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Addition of α-polyhalides to olefins under mild reaction conditions, catalyzed by $Mo(CO)_6$

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Abstract

$Mo(CO)_6$ was found to be an efficient pre-catalyst in the 1,2-addition reaction of α-polyhalides to various olefins. Significantly, the reaction was run under mild conditions, viz. refluxing acetonitrile, with satisfactory yields. $Cr(CO)_6$ was also studied but found to be inferior relative to the Mo complex. It was assumed that the active catalytic species is $(CH_3CN)_3Mo(CO)_3$, generated in situ. The polyhalides examined were CCl_4 and ethyl trichloroacetate. Acyclic, as well as cyclic olefins, and dienes were studied. A cyclization product, substituted [3.3.0]bicyclooctane, was generated starting from 1,5-cyclooctadiene. Whenever relevant and feasible, the stereochemistry of the addition product was elucidated. A catalytic cycle for the addition reaction was proposed.

Keywords: α-Polyhalides; Olefins; $Cr(CO)_6$; $Mo(CO)_6$; Addition reaction

1. Introduction

Metal salts [1], metal complexes [2–6], as well as free radical initiators (Kharasch reaction) [7], catalyze 1,2-addition of α-polyhalides to olefins, such as described by Eq. 1. Metals and their complexes that are known to be active catalysts in the above reaction are Cu(I) [1], $RuCl_2(PPh_3)_3$ [2], $[CpMo(CO)_3]_2$ [3,4], $[CpFe(CO)_2]_2$ [3,5], $Co_2(CO)_8$ [3], and Pd [6]. While the Kharasch reaction is frequently accompanied by telomeriztion [2b,7,8], the reactions catalyzed by organometallic complexes are more selective. Recently, we have reported on a related reaction where methyl dichloroacetate and various alkenes generated γ-lactones in the presence of a catalytic amount of CuCl and stoichiometric quantity of Fe(0) [9]. In all, the addition reaction is a simple and useful one-step C–C bond forming reaction in organic synthesis.

Group VI metal complexes, such as $[CpMo(CO)_3]_2$ [3], $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ [10] and $Mo(CO)_6$ [3,11], are also known for their catalytic activity in the 1,2-addition of α-polyhalides to olefins and dienes. Using Group VI metal complexes, we were aiming at the simplification of both the reaction conditions, which usually require elevated temperatures (sealed tube), as well as the nature of the known catalysts. Some of the known catalysts were found to be air sensitive and difficult to store, while others were difficult to prepare and commercially unavailable. Thus, a simpler approach is in place.

In our study, the commercial, relatively inexpensive and stable, $M(CO)_6$ complexes (M = Cr and Mo) served as precatalysts. However, they had to be activated with a more labile ligand in order to obtain a reasonably active catalytic species. The known complexes $(CH_3CN)_3M(CO)_3$ (M = Cr and Mo) [12], carrying the readily dissociating nitrile ligands, served our purpose. Ideally, carrying the addition reaction to olefins in refluxing acetonitrile as a solvent in the presence of $M(CO)_6$ would generate the above catalyst in situ. Such a protocol would circumvent the synthesis, isolation, and handling of $(CH_3CN)_3M(CO)_3$ complexes. Furthermore, the use of a ligating solvent in the addition reaction is beneficial in prolonging the lifetime of the active catalytic species in solution during the reaction. The two polyhalides examined in the present study were CCl_4 and ethyl trichloroacetate (ETCA), with a variety of acyclic and cyclic alkenes and dienes, according to the

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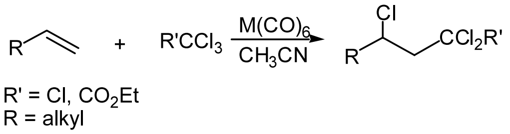
following general reaction for a terminal mono-ene (Eq. 1).



(1)

2. Results and discussion

Since the reaction of $M(CO)_6$ complexes with nitriles was considered to be slow, it was necessary to determine the effect of the pre-complexation period with acetonitrile on the yield (conversion) of the polyhalides addition product to olefins. Thus refluxing the $Cr(CO)_6$ in acetonitrile for various lengths of time, followed by the addition of CCl_4 and an alkene, and then further refluxing for a fixed period of time, generated Graph 1. Clearly, while zero pre-complexation time gave less than 50% conversion, 6 h pre-complexation time seems to be optimal (the reason for the minimum at 4 h pre-complexation time, which is consistent, is not clear). Nevertheless, it must be concluded that the substrates were interfering with the complexation reaction of acetonitrile and $Cr(CO)_6$, while longer complexation time hardly affected the stability of the catalytic species.

Next, it was of interest to examine the *relative* reactivity of the Cr and Mo catalytic systems in the 1,2-addition reactions of polyhalides to olefins in acetonitrile. The results of this study, carried out under standard reaction conditions, are presented in Table 1.

The following conclusion may be drawn from the data of Table 1:

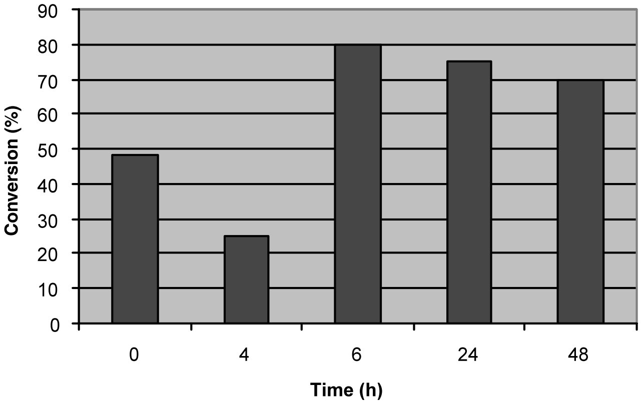


Fig. 1. Complexation times of $Cr(CO)_6$ with acetonitrile. Conditions: Pre-complexation was carried out in refluxing acetonitrile. The reaction mixture was refluxed for 24 h after addition of the reactants. The ratio of reactants: CCl_4:1-octene:$Cr(CO)_6$ was 6.6:1:0.05; [1-octene] = 0.7 M.

1) In variance with the Cr system, the Mo reaction system *does not* require a pre-complexation period (Expts. 1 and 2). We propose that with Mo, fast acetonitrile complex formation occurs under the addition reaction conditions, thus making it kinetically indistinuishable.
2) The Mo system is more reactive than the Cr system.
3) The reaction of ethyl trichloroacetate is slower than that of CCl_4.

The above conclusions directed our study to the more efficient Mo system. The results of the addition reactions of the above mentioned two polyhalides to various cyclic and acyclic olefins, using $Mo(CO)_6$ as precatalyst in various nitrile solvents, are presented in Table 2. The general chemistry of the addition reactions is outlined in Scheme 1.

All substrates combinations were found to be reactive with the new catalytic system, and under mild condition, with satisfactory yields of the 1,2-addition products. Replacing acetonitrile with propionitrile or benzonitrile as the ligating solvents, thereby also raising the reaction temperature, substantially accelerated the reaction rate (Expts. 1–3, Table 2). The same effect was noted in Exp. 5 and 6, and also 7 and 8, although in the latter case it was also accompanied by substantial decrease of the yield.

Cyclohexene was the poorest reacting olefin substrate, resulting in low yields of the addition product. The prolonged reaction time also generated cyclohexene derivative as an HCl elimination product (GC/MS). It also gave rise to two diastereomers in a non-stereoselective manner, exhibiting ^{1}H-NMR signals at 4.46 (multiplet) and 4.94 ppm (wide singlet) in a ratio of ca. 1:1. These signals were assigned to the H atom α to Cl. The above H atom in the cis product has three adjacent H atoms with approximately the same dihedral angle of ca. 60°. Such dihedral angle should generate coupling constant of ca. 1–2 Hz (Karplus graph), and should give rise to ddd. We could not resolve the signals, but from the $W_{1/2}$ of 6 Hz (at 4.94 ppm), versus 17.5 Hz (at 4.46 ppm), the former signal must be assigned to the cis isomer. The dihedral angles in the trans isomer are 60, 180, 180°, that should generate coupling constants of 1, 8, 8 Hz, respectively, in agreement with $W_{1/2}$ of 17.5 Hz for the signal at 4.46 ppm.

The lack of steroselectivity in the above reaction is of mechanistic significance (vide infra).

Cyclooctene, on the other hand, was found to be the most reactive olefin substrate. Our reaction conditions yielded a single isomer (GC, NMR) with both CCl_4 and ETCA, in variance with previous work that gave a mixture of regio and stereoisomers [13]. As to the stereochemistry of this single isomer, again the NMR signal (4.2 ppm) of the H atom α to Cl was used as an indicator. The structures of the cis and trans addition

Table 1
The effect of pre-complexation on the addition reactions [a]

Exp no.	Catalyst (charged)	Solvent	Complex. time (h)	Substrate	Poly halide	Time (h)	Conv. (%)	Yield (%) [b]
1	$Mo(CO)_6$	CH_3CN	0	1-Octene	CCl_4	24	86	85
2	$Mo(CO)_6$	CH_3CN	4	1-Octene	CCl_4	23	89	75
3	$Cr(CO)_6$	CH_3CN	6	1-Octene	CCl_4	40	90	40
4	$Mo(CO)_6$	CH_3CN	4	1-Octene	ETCA	40	90	80
5	$Cr(CO)_6$	CH_3CN	6	1-Octene	ETCA	40	65	27

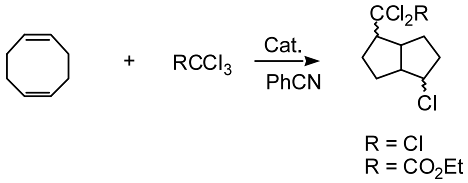
[a] Reaction conditions: pre-complexation was carried out by refluxing the charged catalyst in acetonitrile for the specified time, followed by the addition of 1-octene and the polyhalides, and then continue refluxing for the specified time under dinitrogen. The molar ratio: catalyst–1-octene–polyhalide was 0.05:1:6.6 respectively. [1-octene] = 0.7 M.

[b] The yields were determined by GC quantitative analysis using anisole as internal standard in Experiments 1–3, and 1-methylnaphthalene in Experiments 4 and 5.

products were calculated using MM2 Molecular Modeling program, and the resulting dihedral angles between the H atom α to Cl and the three adjacent H atoms were determined. These angles were correlated with ^{1}H-NMR coupling constants using the Karplus equation. The coupling constants for the cis and trans isomers were 9, 2, 0.5 and 2.5, 2, 1.8 Hz, respectively. The NMR signal in the spectrum of the product appeared as a broad multiplet with $W_{1/2}$ of 25 Hz. Obviously, such signal width should be correlated only with cis product. Mechanistically, this is the expected product (vide infra).

The addition reaction was also examined with dienes, and the results are presented in Table 3. The addition of CCl_4 to 1,5-hexadiene resulted in a mixture of the 1:1 and 1:2 addition products in moderate yields, the latter was obtained as a mixture of diastereomers (Scheme 1). The only catalyst known to induce a 1:2 addition reaction is $RuCl_2(PPh_3)_3$ in 35% yield [2c]. The reaction with ethyl trichoroacetate gave mostly 1:1 addition product, albeit in low yield.

Only 1:1 addition product was obtained with 1,5-cyclooctadiene, both with CCl_4 and ethyl trichloroacetate in benzonitrile as solvent. The reaction was found to proceed according to Eq. 2.



(2)

Two diastereomers of the substituted [3,3,0]bicyclooctane were formed in a 1:4 ratio, as determined by ^{1}H-NMR and GC. The main experimental evidence supporting the above bicyclic structure was the lack of vinyl H signals in the ^{1}H-NMR spectrum on one hand, and on the other hand, the single addition of $RCCl_3$ to the 1,5-cyclooctadiene system, i.e. a 1:1 addition product, as was verified by MS. In addition, PET spectrum indicated the presence of four tertiary CH atoms, in

Table 2
Addition reactions of α-polyhalides to olefins catalyzed by $Mo(CO)_6$ [a]

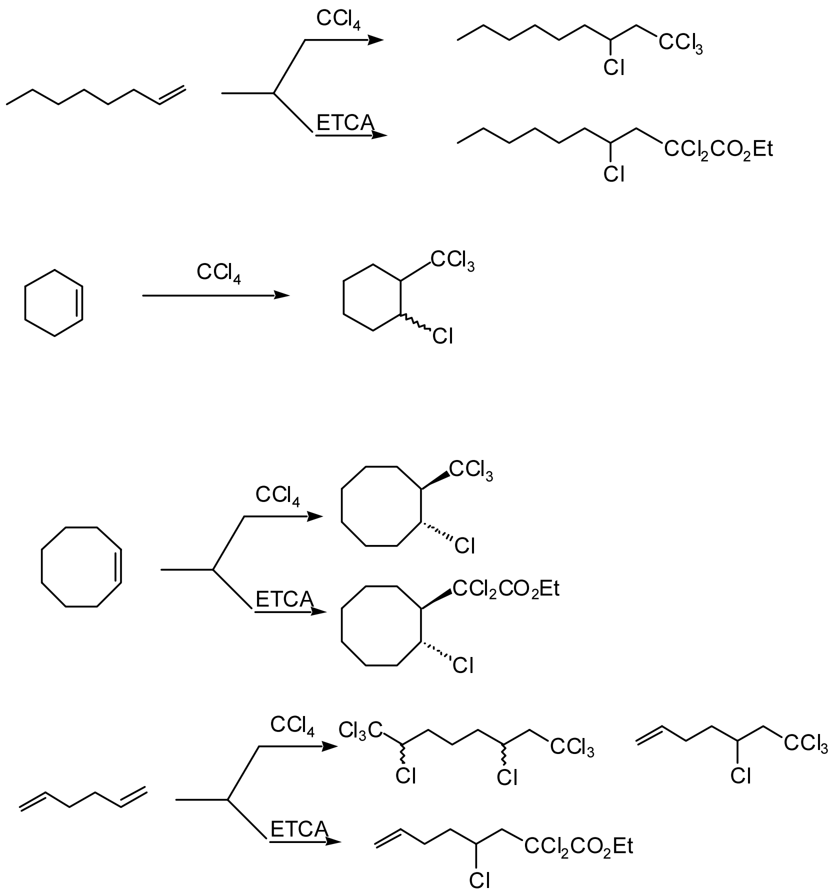
Exp no.	Catalyst (charged)	Solvent	Substrate	Poly-halide	Time (h)	Temperature (°C)	Conv. (%)	Yield (%) [b]
1	$Mo(CO)_6$	CH_3CN	1-Octene	CCl_4	24	80	99	85
2	$Mo(CO)_6$	C_2H_5CN	1-Octene	CCl_4	6.5	90	98	74
3	$Mo(CO)_6$	PhCN	1-Octene	CCl_4	4	100	78	64
4	$Mo(CO)_6$	CH_3CN	1-Heptene	CCl_4	23	80	90	80
5	$Mo(CO)_6$	CH_3CN	Cyclohexene	CCl_4	70	80	52 [c]	23
6	$Mo(CO)_6$	PhCN	Cyclohexene	CCl_4	47	100	58 [d]	38
7	$Mo(CO)_6$	CH_3CN	1-Octene	ETCA	45	80	97	80
8	$Mo(CO)_6$	PhCN	1-Octene	ETCA	8	100	86	54
9	$Mo(CO)_6$	PhCN	Cyclooctene	ETCA	7.5	100	52	22
10	$Mo(CO)_6$	CH_3CN	Cyclooctene	CCl_4	7	80	82	88
11	$Mo(CO)_6$ (hydroquinone)	CH_3CN	Cyclooctene	CCl_4	7	80	83	70
12	$Mo(CO)_6$ (galvinoxyl)	CH_3CN	Cyclooctene	CCl_4	14	80	56	62
13	$Mo(CO)_6$	PhCN	Cyclooctene	CCl_4	4.5	100	95	92

[a] Reaction conditions: The catalyst, substrate and polyhalide in a 0.05:1:6.6 molar ratio respectively, were refluxed under dinitrogen for the specified period of time. [substrate] = 0.7 M.

[b] The yields were determined by quantitative GC analysis using anisole as internal standard in Experiments 1,2,4,5,6, and 1-methylnaphthalene in Experiments 3,7, and 13.

[c] Diastereomers cis–trans in 3:4 ratio (GC).

[d] Diastereomers cis–trans in 1:1 ratio (GC).



Scheme 1. The reactions are in a nitrile solvent with $Mo(CO)_6$.

agreement with the above structure. The diastereomeric mixture was not separated. The stereochemistry of the two isomers is of interest. The system contains four chiral centers and could generate eight racemic diastereomers. Again we resorted to the ^{1}H-NMR spectrum of the H atom α to Cl, the only clearly visible and separated signal. The structures of all eight addition products were calculated using MM2 Molecular Modeling program, and the resulting dihedral angles between the H atom α to Cl and the three adjacent H atoms were determined. These angles were correlated with ^{1}H-NMR coupling constants (Karplus equation). The two stereoisomers, with both CCl_4 and ETCA, were obtained in a 1:4 ratio (NMR and GC). The NMR signal of the major product appeared as an unresolved singlet, while that of the minor isomer as a double doublet with $J = 8$ and 9 Hz. The two isomers were assigned structures **A** and **B** in accordance with the calculated coupling constants of 6, 4 and 0.5 Hz for **A** and 9, 7, and 6 Hz for **B**.

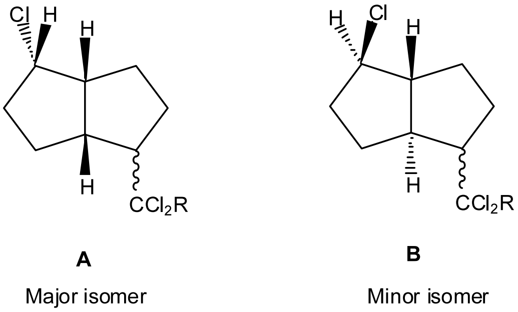
Table 3
Addition reactions of α-polyhalides to dienes catalyzed by $Mo(CO)_6$ [a]

Exp no.	Catalyst (charged)	Solvent	Substrate	Poly-halide	Time (h)	Temperature (°C)	Yield % 1:1 product	Yield % [b] 1:2 product
1	$Mo(CO)_6$	CH_3CN	1,5-Hexadiene	CCl_4	22	80	20	22 [c]
2	$Mo(CO)_6$	CH_3CN	1,5-Hexadiene	ETCA	65	80	25	9
3	$Mo(CO)_6$	PhCN	1,5-Cyclo octadiene	CCl_4	69	100	64	–
4	$Mo(CO)_6$	PhCN	1,5-Cyclo octadiene	ETCA	68	100	42	–

[a] Reaction conditions: The catalyst, substrate and polyhalide in a 0.05:1:6.6 molar ratio respectively, were refluxed under dinitrogen for the specified period of time. [substrate] = 0.7 M.

[b] The yields were determined by GC quantitative analysis using anisole as internal standard in Experiments 1, and 1-methylnaphthalene in Experiments 2–4.

[c] Diastereomers in 1:1 ratio (GC).

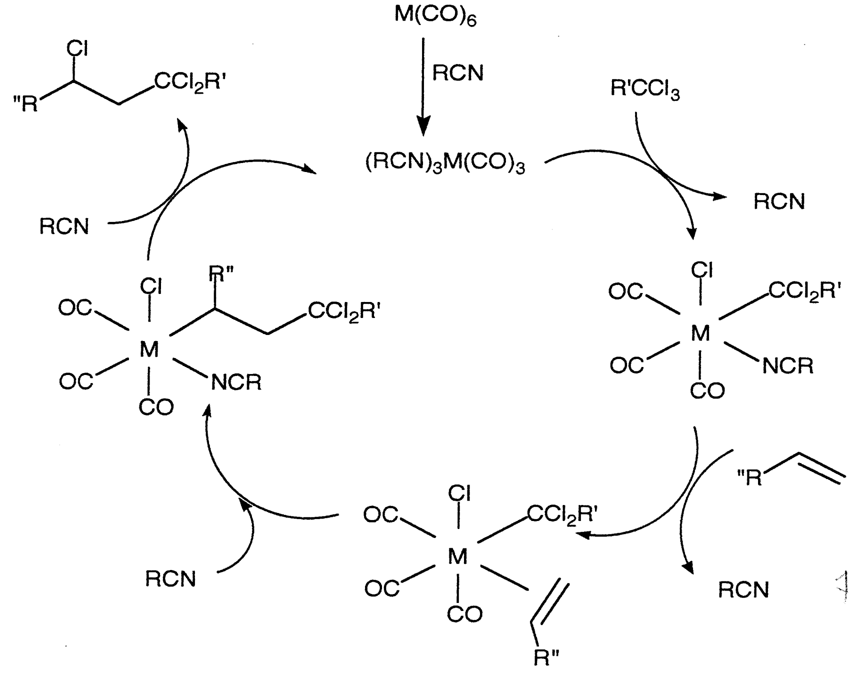


It was impossible to ascertain the stereochemistry of the CCl_2R group, as its orientation did not affect the coupling pattern of the H atom α to Cl. Since no double addition products were formed in the above reaction, it is logical to assume a concerted coordination of the Mo atom to both double bonds, and concerted delivery of the Cl and CCl_2R groups, with either cis or trans ring closure.

We would like to comment on the mechanism of the addition reaction that has not yet been definitely established in the chemical literature. The central question is whether the mechanism involves free radicals, or is it classical organometallic reaction mechanism. An ionic mechanism, in which a negatively charged complex resulting from the addition of Cl anion to the metal atom (Lewis acid) is formed, should also be considered. The free radical mechanism can be ruled out, since addition of hydroquinone or galvinoxyl (Table 2, Expts. 11 and 12) has hardly inhibited the reaction. The possibility of ionic mechanism was checked by carrying out an addition reaction with 1-octene, CCl_4 and $Mo(CO)_6$ in acetonitrile in the presence of a large excess of finely ground NaCl. The possible participation of the added Cl anion should have inhibited the addition reaction. However, after 3.5 h reaction time, the addition product was obtained in 65% yield. Thus, the reaction seems to be indifferent to the presence Cl anion, and it is concluded that the mechanism is neither ionic.

We therefore conclude that most probably the mechanism is of a classical organometallic nature, as proposed by the following catalytic cycle. The formation of the active catalyst, $(CH_3CN)_3Mo(CO)_3$, is followed by oxidative addition of the α-polychloride to the Mo atom, after the dissociation of two nitrile ligands. Next, an olefin substrate coordinates to the metal atom, after vacation of another nitrile coordination site. It is followed by an insertion reaction of the olefin into the M–C bond. Subsequent reductive elimination and back coordination of the nitrile ligands generates the final addition product, and regenerates the active catalytic species. It is evident that this mechanism depends on the facile dissociation and complexation of the nitrile ligands, made feasible by running the reaction in a nitrile solvent.

In conjunction with the above mechanism, when cyclic alkene substrates are being used, stereospecificity



Proposed catalytic cycle

should be anticipated. This is true, since insertion of olefin to the M–C bond should occur in a syn mode from the Mo atom which is coordinated to one face of the double bond. The subsequent reductive elimination should occur with retention of the carbon atom configuration. The resulting product should therefore have the Cl and CCl_2R substituents in cis stereochemistry.

However, with cyclohexene a diastereomeric mixture of cis and trans isomers was obtained, while with cyclooctene, only the cis isomer was generated. We have no experimental proofs to support any explanation for the cyclohexene case. However, one may speculate that isomerization of the initially formed cis product may have taken place. The Mo atom is known for its electrophillicity that may account for such isomerization by ionizing the Cl atom in the polar nitrile solvent, consequently scrambling the configuration. Alternatively, the Mo atom may oxidatively add to the C–Cl bond leading to configuration inversion of the C atom followed by reductive elimination with configuration retention. Some experimental support for this hypothesis may be gained from the observation that the content of the cis isomer diminishes with longer reaction time (Expt. 5 and 6, Table 2) using cyclohexene, while with cyclooctene the reaction time is substantially shorter, and therefore only the kinetic cis isomer was obtained.

In conclusion, $Mo(CO)_6$ in nitrile solvents, such as acetonitrile, propionitrile and benzonitrile, function as a precatalyst in the addition reaction of α-polyhalides to olefins. The use of the commercially and relatively inexpensive $Mo(CO)_6$ substantially simplifies the process. The yields of the addition products are satisfactory. The reaction conditions are mild, viz. refluxing in acetonitrile in an open system. Non-conjugated acyclic dienes gave mixtures of 1:1 and 1:2 addition products. 1,5-cyclooctadiene resulted in the selective formation of an intramolecular cyclization product.

3. Experimental

All reactions and preparative manipulations were carried under nitrogen atmosphere, using Schlenck techniques. Acetonitrile was distilled from P_2O_5 prior to use. Propionitrile and benzonitrile, reagent grade, were used without purification.

In a typical reaction, the catalyst, olefin substrate and the polyhalide, in a molar ratio of 0.05:1:6.6, were refluxed in the solvent under dry nitrogen atmosphere for the time specified in Tables 1–3; [olefin substrate] = 0.7 M.

Isolation of the product was conducted by distilling the solvent and the excess polyhalide, followed by precipitation of the catalyst (oxidized) with pet ether followed by passing the resulting clear solution through a short silica column. Isolation of addition products with ETCA was followed by trituration with 1:1 ethyl acetate–pet ether. The crude product was then purified by vacuum distillation.

^1H- and ^{13}C-NMR spectra of the products were measured on a Bruker AC-200 spectrometer, in $CDCl_3$ solution with Me_4Si as internal standard, and are expressed in ppm.IR spectra were recorded on a Nicolet 1600 FT-IR spectrometer.

GC analyses were performed on a HP 5890 instrument fitted with a FID detector and an Altech capillary column, Elcho-cap. SE-30 (30 m × 0.25 mm).GC–MS analysis was performed on a Varian 3400 instrument with a DB-1 column (30 m × 0.25 mm), connected to a Finnigan mat ITD 800 ion trap detector.Mass Spectra were recorded on a VG-Autospec. M-250 mass spectrometer.

3.1. *1,1,1,3-Tetrachlorononane (Tables 1 and 2, 1–3)*

B.p. = 112 °C/1 mmHg. ^1H-NMR: $\delta = 0.9$ (t, 3H), 1.4 (m, 8H), 1.9 (m, 2H), 3.2 (ddd, 2H), 4.2 (m, 1H). MS: m/z (%) = 223(19), 193(29), 185(35), 157(100), 149(29), 132(58), 121(94), 109(73).

3.2. *1,1,1,3-Tetrachlorooctane (Table 2, 4)*

B.p. = 54 °C/0.1 mmHg. ^1H-NMR: $\delta = 0.9$ (t, 3H), 1.5 (m, 6H), 1.9 (m, 2H), 3.2 (ddd, 2H), 4.2 (m, 1H). MS: m/z (%) = 223(7), 187(11), 179(23), 143(54), 107(51), 97(43), 82(58), 69(67), 55(97), 41(100).

3.3. *1-Chloro-2-trichloromethylcyclohexane (Table 2, 5–6)*

B.p. = 53 °C/0.05 mmHg. ^1H-NMR: $\delta = 1.1–2.3$ (m, 12H), 2.60 (m, 1H), 2.63 (m, 1H), 4.47 (m, 1H), 4.95 (s, 1H). MS: m/z (%) = 199(11), 163(43), 127(35), 109(10), 91(26), 81(100).

3.4. *1-Chloro-2-trichloromethylcyclooctane (Table 2, 10–13)*

B.p. = 80–90 °C/0.3 mmHg. ^1H-NMR: $\delta = 1.2–2.7$ (m, 13H), 4.2 (m, 1H). MS: m/z (%) = 262(1), 191(100), 155(86), 119(36), 109(50), 93(6), 81(7), 67(10).

3.5. *Ethyl 2,2,4-trichlorodecanoate (Table 1, 4–5, and Table 2, 7–8)*

B.p. = 94 °C/0.1 mmHg. ^1H-NMR: $\delta = 0.9$ (t, 3H), 1.4 (m, 11H), 1.8 (m, 2H), 2.9 (ddd, 2H), 4.2 (m, 1H), 4.3 (q, 2H). IR (neat): $v = 1762$(s), 1748(sh), 1467, 1256, 1201, 1027 cm^{-1}. MS: m/z (%) = 231(13), 195(7), 156(81), 128(27), 121(39), 97(28), 81(27), 69(55), 55(100), 43(89).

3.6. Ethyl dichloro(2-chlorocyclooctyl)ethanoate (Table 2, 9)

B.p. = 118 °C/0.3 mmHg. ^{1}H-NMR: $\delta = 1.3$–2.6 (m, 16H), 4.2–4.4 (m, 1H + 2H). ^{13}C-NMR: $\delta = 13.9$, 22.3–36.5, 48.8, 61.9(d), 63.8, 91.6, 166.0. IR (neat): $\nu = 1760$, 1468, 1446, 1235(br), 1029 cm^{-1}. MS: *m*/*z* (%) = 301(19), 281(11), 265(90), 229(100), 201(16), 193(88), 156(32), 119(23), 109(25), 91(7), 79(9).

3.7. 1,1,1,3-Tetrachloro-7-heptene (Table 3, 1, 1:1 addition product)

b.p. = 39 °C/0.1 mmHg. ^{1}H-NMR: $\delta = 1.9$ (m, 2H), 2.3 (m, 2H), 3.2 (ddd, 2H), 4.2 (m, 1H), 5.1 (m, 2H), 5.8 (m, 1H). MS: *m*/*z* (%) = 199(11), 163(27), 149(13), 127(60), 109(37), 91(45), 67(89), 55(85), 41(100).

3.8. 1,1,1,3,6,8,8,8-Hexachlorooctane (Table 3, 1, 2:1 addition product)

B.p. = 114–120 °C/0.3 mmHg. ^{1}H-NMR: $\delta = 1.6$–2.4 (m, 4H), 3.2 (dddd, 4H), 4.3 (m, 2H). MS: *m*/*z* (%) = 317(50), 281(33), 245(50), 221(30), 183(28), 159(31), 143(55), 123(44), 109(100), 87(33), 75(58), 61(23), 43(58).

3.9. Ethyl 2,2,4-trichloro-7-octenoate (Table 3, 2, 1:1 addition product)

B.p. = 69 °C/0.2 mmHg. ^{1}H-NMR: $\delta = 1.4$ (t, 3H), 1.9 (q, 2H), 2.2 (m, 2H), 3.1 (ddd, 2H), 4.3 (m, 3H), 5.0 (m, 2H), 5.8 (m, 1H). ^{13}C-NMR: $\delta = 13.7$, 30.1, 37.6, 52.8, 57.3, 64.0, 82.7, 116.1, 136.4, 165.4. IR (neat): $\nu =$ 1768, 1725(sh), 1446, 1255(br), 1202, 1097, 1027, 918, 697 cm^{-1}. MS: *m*/*z* (%) = 237(45), 201(23), 156(54), 127(30), 109(19), 91(37), 81(56), 67(61), 55(33), 41(100).

3.10. Ethyl ethyl 2,2,4,7,9,9-hexachlorodecanedioate (Table 3, 2, 2:1 addition product)

B.p. = 124 °C/0.1 mmHg. ^{1}H-NMR: $\delta = 1.4$ (t, 6H), 2.1 (m, 4H), 2.7 (dddd, 4H), 4.3 (m, 6H). ^{13}C-NMR: $\delta = 13.7$, 30.5, 33.8–35.3, 49.8, 52.5(d), 56.9, 57.3, 64.1, 82.3, 165.2. IR (neat): $\nu =$ (1797)*, 1756, 1748(sh), 1445, 1396, 1255, 1201, 1097, 1024, 963. *GC–MS: *m*/*z* (%) = 392(6), 355(6), 321(29), 283(25), 245(29), 209(31), 183(29), 156(49), 122(45), 91(66), 75(100), 51(60).

*The 2:1 addition product was partially decomposed during its work-up, to give (assumably) the lactone. Thus, distillation of the reaction mixture afforded a mixture of these two products.

3.11. 2-Trichloromethyl-6-chlorobicyclo[3.3.0]octane (Table 3, 3)

B.p. = 70 °C/0.1 mmHg. ^{1}H-NMR: $\delta = 1.7$–2.3 (m, 8H), 2.8 (m, 3H), 4.2 (m, 1H). ^{13}C-NMR (J MOD): $\delta =$ 31.1(d, o), 32.1(o), 34.9(o), 45.5(e), 55.9(e), 65.3(e), 69.0(e), 103.5(o). IR (neat): $\nu = 1450$, 1303, 1237, 1064, 1031, 845, 812, 779, 719. MS: *m*/*z* (%) = 262(1), 224(6), 198(17), 189(42), 153(46), 143(87), 117(24), 107(100), 91(31), 79(81), 67(33), 59(22), 51(17), 39(34).

3.12. Ethyl dichloro(2-bicyclo[3.3.0]-6-chlorooctyl)ethanoate (Table 3, 4)

B.p. = 90 °C/0.05 mmHg. ^{1}H-NMR: $\delta = 1.4$ (t, 3H), 1.6–2.2 (m, 8H), 2.6–2.8 (m, 3H), 4.1 (m, 1H), 4.3 (q, 2H). ^{13}C-NMR: $\delta = 31.1$(t), 35.2(d), 49.9, 56.0, 59.4, 60.3, 62.4, 65.4, 88.1, 170.5. IR (neat): $\nu = 1756$, 1451, 1369, 1296, 1242(br), 1023, 847,830, 693 cm^{-1}. MS: *m*/*z* (%) = 300(1), 263(14), 227(11), 189(58), 156(100), 128(24), 117(44), 107(39), 91(35), 79(49), 67(25), 53(14), 41(23).

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