REDUCTION OF 1,1,1-TRICHLOROETHANE AND ITS ADDITION TO 1-HEPTENE INITIATED BY tert-BUTYL PEROXIDE OR $Fe(CO)_5$ IN THE PRESENCE OF TRIETHYLSILANE

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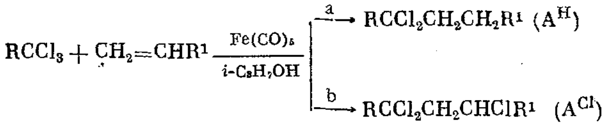
The addition of $RCCl_3$ to α-olefins initiated by $Fe(CO)_5$ and a nucleophilic cocatalyst such as isopropyl alcohol yields A^H and A^{Cl} adducts



$$RCCl_3 + CH_2{=}CHR^1 \xrightarrow[i\text{-}C_3H_7OH]{Fe(CO)_5} \begin{cases} \xrightarrow{a} RCCl_2CH_2CH_2R^1 \ (A^H) \\ \xrightarrow{b} RCCl_2CH_2CHClR^1 \ (A^{Cl}) \end{cases} \tag{1}$$

The fraction of the A^H adduct is about 2% when the olefin/i-C_3H_7OH ratio is 1:3 [1]. Silicon hydrides are known to be active hydrogen donors in the reduction of the CCl_3 group to $CHCl_2$ [2]

$$RCCl_3 + HSiEt_3 \xrightarrow{\text{initiator}} RCHCl_2 + ClSiEt_3 \tag{2}$$

Silyl radical presumably are involved in radical reactions with silicon hydrides initiated by peroxides [3, 4]

$$Et_3SiH + RO^{\cdot} \rightarrow ROH + Et_3\dot{S}i$$

Silyl radicals were detected by ESR spectroscopy in $HSiEt_3$—tert-butyl peroxide (TBP) [5], $HSiEt_3$—$Fe(CO)_5$ [6], and $EtSiCl_3H$—$Fe(CO)_5$ systems [6, 7]

$$Et_3SiH + Fe(CO)_5 \rightarrow Et_3\dot{S}i + H\dot{F}e(CO)_4$$

$R\dot{C}Cl_2$ radicals are also generated from $RCCl_3$ compounds by the action of these systems [7].

It was of interest to elucidate the course of the reaction in the $RCCl_3$—olefin—$HSiEt_3$ system and evaluate the competition of the reduction (Eq. (2)) and addition (Eq. (1)) reactions as well as the distribution of A^H and A^{Cl} adducts relative to the amount of $HSiEt_3$.

Under comparable conditions, we studied the reduction of 1,1,1-trichloroethane (I) by triethylsilane (II) and the addition of CCl_3CH_3 to 1-heptene (III) in the presence of $HSiEt_3$ in the CCl_3CH_3—1-heptene—$HSiEt_3$ systems. The initiator was either 20-30 mole % TBP or 2-10 mole % $Fe(CO)_5$ relative to (I) (in the reduction reaction) and to (II) (in the addition reaction) at 130-145°C.

1,1,1-Trichloroethane is reduced in the presence of 20 mole % TBP by an equimolar amount of triethylsilane to 1,1-dichloroethane (IV) in good yield and high conversion (Table 1, experiment 1). When this reaction is initiated by $Fe(CO)_5$, the conversion of (I) and yield of (IV) are dependent on the amount of initiator (experiments 2, 4, and 5). Thus, the conversion of (I) does not exceed 80% with 2-6 mole % $Fe(CO)_5$, which hinders the purification of (IV). High conversion of (I) (95-98%) and yields of (IV) (up to 84%) in the reduction of (I) are achieved by the use of 9-11 mole % $Fe(CO)_5$. These conditions are suitable for the preparative synthesis of (IV) (see experiment 5 and the Experimental section).

The addition of CCl_3CH_3 to 1-heptene when taken in 5:1 molar ratio was studied in the presence of from 0 to 3 moles $HSiEt_3$ per mole of the olefin (Table 2).

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TABLE 1. Reduction of CCl_3CH_3 (I) by Triethylsilane Initated by TBP or $Fe(CO)_5$ over 5 h

Experiment no.	Reagents, mmoles			Conversion, *%		Yield* of $CHCl_2CH_3$ (IV), %
	(I)	(II)	initiator	(I)	(II)	
TBP (130–140°)						
1	2,0	2,0	0,41	93	90	70,0
$Fe(CO)_5$ (140–145°)						
2	3,3	3,4	0,06	53	47	31,6
3	10,0	2,0	0,05	28	63	8,6(41) †
4	35,5	38,1	2,14	79	76	69,5
5	3,0	3,0	0,29	98	93	84
6	10,0	2,1	0,22	29	70	10(47) †

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*Conversions and yields determined by gas-liquid chromatography.

†The yield of (IV) relative to (II).

TABLE 2. The Reaction of CCl_3CH_3 (I) (5-10 mmoles) with 1-Heptene and $HSiEt_3$ (II) Initiated by TBP or $Fe(CO)_5$ over 5 h ((I):1-heptene mole ratio = 5:1)

Experiment	$HSiEt_3$, moles per mole 1-heptene	Initiator, mole % rel. to 1-heptene	Conversion, %*			Reaction products and their yield,%*		
			(I)	1-heptene	(II)	(IV)	(V)	(VI)
TBP (130–140°)								
1	0	30	53	64	–	Trace	2,2	12.5
2	3	30	41	83	23	12,4 (20,6) †	32,2	8,7
$Fe(CO)_5$ (140–145°)								
3	0	2,2	30	83	–	2,4	3,4	33,4
4	0,5	2	34	74	52	2,3	2,9	55
5	1	2	50	81	46	4,0	2,9	60,6
6	3	2	46	71	15	10,5 (17,6) †	3,4	56
7	0	5	–	90	–		5,8	33,3
8	0	10	39	100	–	1	7,9	32,4
9	0,5	10	52	88	100	3,5	5,0	63,6
10	0,7	9,2	43	93	96	5,1	4,6	61
11	1	10	43	95	62	9,6	4,0	66,2
12	2,7	10	57	97	44	25 (40) †	4,6	61

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*Conversions and yields determined by gas-liquid chromatography.

†The yield of (IV) is calculated relative to (II).

As in other cases reported [2], (I) does not add readily to 1-heptene in the case of TBP initiation. Thus, the yield of 2,2-dichlorononane (V) in the presence of 30 mole % TBP is only about 3% while the yield of 2,2,4-trichlorononane (VI) is about 13%. The addition of 3 moles $HSiEt_3$ per mole olefin leads to a tenfold increase in the yield of (V), while the yield of (VI) is virtually unchanged (see Table 2, experiments 1 and 2). In this case, (I) is partially reduced to (IV) but to a significantly less extent than in the absence of olefin (see Table 1).

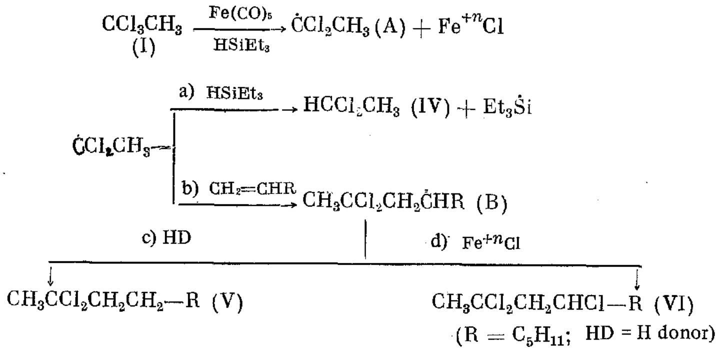
The addition of CCl_3CH_3 to 1-heptene in the case of $Fe(CO)_5$ initiation is not affected by the amount of initiator (2, 5 and 10 mole % per mole (III), see Table 2, experiments 3, 7, and 8) but is accompanied by tar formation of the reaction mixture. The overall yields of (V) and (VI) does not exceed 40% in the case of 80-100% olefin conversion.

The addition of 50-100 mole % $HSiEt_3$ per mole 1-heptene eliminated tar formation and increased the yield of (VI) to 55-66% (see Table 2, experiments 4, 5, 9-11). The yield of

(V) [93-7%] virtually does not change during the reaction initiated by TBP (experiment 2). The reduction of (I) is also suppressed under these conditions (see experiments 4 and 5 in Table 1).

An increase in the amount of (II) to 3 moles per mole olefin does not have a significant effect on the yields of adducts (V) and (VI) (see Table 2, experiments 6 and 12). However, the competitive reduction of CCl_3CH_3 becomes significant in the case of a concurrent increase in the $Fe(CO)_5$ concentration to 10 mole % since this reduction depends on the initiator concentration (experiments 11 and 12, Table 2 and experiments 3 and 6, Table 1).

The addition of (I) to 1-heptene in the presence of (II) may be described by the following scheme



The 1,1-dichloroethyl radical (A) formed in the case of initiation by both TBP and $Fe(CO)_5$ may react by two pathways depending on the concentration of the reagents: It may be reduced by triethylsilane to 1,1-dichloroethane (IV) (this pathway becomes predominant in the absence of olefin), and b) it may add to the olefin double bond to form the radical adduct (B).

The further transformations of radical adduct (B) are related to the nature of the initiator. In the case of peroxide initiation, radical (B) is stabilized to a considerable extent by the loss of hydrogen to form 2,2-dichlorononane (V) (steps b and c). In this case, $HSiEt_3$ may apparently be a hydrogen donor.

When the addition of (I) to 1-heptene is initiated by iron pentacarbonyl, the presence of small amounts of (II) facilitates the formation of 2,2,4-trichlorononane (VI) as the major product (steps b and d). Under these conditions in the presence of $Fe(CO)_5$, chlorine is transferred to radical adduct (B) more efficiently than H from (II) even in the case of a threefold molar excess of (II).

It is interesting that the yield of adduct (VI) for any concentrations of $Fe(CO)_5$ and (II) in the reaction of (I) with 1-heptene initiated by $Fe(CO)_5$ in the presence of (II) is always higher (55-66%, see Table 2, experiments 4-6, 9-12) than the yield of (VI) in experiments without (II) (32-33%, experiments 3, 7, 8).

This reaction is the first example of the action of an electrophilic additive ($HSiEt_3$) on an addition reaction initiated by iron pentacarbonyl.

The products of the reaction of (V) and (VI) were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The signals for the $CH_3CCl_2CH_2CH_2$ and $CH_3CCl_2CH_2CHClCH$ fragments of adducts of (V) and (VI) are in accord with the data reported in our previous work [8] and calculations taking account of the α, β, and γ effect of chlorine [9].

EXPERIMENTAL

All the experiments were carried out in sealed glass ampuls filled by the freeze—evacuation—argon filling—thawing method. The ampuls were placed in metal tubes with counterpressure and heated for 5 h at 130-145°C.

The gas-liquid chromatographic analysis of the starting compounds of the reaction mixtures and the reaction products was carried out on an LKhM-8MD chromatograph in a helium stream with thermal conductivity detector on steel columns: 1) 3 × 2000 mm packed with silicone E-301 and 2) 3 × 1000 mm packed with 15% Carbowax 20M. The internal standards were CCl_3CH_2Cl for (I), (II), and (IV), 1-octene for 1-heptene, and $CHCl_2(CH_2)_3{-}CH_2Cl$ for (V)-(VII).

TABLE 3. ^{13}C NMR Parameters for $\overset{1}{CH_3}\,\overset{2}{CCl_2}\,\overset{3}{CH_2}\,\overset{4}{CH(X)}\,\overset{5}{CH_2}\,\overset{6}{CH_2}\,\overset{7}{CH_2}\,\overset{8}{CH_2}\,\overset{9}{CH_3}$

Compound	δ, ppm, $\frac{\text{Found}}{\text{Calculated}}$								
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
(V), X=H	$\frac{37,2}{37,2}$	$\frac{89,8}{89,5}$	$\frac{49,7}{49,6}$	$\frac{28,9}{29,4}$	$\frac{31,7}{}$	$\frac{28,9}{}$	25,5	22,4	13,9
(VI), X=Cl	$\frac{37,3}{37,2}$	$\frac{88,2}{85,9}$	$\frac{57,7}{57,0}$	$\frac{57,7}{57,5}$	$\frac{39,3}{39,1}$	$\frac{25,6}{26,3}$	$\frac{31,7}{32,0}$	$\frac{22,3}{22,7}$	$\frac{13,9}{13,8}$

The separation and purification of the compounds were carried out by preparative gas-liquid chromatography on column 3) 9 × 2000 mm packed with 15% silicone E-301. The solid support was Chromatone N-AW 0.16-0.20 and 0.20-0.25 mm.

The ^1H and ^{13}C NMR spectra were taken for 20-70% solutions in CCl_4 and $CHCl_3$ on a Perkin-Elmer R-12 spectrometer at 60 MHz and Bruker HX-90 spectrometer using the δ scale relative to TMS.

Addition of 1,1,1-Trichloroethane (I) to 1-Heptene in the Presence of TBP and $HSiEt_3$ (II). A mixture of 5 g olefin, 33.4 g (I), 17 g (II), and 1.5 g TBP was heated at 130-140°C. Gas-liquid chromatographic analysis of the reaction products on column 1 at 155°C indicated the formation of 3.3 g (33%) 2,2-dichlorononane (V) and 1.2 g (10%) 2,2,4-trichlorononane (VI). The mixture was fractionated after washing with dilute hydrochloric acid, water, extraction, and drying. The fraction with bp 106-111°C (16 mm) (7.6 g) was subjected to preparative gas-liquid chromatography on column 3 at 125°C to give adduct (V), n_D^{20} 1.4470, d_4^{20} 0.9800. Found: C 55.50; H 9.36; Cl 35.09%, MR 53.75. Calculated for $C_9H_{18}Cl_2$: C 54.82; H 9.20; Cl 35.97%, MR 53.49. PMR spectrum (δ, ppm): 0.84 m, 1.2 m (CH_3, $6CH_2$, 15H), 2.0 s (CH_3CCl_2, 3H) [10].

The same fraction upon similar treatment on column 3 at 140°C gave hexaethyldisiloxane (VII), n_D^{20} 1.4342, d_4^{20} 0.8249 [11]. Found: C 58.94; H 12.47; Si 22.60%, MR 76.10. Calculated for $C_{12}H_{30}Si_2O$: C 58.45; H 12.26; Si 22.79%, MR 76.77. PMR spectrum (δ, ppm): 0.49 t ($6CH_3$, 18H), 0.84 q ($6CH_2$, 12H).

The fraction with bp 112-116°C (16 mm) (4.6 g) was subjected to chromatography on column 3 at 145°C to yield adduct (VI). PMR spectrum (δ, ppm): 2.18 s (CH_3CCl_3, 3H), 2.6 d (CCl_2·CH_2, 2H), 4.0 m (CHCl, 1H), and 0.94 m and 0.9 m ($4CH_2$, CH_3, 11H).

Addition of CCl_3CH_3 (I) to 1-Heptane in the Presence of $Fe(CO)_5$ and (II). a) A mixture of 5.1 g olefin, 35.6 g (I), 4 g (II), and 0.5 g $Fe(CO)_5$ was heated to 140-145°C and 0.3 g precipitate was separated. The solution was washed with dilute hydrochloric acid and water and dried over Na_2SO_4. The aqueous layers were extracted with chloroform and the solvent was distilled off. According to gas-liquid chromatographic analysis on column 1 at 155°C, the residue (20 g) contained 0.8 g (~1%) (V), 7.1 g (59%) (VI), and 2.4 g (VII). Products (V) and (VII) were identified relative to authentic samples on columns 1 and 2 at 155°C.

Fractional distillation at 10 mm gave a fraction with bp 108-112°C containing 66% (VI) and 30% (VII). This fraction was subjected to preparative gas-liquid chromatography on column 3 at 150° to give (VI), n_D^{20} 1.4650, d_4^{20} 1.0952. Found: C 46.81; H 7.42; Cl 45.64%, MR 58.47. Calculated for $C_9H_{17}Cl_3$: C 46.69; H 7.39; Cl 45.93%, MR 58.36. PMR spectrum (δ, ppm): 2.2 s (CH_3CCl_2, 3H), 2.7 d (CCl_2CH_2, 2H), 4.1 m (CHCl, 1H), 1.3 m and 0.9 m ($4CH_2$, CH_3, 11H).

b) In order to identify unreacted (II), the solvent, (I), the fraction with bp 90-105°C (2.9 g) containing 60% (II) and the fraction with bp 108-112°C (12 mm) (2.9 g) containing (V), (VI) (63%) and (VII) were distilled off the combined mixture (see Table 2, experiments 4-6, 9-12) without work-up. Triethylsilane was purified on column 3 at 112°C, n_D^{20} 1.4090,

d_4^{20} 0.7282, MR 39.47 (found), 39.76 (calculated) [3]. PMR spectrum (δ, ppm): 0.73 t, 1.0 q ($3CH_3$, $3CH_2$, 15H), 3.67 br. s (SiH, 1H). For authentic $HSiEt_3$ (δ, ppm): 0.8 t, 1.06 q ($3CH_3$, $3CH_2$, 15H), 3.71 br. s (SiH, 1H).

Reduction of CCl_3CH_3 (I) by Triethylsilane (II) in the Presence of $Fe(CO)_5$. A mixture of 10.5 g (I), 9.8 g (II), and 1.6 g $Fe(CO)_5$ was heated at 140-145°C. Gas-liquid chromatographic analysis indicated 97% conversion of (I) and 95% conversion of (II) and a yield of 5.7 g (73.5%) 1,1-dichloroethane (IV). The precipitate was filtered off. The fraction with bp 47-66°C (6.6 g) containing 4.5 g (59.4% yield) (IV) was distilled off. PMR spectrum (δ, ppm): 5.82 q ($CHCl_2$, 1H), 1.98 d (CH_3, 3H). A sample of 5 g triethylchlorosilane with bp 74-76°C (68 mm), n_D^{20} 1.4310 and d_4^{20} 0.8947 [11] was distilled from the residue (11 g).

CONCLUSIONS

1. 1,1,1-Trichloroethane is reduced by triethylsilane with initiation by either tert-butyl peroxide or $Fe(CO)_5$ to give 1,1-dichloroethane in high yield and high trichloroethane conversion.

2. 1,1,1-Trichloroethane reacts with 1-heptene in the presence of triethylsilane upon initiation either by tert-butyl peroxide or $Fe(CO)_5$ to form 2,2-dichlorononane and 2,2,4-trichlorononane. The ratio of these products depends on the nature of the initiator. The major product with TBP as initiator is 2,2-dichlorononane while the major product with $Fe(CO)_5$ as initiator is 2,2,4-trichlorononane.

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