Brief Communications

Metal phthalocyanine-catalyzed addition of polychlorine-containing organic compounds to C=C bonds

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Organopolychlorine compounds (CCl_4, CCl_3CO_2Et, CCl_3CHO) add at the double bond of various olefins under the catalysis of the metal phthalocyanine complexes. A possibility of quantitative catalyst recovery was shown.

Key words: phthalocyanines, olefins, polychlorine-containing organic compounds, tetrachloromethane, Kharasch reaction, copper complexes, cobalt complexes.

The addition of organic polyhalides to unsaturated compounds (the Kharasch reaction) is a convenient and satisfactorily developed method for functionalization of organic compounds. The intermediate products obtained can serve as precursors of higher carboxylic acids, amino acids, and various heterocyclic compounds.

Copper and its salts,[1—3], metal carbonyls,[4—6] ferrocene,[7,8] *etc.* were used as catalysts of the process. Among drawbacks of these catalysts is that they cannot be recovered after the reaction.

At the same time, metal phthalocyanine complexes are known to be used as catalysts of diverse organic reactions, for example, oxidation,[9] reduction with sodium boron hydride,[10] Kabachnik—Fields reactions,[11] and chlorination of aromatic compounds.[12,13] The purpose of the present work is to study the catalytic activity of phthalocyanines in the Kharasch reaction.

We found that in the presence of 0.1—1.0 mol.% copper tetra-*tert*-butylphthalocyanine or copper octabutylphthalocyanine CCl_4 adds to acrylonitrile to form 2,4,4,4-tetrachlorobutyronitrile in a yield up to 65% (Scheme 1). The reaction involving hex-1-ene and styrene proceeds similarly. As a result, 1,1,1,3-tetrachlorohexane and 1,1,1,3-tetrachloro-3-phenylpropane, respectively, are formed.

The reaction occurs on heating a mixture of the reactants in acetonitrile in a sealed vessel at 140 °C. An attempt to carry out the process by refluxing the reactants in acetonitrile or butyronitrile under atmospheric pressure was unsuccessful: no addition products were formed.

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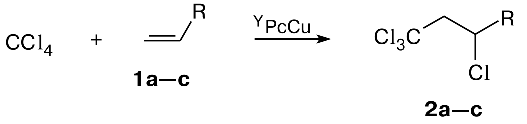
Scheme 1



R = CN (**a**), Bu (**b**), Ph (**c**)
Y = Bu^t_4, Bu^n_8

The catalyst is quantitatively recovered after the target compound was separated by the elution of the column with polar solvents, which is seen from the weight of the product, its unchanged electronic absorption spectrum, and reproducible yields of the adducts when the phthalocyanine complex is used repeatedly.

Along with copper phthalocyaninates, we studied catalytic properties of planar and sandwich phthalocyanine complexes and the free tetra-*tert*-butylphthalocyanine ligand. The results of CCl_4 addition to hex-1-ene in various solvents in the presence of these additives are given in Table 1.

As can be seen from Table 1, no adducts are formed in the reaction of rare-earth metal diphthalocyanines and the free ligand, which indicates that the reaction occurs on the sterically accessible metal site of the catalyst. Note that the addition in the presence of unsubstituted copper phthalocyanine cannot be carried out, because the latter is insoluble under the reaction conditions.

Cobalt tetra-*tert*-butylphthalocyanine is an active catalyst along with the copper complexes, which was confirmed for other unsaturated compounds as well. The comparative yields of CCl_4 addition to various substrates in the presence of the copper and cobalt catalysts are listed in Table 2.

Table 1. Yields of 1,1,1,3-tetrachloroheptane (**2b**) with the use of various metal complexes (0.5 mol.%) and solvents

Metal phthalocyanine	Yield **2b** (%)			
	MeCN	Propan-2-ol	CCl_4*	Hex-1-ene*
$^{Bu^t}$PcCu	76	75	73	64
$^{Bu^n}$PcCu	74	73	—**	—**
$^{Bu^t}$PcCo	84	85	78	66
$^{Bu^t}$PcNi	3	4	3	3
$^{Bu^t}$PcPt	8	9	10	10
$^{Bu^t}$PcPd	7	8	6	7
$^{Bu^t}$PcMn	13	12	11	14
$^{Bu^t}$PcCr	4	5	4	3
$^{Bu^t}$PcZn	3	3	3	3
$^{Bu^t}$PcH$_2$	0	0	0	0
$^{Bu^t}$Pc$_2$Lu	0	0	0	0
$^{Bu^t}$Pc$_2$Eu	0	0	0	0

* An excess of the corresponding reactant was used as the solvent.
** Experiment was not carried out.

Table 2. Yields of the addition products of CCl_4 to unsaturated substrates in the presence of Cu and Co tetra-*tert*-butylphthalocyanines (0.5 mol.%)

Substrate	Yield (%)	
	$^{Bu^t}$PcCu	$^{Bu^t}$PcCo
NC—CH=CH$_2$	65	64
Bu—CH=CH$_2$	76	84
Ph—CH=CH$_2$	72	69

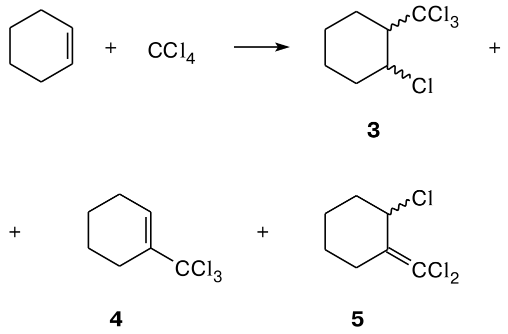
The reactions described above concern terminal olefins. In order to extend the range of involved olefins, we studied the addition of CCl_4 to cyclohexene under the conditions determined earlier (sealed vessel, 140 °C, 8 h). The products were identified on the basis of GC-MS data. The chromatograms of the reaction mixtures exhibit three peaks with the retention times 12.5, 15, and 17 min in a ratio of 1 : 2 : 1.5. The mass spectrum of the first product contains peaks of the molecular ion of $[C_7H_{10}Cl_4]^+$ with *m/z* 234, 236, 238, and 240, which corresponds to four chlorine atoms in the molecule. Therefore, this signal is assigned to adduct **3** of cyclohexene and tetrachloromethane (Scheme 2). The mass spectra of two other compounds contain signals with *m/z* 198, 200, and 202 corresponding to the $[C_7H_9Cl_3]^+$ ion. However, the second product contains predominantly light fragments (*m/z* 80 for cyclohexadiene and *m/z* 78 for benzene), which indicates that the structure contains the trichloromethyl group. Based on these data, the structure of 1-trichloromethylcyclohexene (**4**) can be ascribed to the second product. Ions with *m/z* 162, 164, and 166 are observed in the mass spectrum of the latter compound along with the molecular ion peak with *m/z* 198, 200, and 202. This corresponds to the elimination of hydrogen chloride from the molecular ion and indicate the allylic migration of chlorine in 1-trichloromethylcyclohexene (**4**), resulting in 1-chloro-2-dichloromethylidenecyclohexane (**5**).

An increase in the reaction duration to 12 h and the temperature decrease to 100—110 °C induce no substantial change in the composition of the products. Therefore, it can be supposed that all the three compounds are formed from the same precursor rather than consecutively (see Scheme 2).

Note that we found no 1-chlorocyclohex-2-ene, which is the by-product formed upon the addition of CCl_4 to cyclohexene in the presence of the CuCl complex with triphenylphosphine.[14,15]

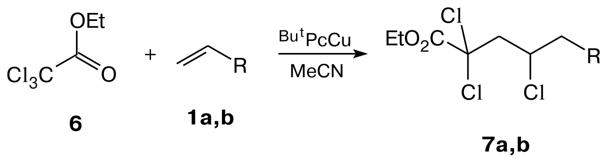
Under the conditions determined, chloroform does not add to alkenes, whereas more reactive addends react

Scheme 2



in the process under study. For instance, we carried out the addition of ethyl trichloroacetate (**6**) to acrylonitrile and hex-1-ene in 67 and 77% yields, respectively (Scheme 3).

Scheme 3

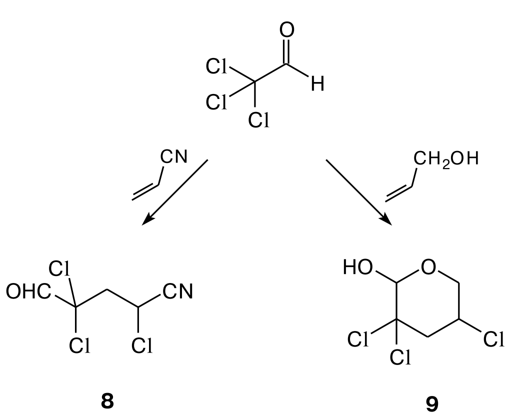


R = CN (**a**), Bu (**b**)

In the case of ethyl trichloroacetate addition to styrene (**1c**) at the quantitative olefin conversion, a large amount of resinous compounds are formed, which prevents isolation of the target product.

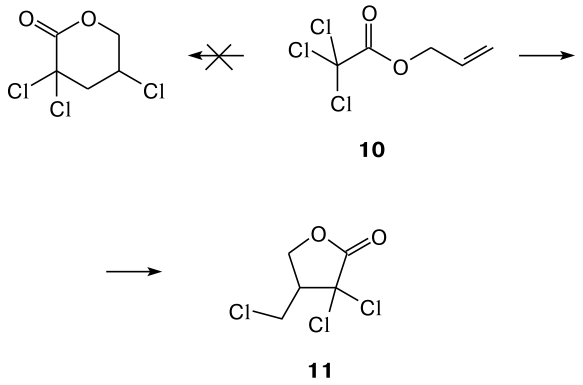
Chloral reacts with acrylonitrile and allyl alcohol to yield earlier described 2,2,4-trichloro-5-oxovaleronitrile (**8**)[1] and 2-hydroxy-3,3,5-trichlorotetrahydropyrane (**9**),[2,4] respectively (Scheme 4).

Scheme 4



We established that the phthalocyanine complexes catalyze both the intermolecular and intramolecular Kharasch reaction. The cyclization of allyl trichloroacetate in the presence of copper and cobalt tetra-*tert*-butylphthalocyanines affords not 3,3,5-trichlorodihydropyran-2-one (**10**) but 3,3-dichloro-4-chloromethyldihydrofuran-2-one (**11**), as in the presence of univalent copper salt[3] (Scheme 5).

Scheme 5



This suggests that the addition of polychlorine-containing organic compounds to alkenes in the presence of the phthalocyanine catalysts proceeds as a radical process. Note that the addition of tetrachloromethane and other addends to olefins is not inhibited by hydroquinone, which makes it possible (with a sufficient probability) to exclude the free radical mechanism of such a reaction. This fact additionally indicates that the addition occurs in the coordination sphere of the metal.

In summary, a new efficient and easily recoverable catalysts were found for the addition of organopolychlorine compounds to carbon—carbon double bonds.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-300 spectrometer relative to Me_4Si, using $CDCl_3$ as the solvent. The GC-MS spectra were measured on a Finnigan MAT INCOS-50 instrument (EI, 70 eV), using nitrogen as a carrier gas (30 cm^3 min^{-1}), glass columns 3500S3 mm with 5% XE-60 on Inerton-super (0.20—0.25 mm), and the temperature-programmed regime from 50 to 250 °C with a rate of 20 °C min^{-1}.

Thin layer chromatography was carried out on Silufol UV-254 plates (Merck).

All reagents used were high-purity, reagent, and analytically pure grade. Prior to use the solvents were distilled and (if necessary) dried.

The phthalocyanine complexes were synthesized according to procedures described earlier.[16]

Allyl trichloroacetate (10) was synthesized in 60% yield according to a known procedure.[3]

Reaction of CCl_4 with unsaturated compounds (general procedure). A solution of an unsaturated compound (10 mmol), a polychloro derivative (10 mmol), and a catalyst (0.01—0.10 g) in acetonitrile (total volume 10 mL) was heated for 4—8 h at 140 °C in a sealed tube. After cooling, the tube was opened, and the solvent and unreacted starting compounds were evaporated *in vacuo*. The residue containing the target product and the catalyst were purified by column chromatography (SiO_2, 60—200 mesh). After the eluent was evaporated, the corresponding adduct was obtained as a yellowish liquid. The yields of the adducts are presented for the $^{Bu^t}$PcCu-catalyzed reaction. After the adduct was isolated from the chromatographic column, the catalyst was eluted with ethyl acetate, which allowed its quantitative recovery to be performed.

2,4,4,4-Tetrachlorobutyronitrile (2a). The eluent for the chromatographic isolation of the adduct was C_6H_6—hexane (1 : 1, vol.). The yield was 65%. ^{1}H NMR, δ: 4.87 (dd, 1 H, CHCl, ^3J = 4.7 Hz, ^3J = 8.7 Hz); 3.63 (dd, 1 H, CH_2, ^2J = 15.2 Hz); 3.37 (dd, 1 H, CH_2). ^{13}C NMR, δ: 115.8 (CN), 93.8 (CCl_3), 59.1 (CH_2), 37.95 (CHCl).

1,1,1,3-Tetrachloroheptane (2b). The eluent for the chromatographic isolation of the adduct was C_6H_6—hexane (1 : 1, vol.). The yield was 76%. ^{1}H NMR, δ: 4.27 (m, 1 H, CHCl); 3.65 (dd, 1 H, CCl_3—CH_2, ^2J = 15.5 Hz, $^3J_{vic}$ = 5.5 Hz); 3.13 (dd, 1 H, CCl_3—CH_2, ^3J = 4.6 Hz); 1.83—1.98 (m, 2 H, CH_2—CHCl); 1.27—1.58 (m, 4 H, CH_2—CH_2); 0.95 (t, 3 H, Me, ^3J = 7.3 Hz). ^{13}C NMR, δ: 97.1 (CCl_3), 62.5 (CCl_3—$C\underline{H}_2$), 57.8 (CHCl), 38.9, 28.2, 22.1 (3 CH_2), 14.0 (Me).

1,1,1,3-Tetrachloro-3-phenylpropane (2c). The eluent for the chromatographic isolation of the adduct was C_6H_6—hexane (1 : 1, vol.). The yield was 72%. ^{1}H NMR, δ: 7.35—7.49 (m, 5 H, CH arom.); 5.33 (dd, 1 H, CHCl); 3.65 (dd, 1 H, CCl_3—CH_2, ^2J = 15.2 Hz, ^3J = 5.5 Hz); 3.56 (dd, 1 H, CCl_3—CH_2, ^3J = 6.4 Hz). ^{13}C NMR, δ: 163.3 (C arom.), 140.5 (C arom.), 129.0 (C arom.), 127.5 (C arom.), 96.3 (CCl_3), 62.8 (CH_2), 58.4 (CHCl).

Ethyl 2,2,4-trichloro-4-cyanobutanoate (7a). The eluent for the chromatographic isolation of the adduct was ethyl acetate—hexane (1 : 2, vol.). The yield was 67%. ^{1}H NMR, δ: 4.88 (dd, 1 H, CHCl); 4.32 (q, 2 H, $CH_3C\underline{H}_2O$); 4.20 (m, 1 H, CHCl); 3.11 (m, 2 H, CHCl—$C\underline{H}_2$—CCl_2); 1.36 (t, 3 H, $C\underline{H}_3CH_2O$).

Ethyl 2,2,4-trichlorooctanoate (7b). The eluent for the chromatographic isolation of the adduct was C_6H_6—hexane (1 : 1, vol.). The yield was 77%. ^{1}H NMR, δ: 4.32 (q, 2 H, $CH_3C\underline{H}_2O$, ^3J = 6.97 Hz); 4.20 (m, 1 H, CHCl); 2.95 (ddd, 2 H, CHCl—$C\underline{H}_2$—CCl_2); 1.79 (m, 2 H, CH_2); 1.40 (m, 2 H, CH_2CH_2); 1.36 (t, 3 H, $C\underline{H}_3CH_2O$); 0.92 (t, 3 H, $CH_2CH_2C\underline{H}_3$, ^3J = 6.4 Hz).

2,4,4-Trichloro-5-oxopentanonitrile (8). The eluent for the chromatographic isolation of the adduct was ethyl acetate—hexane (3 : 1, vol.). The yield was 45%. ^{1}H NMR, δ: 9.25 (s, 1 H, CHO); 4.88 (dd, 1 H, CHCl, ^3J = 6.2 Hz, ^3J = 7.3 Hz); 3.00 (m, 2 H, $C\underline{H}_2$—CCl_2).

2-Hydroxy-3,3,5-trichlorotetrahydropyrane (9) was purified by distillation *in vacuo*, b.p. 120 °C (0.12 Torr). The yield was 34%. ^{1}H NMR, δ: 4.14 (s, 1 H, H_{ax}(2)); 3.66 (m, 1 H, H_{ax}(4)); 3.59 (m, 1 H, H_{ax}(5)); 2.68 (m, 1 H, H_{ax}(6)); 2.59 (m, 1 H, H_{eq}(4)); 1.91 (m, 1 H, H_{eq}(6)).

3,3-Dichloro-4-chloromethyl-4,5-dihydro-3*H*-furan-2-one (11). The eluent for the chromatographic isolation of the adduct was ethyl acetate—hexane (2 : 1, vol.). The yield was 67%. ^{1}H NMR, δ: 4.65 (dd, 1 H, CHO, ^2J = 9.3 Hz, ^3J = J = 7.1 Hz, ^2J = 9.3 Hz); 4.23 (dd, 1 H, CHO, ^3J = 8.8 Hz, J = 9.3 Hz); 3.99 (dd, 1 H, CHCl, ^3J = 4.6 Hz, ^3J = 11.5 Hz); 3.75 (dd, 1 H, CHCl, J = 7.1 Hz, J = 9.3 Hz); 3.32—3.41 (m, 1 H, CCl_2CH).

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