

ADDITION OF CARBON TETRACHLORIDE TO CONJUGATED 1,3-DIENES CATALYZED BY
DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) ¹

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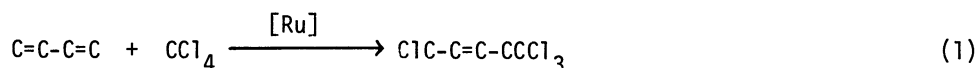
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Addition of carbon tetrachloride to conjugated 1,3-dienes such as 1,3-butadiene, 1,3-pentadiene, isoprene, 1,3-cyclohexadiene and 1,3-cyclooctadiene proceeded smoothly under mild conditions in the presence of dichloro-tris(triphenylphosphine)ruthenium(II) to give the corresponding 1,4-addition products as 1:1 adducts in excellent yields.

Although much attention has been directed to the addition of carbon tetrachloride across the double bonds of olefins,² the addition to conjugated 1,3-dienes has been not yet reported except for one case. Thus, Asscher and Vofsi reported that the addition to 1,3-butadiene was successfully achieved with the use of cupric or ferric chloride as a catalyst to afford the expected 1:1 adduct,³ However, even in this single example, the use of a cocatalyst and a polar solvent is necessary to attain a satisfactory product yield.³ We report herein our finding that the addition of carbon tetrachloride to a variety of conjugated 1,3-dienes can be best effected by a homogeneous ruthenium catalyst, dichlorotris(triphenylphosphine)ruthenium(II).¹

Typically, 8.61g (126 mmol) of 1,3-pentadiene, 65g (420 mmol) of carbon tetrachloride and 0.26g (0.27 mmol) of the ruthenium(II) complex were introduced into a stainless steel vessel. The vessel was then sealed and heated at 80°C for 5 h. The resulting mixture was diluted with 40 ml of n-pentane and the precipitated catalyst was removed by filtration. After evaporation of low boiling materials, distillation gave 23g (82% yield based on the diene charged) of a colorless liquid boiling at 61-62°C (0.4 mm) identified as 1,1,1,5-tetrachlorohexene-3 by its NMR and IR spectra and elemental analysis: NMR (CCl₄) δ 5.83 (m, 2H, -CH=CH-), 4.50 (quintet, 1H, -CHCl-), 3.42 (d, 2H, -CH₂CCl₃) and 1.62 (d, 3H, -CH₃); IR (neat) 3000-2960, 1645 (C=C), 1500, 1255, 1035, 970 and 905 cm⁻¹; Anal. Calcd for C₆H₈Cl₄: C, 32.47; H, 3.63; Cl, 63.90. Found: C, 32.58, H, 3.92; Cl, 63.5.

The results of other reactions are summarized in the Table and it is seen that, in all cases, only 1,4-addition products were produced and the yields were excellent. Further, it



was found that the addition to isoprene proceeded with a high regioselectivity to give 1,1,1,5-tetrachloro-3-methylpentene-3 only.

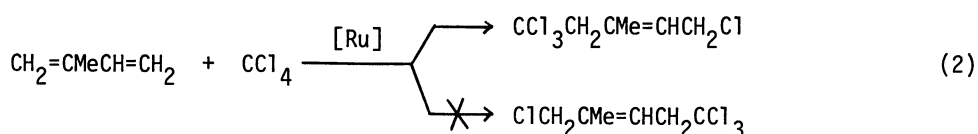

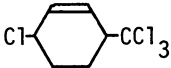

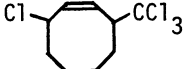


Table Addition of Carbon Tetrachloride to Conjugated 1,3-Dienes in the Presence of Dichlorotris(triphenylphosphine)ruthenium(II).^a

Diene	Time (h)	1:1 Adduct ^b	Yield,% ^c
CH ₂ =CHCH=CH ₂	4	ClCH ₂ CH=CHCH ₂ CCl ₃	86
CH ₃ CH=CHCH=CH ₂ ^d	5	CH ₃ CHClCH=CHCH ₂ CCl ₃	82
CH ₂ =CMeCH=CH ₂	5	CCl ₃ CH ₂ CMe=CHCH ₂ Cl	85
	8		81 ^e
	9		83

^aThe addition reactions were carried out at 80°C in a sealed stainless steel vessel using a 1:3:0.002 mixture of a diene, the chloride and the ruthenium(II) complex.

^bNMR and IR spectra and elemental analyses were in agreement with the assigned structures. Stereochemistry of the adducts, however, was not determined. ^cUnless otherwise stated, isolated yields are given. ^dA mixture of cis- and trans-isomers was used. ^eDetermined by GLC

For comparison purposes, benzoyl peroxide-catalyzed addition reactions of carbon tetrachloride with 1,3-pentadiene, isoprene, 1,3-cyclohexadiene and 1,3-cyclooctadiene were carried out at 80-100°C for 15-24 h in a sealed stainless steel vessel using a 1:5:0.05 mixture of a diene, the chloride and the peroxide. These reactions, however, gave mostly undistillable viscous materials and the yields of the expected 1:1 adducts never exceeded 5%.

In summary, the present results show that the ruthenium(II) complex is an excellent catalyst to initiate the addition of carbon tetrachloride to easily polymerizable 1,3-dienes.

References

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