results indicate that the ruthenium catalysis technique provides an excellent method of preparation of trans-1-trichloromethyl-2-chlorocyclohexane. The high yield and high stereoselectivity exhibited by the present system is likely to be associated with the favorable arrangement of the reactant molecules in the coordination sphere and mechanistic consideration on the reaction is under investigation.

Satisfactory elemental analyses and supporting spectral data have been obtained for all the products.

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5) Previous workers reported that dehydrobromination of 1-trichloromethyl-2-bromocyclohexane was utilized for confirming geometrical isomerism (J. G. Traynham, A. G. Lane and N. S. Bhacca, J. Org. Chem., 34, 1302 (1969)). However, we found that stereoselective dehydrochlorination could not be easily accomplished in the case of 1 . In fact, treatment

of a 53:47 mixture of trans and cis <u>1</u> with 0.5 molar equiv of KOH in DMSO-H_2O solvent under comparable conditions gave only a 63:37 mixture of starting isomers.

6) For 1-trichloromethyl-2-bromocyclohexane, it was found that the NMR signal for H^mCCl_3 in the trans isomer is downfield from that in the cis isomer and that the signal for H^nCBr in the former is upfield from in the latter. In this case, J_{mn} of the trans isomer is larger than that of the cis isomer: ref. 5.