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Telechelic Oligomers by Halogen Atom Transfer Radical Addition

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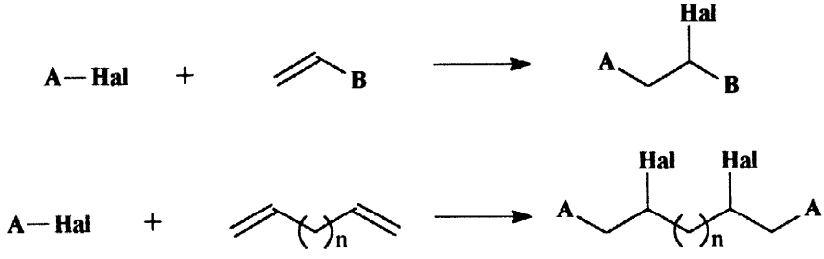
Abstract

Monodispersed telechelic oligomers have been efficiently prepared by Fe^0-$FeCl_3$ promoted halogen atom transfer radical of functional telogens and taxogens.

Keywords: Radicals and radical reactions; oligomers; Halogens and compounds; Iron and compounds.

Monodispersed telechelic oligomers, especially diols, are widely used as anti-wear and anti-tear additives for metallic surfaces, greasiness grade improvers for hydrocarbons, prepolymers for paints[1-2], and in the preparation of polyesters and polyurethanes[3-5].

The preparation of telechelic chlorinated oligomers with remarkable properties[1-5] has been deeply investigated by B. Boutevin, who devised two synthetic strategies based on halogen atom transfer radical addition (HATRA)[3-5]: *i*) the monoaddition of a functional telogen to a functional taxogen, and *ii*) the addition of a functional telogen to both ends of a nonconjugated diene (Scheme 1).

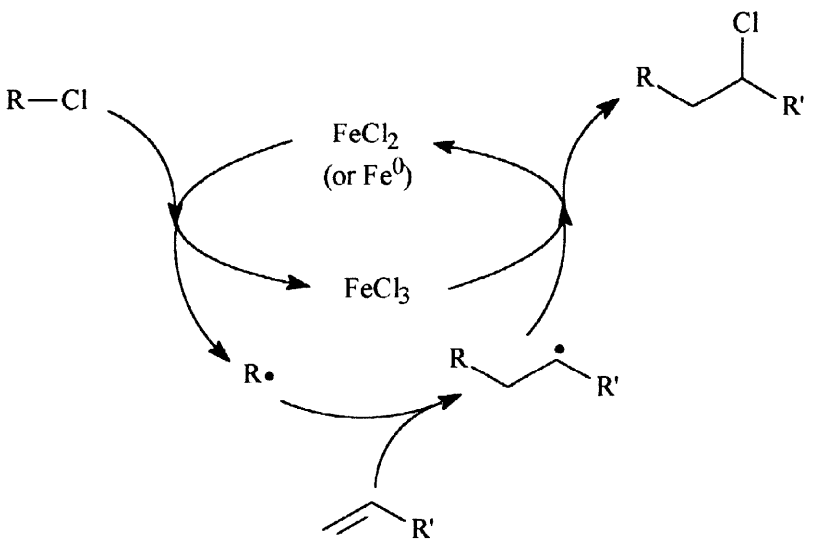


Scheme 1

PII: S0040-4020(98)00419-0

On using redox catalysts, such as CuCl, $FeCl_3$-benzoin and especially $RuCl_2(PPh_3)_3$[1-9], much more selective reactions have been obtained with respect to the classical peroxides initiation[10-11]. Even if high temperatures were required for the reaction, the results were satisfactory, except from trichloroethanolacetate (TCEA), one of the most important telogens[3-5].

Recently we have investigated on Fe^0 promoted Kharasch additions of CCl_4[12] or methyl 2,2-dihalocarboxylates[13-14] to terminal olefins obtaining useful synthetic intermediates; however, starting from allyl acetate, a valuable taxogen for the preparation of telechelic oligomers, a high amount of telomers with order>1 was also obtained. The formation of these telomers was inhibited by adding $FeCl_3$ to Fe^0, giving rise to a conproportionation to $FeCl_2$, another efficient reducer for the halogen atom transfer radical addition promotion[15-17]; it must be pointed out, however, that the ferric halide also efficiently traps the intermediate radical adduct through a ligand-transfer, thus preventing the attack to another olefinic bond (Scheme 2).



Scheme 2

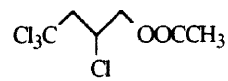
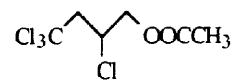
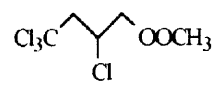
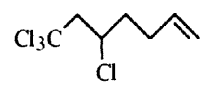
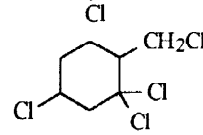
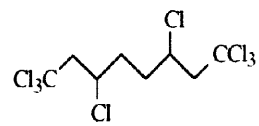
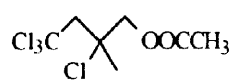
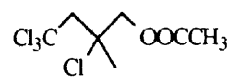
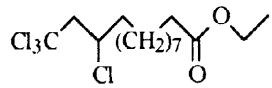
The Fe^0-$FeCl_3$ reagent system also promotes the efficient cyclization of protected N-allyl-2,2-dihaloamides to 2-pyrrolidinone[18]. Now we report that by the same reagent monodispersed telechelic oligomers are obtained in high yields at moderate temperature, through the halogen atom transfer radical addition of functional telogens to functional taxogens. As far as we know the use of this promoter in HATRA has been reported only in few patents[19-23]

Results and discussion

We tested CCl_4, TCEA, and methyl α-polyhalocarboxylates as telogens for the Kharasch's

addition to functional taxogens. Working on CCl_4 and allyl acetate[1], we obtained the best results at high substrate concentration in dimethylformamide (DMF) with a 1:2 Fe^0:$FeCl_3$ ratio (Table 1). With respect to the old procedure with Fe^0 alone (Table 1, items 1, 7) the lower amount of iron atoms now requested for total conversion (Table 1, item 2 and 8) is remarkable; furthermore on adding $FeCl_3$, the selectivity of the transformation is much higher since oligomers with order >1 are virtually absent, and yields increase significatively. The quality (filings or the much more pure turnings) of the iron metal has no influence on the reaction as shown by items 2 and 3 of

Table 1
CCl_4 addition to different taxogens[a)]

item	Taxogen (mmol/mmol CCl_4)	product	Fe^0 kind[c)]	time h	conv. %[d)]	yield[b)] %
1[e)]	Allylacetate (32/48)		filing	5	100	75 (17)
2	Allylacetate (32/48)		turning	5	100	92 (1)
3	Allylacetate (32/48)		filing	5	100	93 (2)
4	1,5-hexadiene (72/24)		filing	5	[f)]	53
5	1,5-hexadiene (72/24)		filing	24	[f)]	71
6	1,5-hexadiene (16/48)		filing	5	[f)]	83
7[e)]	Metallylacetate (32/48)		filing	5	99	72 (6)
8	Metallylacetate (32/48)		filing	5	100	82 (2)
9[g)]	Ethyl ω-undecenoate (32/48)		turning	5	99	84 (3)

a) all reactions were carried out in DMF (4.5 ml) under argon at 80°C. using 0.075 [moles/CCl_4 moles] of Fe^0 and 0.15 [moles/CCl_4 moles] of $FeCl_3$; b) yield of isolated material: in parenthesis the yield of the telomer of order 2; c) iron filing BDH, iron turning Fluka; d) GC value; e) the reaction was carried out in DMF (4.5 ml) under argon at 80°C, using 0.333 [moles/CCl_4 moles] of Fe^0; f) not determined; g) 7 ml of DMF were used.

[1]Unsatisfactory results are obtained when the hydroxyl group is unprotected[12].

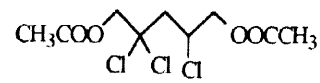
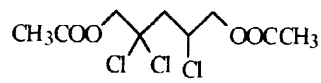
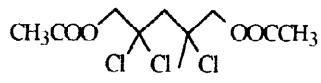
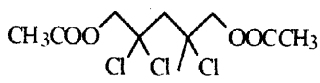
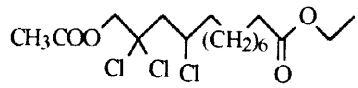
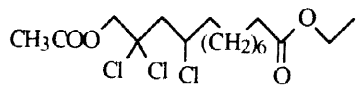
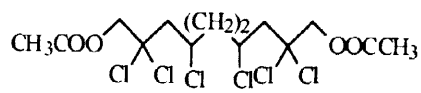
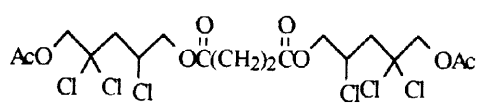
Table 1. The procedure has been extended to a number of functionalized taxogens affording excellent results in any case (Table 1).

The reaction on 1,5-hexadiene deserves some comment[1-2]. This substrate has indeed two identical olefinic end groups and two different products can be selectively obtained by modifying the reagents ratio: on using an excess of 1,5-hexadiene the monoadduct is produced (Table 1, item 4), whereas with an excess of CCl_4 the diadduct is obtained in high yield (Table 1, item 6).

On working with olefin excess (72:24 1,5-hexadiene:CCl_4) but extending the time from 5h to 24h, the 1,1,5-trichloro-2-chloromethylcyclohexane is smoothly obtained (Table 1, item 5), showing that Fe^0-$FeCl_3$ is able to extract a Cl atom even from a trichloromethyl group. Unlike a previous report[11], no C5 or C7 carbocycle is observed.

Table 2

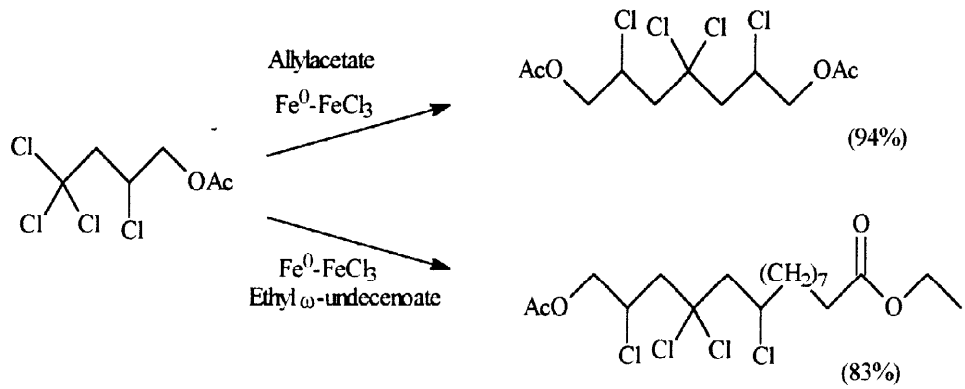
TCEA addition to different taxogens[a)]

item	Taxogen (mmol/mmolTCEA)	product	Fe^0 kind[c)]	conv. %[d)]	yield[b)] %[e)]
1	Allylacetate (32/40)		turning	97	93 (1)
2	Allylacetate (32/40)		filing	100	93 (1)
3	Metallylacetate (32/40)		turning	95	86 (3)
4	Metallylacetate (32/40)		filing	92	90 (3)
5	Ethyl ω-undecenoate (32/40)		turning	95	83
6	Ethyl ω-undecenoate (32/40)		filing	98	88
7	1,6-hexadiene (16/48)		filing	f)	89
8	Diallyl succinate (16/48)		filing	100	70

a) all reactions were carried out in DMF (4.5 ml) under argon at 100°C (24 h), using 0.075 [moles/TCEA moles] of Fe^0 and 0.15 [moles/TCEA moles] of $FeCl_3$; b) in parenthesis the yield of the telomer of order 2; c) iron filing BDH, iron turning Fluka; d) GC value; e) yield of isolated material; f) not determined.

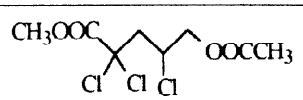
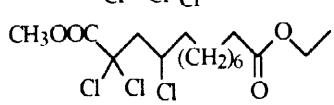
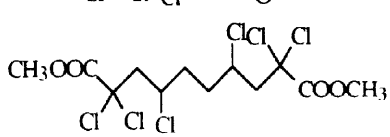
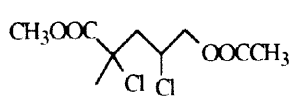
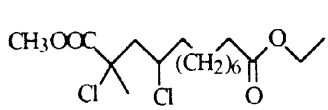
[1] A dangerous explosion took place when CCl_4 addition to 1,5-hexadiene was tried with Fe^0 turnings from Fluka.

The efficiency of the Fe^0-$FeCl_3$ system has prompted its use with trichloroethanol (TCE), a typical functional telogen, for carrying out the preparation of telechelic diols; poor results have been, however, observed. On protecting the TCE hydroxy group by acetylation, excellent yields have been obtained with a number of functionalized taxogens (Table 2). Owing to the lower reactivity of this acetate (TCEA) with respect to CCl_4, a lower amount of telogen is now necessary, while temperature being increased to 100°C for speed up the halo-addition. Under the same reaction conditions even the heavy functionalized 2,4,4,4-tetrachlorobutyl acetate (Scheme 3), a telechelic adduct from the Kharasch's addition of CCl_4 to allyl acetate (Table 1, item 2), gives rise to high yields transformation.



Scheme 3

Table 3. Methyl α-polyhalocarboxylates addition to different taxogens.

item	Taxogen (mmol telogen/mmol)	product	T °C	conv. %[a]	yield %[b]
1[c]	Allylacetate (32/48)		100	91	83
2[c]	Ethyl ω-undecenoate (32/48)		100	99	93
3[c]	1,5-hexadiene (16/48)		100	100	76
4[d]	Allylacetate (6/4)		120	94	89
5[d]	Ethyl ω-undecenoate (4.4/4)		120	82	63

a) GC value; b) yield of isolated material; c) reaction was carried out in DMF (4.5 ml) under argon (24 h), using 0.075 [moles/MTCA moles] of Fe^0 and 0.15 [moles/MTCA moles] of $FeCl_3$; d) reactions 4 and 5 were carried out in DMF/dichloroethane (1 and 4 ml respectively) under argon (17 h), using 0.05 [moles/MDCP moles] of Fe^0 and 0.1 [moles/MDCP moles] of $FeCl_3$.

Finally, Fe^0-$FeCl_3$ promotes also the efficient addition of methyl trichloroacetate (MTCA) or methyl 2,2-dichloropropanoate (MDCP) to allyl acetate or ethyl ω-undecenoate (Table 3). MDCP, giving rise to a more smooth radical generation and being also more expensive than the used taxogens, has been telomerized in high yield even with an unusual telogen:taxogen ratio > 1 (Table 3, items 4 and 5).

Experimental part

^1H NMR spectra were recorded on a Bruker WP80 spectrometer. Mass spectra were obtained on a combined HP 5890 GC - HP 5989A MS Engine. Iron filings (90%) were purchased from BDH and iron turnings (>99%) from Fluka; other reagents and solvents were standard grade commercial products and used without further purification. DMF was dried over three batches of 3Å sieves (5% w/v, 12 h). Methyl 2,2-dihalocarboxylates were prepared according to a literature procedure[24-25]. Known products were identified by comparison of spectral data with those of samples prepared according to literature[3-5, 12].

General procedure for alkyl-halo-additions using CCl_4 or TCEA: preparation of 2,4,4,4-tetrachlorobutyl acetate. Iron filings (3.6 mmol) were weighted in a Schlenk tube[1] and then 26 % (w/v) $FeCl_3$ in DMF (4.5 ml), allylacetate (32 mmol), and CCl_4 (48 mmol) were added under argon. The mixture was stirred at 80°C and after 5 h diluted with 2.5% HCl (15 ml) and extracted with CH_2Cl_2 (2 x 8 ml). The organic layers were collected, dried over Na_2SO_4 and then evaporated. The crude oil was distilled under vacuum, affording 6.91 g of 2,4,4,4-tetrachlorobutyl acetate (92%).

1,1,5-trichloro-2-chloromethyl-cyclohexane

^1H NMR δ ($CDCl_3$): 1.35-1.85 (2H, m, -CHC$\underline{H_2}$C$\underline{H_2}$CHCl-); 2.17-2.46 (3H, m, -CHC$\underline{H_2}$C$\underline{H_2}$CHCl-); 2.50 (1H, dd, J=11.0, 13.8 Hz, -CCl_2C$\underline{H_2}$CHCl-); 3.15 (1H, dq, J=2.1, 4.0, 13.8 Hz, -CCl_2C$\underline{H_2}$CHCl-); 3.42 (1H, dd, J=9.8, 11.0 Hz, CHC$\underline{H_2}$Cl); 4.12 (1H, m, -CH_2C$\underline{H}$ClCH_2-); 4.23 (1H, dd, J=2.7, 11.0 Hz, CHC$\underline{H_2}$Cl). MS (EI, 70 eV) m/z: 199 (10%), 163 (100%), 127 (42%), 91 (45%). Found: C, 35.5; H, 4.4. $C_7H_{10}Cl_4$ requires C, 35.63; H, 4.27. Oil.

ethyl 10,12,12,12-tetrachloro-dodecanoate

^1H NMR δ ($CDCl_3$): 1.25 (3H, t, -$OCH_2C\underline{H_3}$); 1.30-2.05 (14H, m, -($C\underline{H_2}$)$_7$CHClCH_2CCl_3); 2.31 (2H, m, -$CH_2C\underline{H_2}COOCH_2CH_3$); 3.12 (1H, dd, -CHCl$C\underline{H_2}CCl_3$); 3.27 (1H, dd, -CHCl$C\underline{H_2}CCl_3$); 4.15 (2H, q, -$OC\underline{H_2}CH_3$); 4.23 (1H, m, -$CH_2C\underline{H}ClCH_2CCl_3$). MS (EI, 70 eV) m/z: 175 (4%), 157 (3%), 147 (3%), 133 (3%),

[1] High headspaces negatively affect the reaction, owing to the partition of olefin and polyhalomethane between liquid and vapour phases. The best yields are obtained on working with Schlenk capacity little higher than the reaction volume.

101 (25%); 88 (100%); 70 (15%). Found: C, 45.9; H, 6.7%. $C_{14}H_{24}Cl_4O_2$ requires C, 45.92; H, 6.61%. Oil.

di 5-acetoxy-2,4,4-trichloro-pentyl succinate

^{1}H NMR δ ($CDCl_3$): 2.18 (6H, s, 2 x $C\underline{H}_3COO$-); 2.75 (4H, s, 2 x -$C\underline{H}_2COO$-); 2.81 (4H, d, 2 x -$CHClC\underline{H}_2CCl_2$-); 4.30-4.53 (6H, m, 2 x -$COOC\underline{H}_2C\underline{H}ClCH_2$-); 4.57 (4H, s, 2 x -$COOC\underline{H}_2CCl_2$-). MS (EI, 70 eV) m/z: 318 (3%); 231 (7%); 229 (8%); 143 (47%);101 (100%). Found: C, 37.1; H, 4.0%. $C_{18}H_{24}Cl_6O_8$ requires C, 37.20; H, 4.16%. Oil.

1,5-diacetoxy-2,2,4-trichloro-4-methyl-pentane

^{1}H NMR δ ($CDCl_3$): 1.83 (3H, s, -($C\underline{H}_3$)CCl-); 2.13 (3H, s, $C\underline{H}_3COO$-); 2.16 (3H, s, $C\underline{H}_3COO$-); 2.90 (1H, d, J=32 Hz, -CCl_2-$C\underline{H}_2(CH_3)CCl$-); 2.99 (1H, d, J=32 Hz, -CCl_2-$C\underline{H}_2(CH_3)CCl$-); 4.33 (2H, s, -$COOC\underline{H}_2C(CH_3)Cl$-); 4.58 (2H, s, -$COOC\underline{H}_2CCl_2$-). MS (EI, 70 eV) m/z: 274 (2%); 232 (2%); 196 (7%); 161 (4%); 136 (4%); 118 (5%); 73 (10%); 43 (100%). Found: C, 39.3; H, 5.1%. $C_{10}H_{15}Cl_3O_4$ requires C, 39.30; H, 4.95%. Oil.

ethyl 13-acetoxy-10,12,12-trichloro-tridecanoate

^{1}H NMR δ ($CDCl_3$): 1.28 (3H, t, -$OCH_2C\underline{H}_3$); 1.30-1.95 (14H, m, -$(C\underline{H}_2)_7CHClCH_2$-); 2.18 (3H, s, $C\underline{H}_3COO$-); 2.32 (2H, t, -$C\underline{H}_2COOCH_2CH_3$); 2.69 (1H, dd, J=3.5, 15.7 Hz, -$CHClC\underline{H}_2CCl_2$-); 2.87 (1H, dd, J=7.1, 15.7 Hz, -$CHClC\underline{H}_2CCl_2$-); 4.16 (2H, q, -$OC\underline{H}_2CH_3$); 4.24 (1H, m, -$C\underline{H}ClCH_2CCl_2$-); 4.60 (2H, s, -$COOC\underline{H}_2CCl_2$-). MS (EI, 70 eV) m/z: 403 (1%); 357 (2%); 328 (3%); 247 (4%); 189 (3%); 98 (38%); 88 (100%). Found: C, 50.7; H, 7.3%. $C_{17}H_{29}Cl_3O_4$ requires C, 50.57; H, 7.24%. Oil.

ethyl 15-acetoxy-10,12,12,14-tetrachloro-pentadecanoate

^{1}H NMR δ ($CDCl_3$): 1.37 (3H, t, -$OCH_2C\underline{H}_3$); 1.30-1.95 (14H, m, -$(C\underline{H}_2)_7CHClCH_2$-); 2.18 (3H, s, $C\underline{H}_3CO$-); 2.32 (2H, t, -$CH_2C\underline{H}_2COOCH_2CH_3$); 2.67-3.10 (4H, m, -$CH_2CHClC\underline{H}_2CCl_2C\underline{H}_2CHCl$-); 4.14 (2H, q, -$OC\underline{H}_2CH_3$); 4.2-4.6 (4H, m, -$CH_2C\underline{H}ClCH_2CCl_2CH_2C\underline{H}ClC\underline{H}_2O$-). Found: C, 49.1; H, 7.0%. $C_{19}H_{32}Cl_4O_4$ requires C, 48.94; H, 6.92%. Oil.

methyl, ethyl 2,2,4-trichloro-tridecanoate

^{1}H NMR δ ($CDCl_3$): 1.27 (3H, t, -$OCH_2C\underline{H}_3$); 1.30-1.95 (14H, m, -$(C\underline{H}_2)_7CHClCH_2$-); 2.31 (2H, t, -$CH_2C\underline{H}_2COOCH_2CH_3$); 2.82 (1H, dd, J=3.3, 15.2 Hz, -$CHClC\underline{H}_2CCl_2$-); 3.13 (1H, dd, J=8.8, 15.2 Hz, -$CHClC\underline{H}_2CCl_2$-); 3.91 (3H, s, -$OC\underline{H}_3$); 4.15 (2H, q, -$OC\underline{H}_2CH_3$); 4.18 (1H, m, -$C\underline{H}ClCH_2CCl_2$-); 4.60 (2H, s, -$COOC\underline{H}_2CCl_2$-). MS (EI, 70 eV) m/z: 136 (12%); 121 (11%); 95 (18%); 81 (65%); 69 (100%). Found: C, 49.2; H, 6.9%. $C_{16}H_{27}Cl_3O_4$ requires C, 49.31; H, 6.98%. Oil.

General procedure for alkyl-halo-additions using MTCA: preparation of methyl 5-acetoxy-2,2,4-trichloro-pentanoate. Iron filings (3.6 mmol) were weighted in a Schlenk tube[13] and then 26 % (w/v) $FeCl_3$ in DMF (4.5 ml), allylacetate (32 mmol), and methyl trichloroacetate (48 mmol) were added, under argon. The mixture was stirred at 100°C and after 24 h diluted with 2.5% HCl (15 ml) and extracted with n-hexane (2 x 8 ml). The organic layers were collected, dried over Na_2SO_4 and then evaporated. The crude oil was distilled under vacuum, affording

7.37 g of methyl 5-acetoxy-2,2,4-trichloro-pentanoate (83%).

General procedure for alkyl-halo-additions with MDCP: preparation of methyl 5-acetoxy-2,4-dichloro-2-methyl-pentanoate. Iron filings (0.2 mmol) were weighted in a Schlenk tube and then $FeCl_3$ (0.4 mmol) in 1/1 DMF/DCE (1.0 ml), allylacetate (6 mmol), and methyl 2,2-dichloro-propanoate (4 mmol) were added, under argon. The mixture was stirred at 120°C and after 17 h diluted with 2.5% HCl (10 ml) and extracted with n-hexane (2 x 8 ml). The organic layers were collected, dried over Na_2SO_4 and then evaporated. The crude oil was distilled under vacuum, affording 0.91 g of methyl 5-acetoxy-2,4-dichloro-2-methyl-pentanoate (89%).

dimethyl 2,2,4,7,9,9-hexachloro-decandioate

^{1}H NMR δ ($CDCl_3$): 1.83-2.23 (4H, m, -CH_2CH_2-); 2.88 (2H, dd, -CHCl$\underline{CH_2}CCl_2$-); 3.18 (2H, dd, -CHCl$\underline{CH_2}CCl_2$-); 3.93 (6H, s, -O$\underline{CH_3}$); 4.25 (2H, m, -$CH_2\underline{CH}ClCH_2$-). MS (EI, 70 eV) m/z: 259 (10%); 142 (62%); 59 (85%); 36 (100%). Found: C, 33.1; H, 3.6%. $C_{12}H_{16}Cl_6O_4$ requires C, 32.98; H, 3.69%. Solid (mixture erythro-threo).

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