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# Addition of Diethyl Trichloromethylphosphonate to Olefins Catalysed by Copper Complexes

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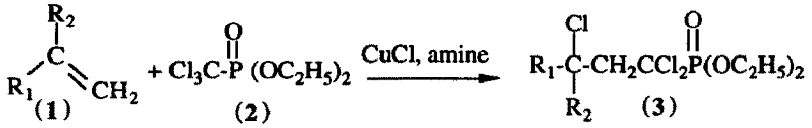
**Abstract:** Diethyl trichloromethyl phosphonate is added on olefins by non-chain catalytic reactions catalysed by copper amine complexes.

Additions of halo compounds, such as tetrachloromethane and methyl trichloroacetate, to olefins providing 1:1 adducts have been reported to proceed with a number of transition metal complexes[1] ( e.g. Cu, Fe , Pd, Ru, Re, Mo, V, Cr, Mn, Ni, Co). In previous papers[2] we have described copper (I) complexes with nitrogen ligands as efficient catalysis in addition reactions. Recently our interest has been focussed on the synthesis of new phosphonates[3]. We report herein that the copper (I) complexes catalyse the addition of diethyl trichloromethyl phosphonate to olefins. This represents a novel synthetic route towards new chlorophosphonate compounds according to **scheme 1.**

**Scheme 1:** Addition of diethyl trichloromethylphosphonate on olefins catalysed by copper



a) $R_1 = COOC_2H_5$ $R_2 = H$
b) $R_1 = CN$ $R_2 = CH_3$
c) $R_1 = (CH_2)_8\,COOC_2H_5$ $R_2 = H$
d) $R_1 = PO\,(OC_2H_5)_2$ $R_2 = H$
e) $R_1 = C_6H_5$ $R_2 = H$
f) $R_1 = CH_2O_2C_6H_4CH_2$ $R_2 = H$
g) $R_1 = C_4H_9$ $R_2 = H$

The yields of substituted trichlorophosphonates (3) are given in **Table I.** Chlorophosphonates are known as biologically active compounds and they are easily transformed to functionalised vinylphosphates which are useful in organic synthesis[4]. To our knowledge, addition of diethyl trichloromethylphosphonate to olefins has not been reported. We have only recorded reductive addition of bromodifluoromethylphosphonate which was recently described[5].

The products (3)[7] are identified by ($^1H$, $^{13}C$, $^{31}P$) NMR, IR, mass spectroscopy and microanalysis.

The advantage of copper(I)-amine complexes as catalysts for addition of halo compounds to olefins is prevention of polymer formation. Nevertheless, high boiling products were found to be heat sensitive and they underwent dehydrochlorination and polymerisation; therefore products obtained from styrene, safrole and ethyl undecenoate were purified by chromatography. For the addition of low reactive olefins like safrole or diethyl vinyl phosphonate, a copper (I) phenanthroline complex (prepared in situ from electroytic copper powder and 1,10-phenanthroline hydrate) was used instead of the copper (I)-2-methylpropylamine catalyst.

**Table 1**: Addition of diethyl trichloromethylphosphonate on olefins

| N° | Olefin (1) | Yield(%) of (**3**) |
|---|---|---|
| **1a** | ethyl acrylate | 59 |
| **1b** | methacrylonitrile | 31 |
| **1c** | ethyl undecenoate | 65 |
| **1d** | diethyl vinyl phosphonate | 52 |
| **1e** | styrene | 64 |
| **1f** | safrole | 45 |
| **1g** | 1-hexene | 55 |

Catalytic additions of halo compounds to olefins are well documented as non-chain reactions[2] in contrast to the classical method based on free-radical chain reaction[6]. The addition of diethyl trichloromethyl phosphonate on olefin allows the synthesis of new chlorophosphonates.

## References and notes

1. Kotora, M.; Adamek, F.; Hàjek, M. *Cat. Lett.* 1993, **18**, 345-348 and references cited.

2. Hàjek, M.; Silhavy, P. *Coll. Czech. Chem. Commun.* 1983, **48**, 1710-1717; Hàjek, M.; Silhavy, P.; Spirkovà, B. *Coll. Czech. Chem. Commun.* 1990, **55**, 2949-2955.

3. Villemin, D.; Thibault-Starzyk, F. *Phosphorus, Sulfur, Silicon.* 1993, **80**, 251-254 and references cited.

4. Minami, T.; Motoyoshiya, J. *Synthesis* 1992, 333-349.

5. Hu Chang-Ming; Chen Jian *J. Chem. Soc. Perkin Trans I* 1993, 327-330.

6. Giese, B. *Radicals in Organic Synthesis : Formation of Carbon-Carbon Bonds;* Pergamon Press, Oxford 1987; Crich, D.; Motherwell,W. *Free-Radical Chain Reaction in Organic Synthesis;* Academic Press, London 1991.

7. In a typical procedure, mixtures of diethyl trichloromethylphosphonate[8], olefin (0.04 mol.), cuprous chloride and 2-methylpropylamine in molar ratio 2:1:0.02:0.04 were stirred in 1,2-dichloroethane and heated to 93-100°C under argon for 5 to 12 hours. In the course of reaction, 2-methylpropylamine was continuously added in a total amount 0.005 to 0.01 mol. The products (1/1 adducts) were isolated by distillation under reduced pressure [bp: **3a**, 118-122 (0.4); **3b**, 118-125 (0.4) ] after treatment of reaction mixture with dilute hydrochloric acid(10%) and water. High boiling products sensitive to heating were isolated and purified by column chromatography on Florisil® ($CH_2Cl_2$:$CH_3OH$= 98:2).

   Typical spectra: (**3e**) PMR($CDCl_3$), δ : 1.4 (m, 6H, $CH_3$ $CH_2$); 3.3 (m, 2H, CCl); 4.4 (m, 4H, $OCH_2$); 5.5 (t, 1H, $C_6H_5$ CH $CH_2$); 7.4 (m, 5H, $C_6H_5$); CMR, δ: 16.40 ($CH_3$); 51 (CCl); 57.57 ($CCl_2$); 55, 70 ($OCH_2$); 128.74 ($C_6H_5$); $^{31}P$ NMR, δ: 11.94 ; IR (film ): 1400 ; 1210 (P=O); MS (70 Ev): 365, 363, 361, 359 (M+)

8. Kosolapoff, G. M. *J. Amer. Chem. Soc.* 1947, **69**, 1002-1003; Bakkas, S.; Julliard, M.; Chanon, M. *Tetrahedron* 1987, **43**, 501-512.

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