

PALLADIUM AND NICKEL-CATALYZED REACTION OF  
GRIGNARD REAGENTS WITH TRICHLOROETHYLENE.  
A SIMPLE SYNTHESIS OF 1,1-DICHLOROALKENES.

VICTORIN RATOVELOMANANA, GERARD LINSTRUMELLE

E.R. 12 du CNRS, Laboratoire de Chimie, Ecole Normale Supérieure,  
24, rue Lhomond, 75231 Paris Cedex 05. FRANCE

and

JEAN-FRANCOIS NORMANT

Laboratoire de Chimie des Organo-Eléments, Université Pierre et Marie Curie,  
Tour 44, 4 place Jussieu, 75230 Paris Cedex 05. FRANCE.

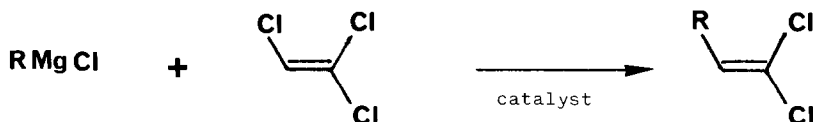
*ABSTRACT* : The palladium (or nickel) catalyzed reaction of Grignard reagents with trichloroethylene affords 1,1-dichloroalkenes in good yield under mild conditions.

The transition metal-catalyzed reactions of organometallics with organic halides have proven to be an efficient approach for carbon-carbon bond formation. Although the substitution of vinyl halides under palladium and nickel catalysis is now well documented<sup>1-4)</sup>, the substitution of polyhalogenoolefins has received little attention.

The selective catalyzed reaction of 1,2-dichloroethylene with organometallics has recently been reported and provides a new procedure for the preparation of vinyl chlorides<sup>5)</sup>. It would be worthwhile to study under similar conditions<sup>6)</sup> the reactivity and selectivity of trichloroethylene which is a cheap compound.

The stoichiometric oxidative addition of palladium complexes has been reported to occur selectively on the monosubstituted carbon<sup>7-9)</sup>. The use of these organometallics as transient reactive species under catalyzed conditions would be interesting in synthesis.

We now report that Grignard reagents react easily at room temperature with trichloroethylene in the presence of palladium or nickel catalysts and lead to 1,1-dichloroolefins in good yield. Thus, when treated with octylmagnesium chloride (1 equiv) and palladium tetrakis(triphenylphosphine)(0.05 equiv) in a mixture ether and benzene at 20° for 6h, trichloroethylene (5 equiv) gave 1,1-dichlorodecene 3 (99% isomeric purity) in 65% yield. In the same conditions, by using nickel tetrakis(triphenylphosphine) as catalyst instead of palladium, the dichloroolefin 3 was also obtained in 75% yield with a slightly lower purity (95%)<sup>10)</sup>. Several examples are given in the Table :



R	Catalyst	Isolated Yield (%)	Purity (%)	b.p.(°C/torr)
n-C <sub>8</sub> H <sub>17</sub>	A	65	99	85/1
n-C <sub>8</sub> H <sub>17</sub>	B	75	95	"
n-C <sub>6</sub> H <sub>13</sub>	A	60	99	63/1.5
n-C <sub>6</sub> H <sub>13</sub>	B	72	95	"
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	B	55	98	148/760
(CH <sub>3</sub> ) <sub>2</sub> CH	B	52	98	118/760
c-C <sub>6</sub> H <sub>11</sub>	A	81	99	85/20

Catalyst A : Pd (PPh<sub>3</sub>)<sub>4</sub><sup>13</sup>. Catalyst B : Ni (PPh<sub>3</sub>)<sub>4</sub><sup>14</sup>.

We may assume that oxidative addition of the transition metal catalysts occur at the monosubstituted site of the trichloroethylene<sup>11)</sup> and that the transient catalytic species reacts with the Grignard reagent to give after reductive elimination the 1,1-dichloroalkene.

The procedure reported herein provides a convenient access to 1,1-dichloroolefins which are useful intermediates in synthesis<sup>12)</sup>.

Typical procedure: 2-cyclohexyl-1,1-dichloroethene

In a three-necked flask fitted with magnetic stirrer, thermometer and serum caps, Pd (PPh<sub>3</sub>)<sub>4</sub> (900 mg, 0.75 mmol) is dissolved in benzene (30 ml)<sup>15)</sup>. Trichloroethylene (9.9 g, 75 mmol) is added to this solution and stirred at room temperature for 30 min. Cyclohexyl magnesium chloride in ether (14.3 ml, 15 mmol) is added dropwise at 20° and stirring is maintained for 6h. Extraction in the usual manner, filtration over neutral alumina and distillation gives 2-cyclohexyl-1,1-dichloroethene, b.p.: 84-85°(20torr); 2.18 g (81%). IR (neat) :  $\nu$  1612 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) :  $\delta$  5.74ppm(1H,d,J=9.5Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) :  $\delta$  118.56 (C-1), 134.77ppm (C-2).

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- 15) For a typical experimental procedure for nickel-catalyzed coupling reactions, see ref 4.