

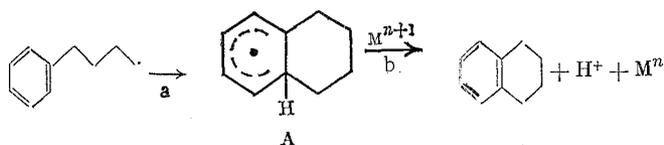
REDOX CYCLIZATION OF ARYLBUTYL RADICALS IN THE PRESENCE OF COMPLEXES
OF IRON OR MOLYBDENUM

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Arylbutyl radicals, which are generated by various methods, are capable of undergoing cyclization to cyclohexadienyl radicals A with subsequent oxidation to compounds of the tetrahydronaphthalene series, according to the following scheme:

Scheme 1



The oxidation of A with equimolar amounts of $\text{Pb}(\text{OAc})_4$, $\text{Cu}(\text{II})$, $\text{Mn}(\text{III})$, and $\text{Ce}(\text{IV})$ has been described [1-4].

A special position in redox cyclization is occupied by $\text{Fe}(\text{CO})_5$. It has been shown that if the reactions of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane with ethylene, vinyl and vinylidene chlorides, methyl acrylate, methyl methacrylate, and styrene are initiated by systems based on $\text{Fe}(\text{CO})_5$ the main products are substituted tetrahydronaphthalenes (or the products from their further transformations) [5]. The difference between $\text{Fe}(\text{CO})_5$ and the above-mentioned metal salts lies in the fact that catalytic amounts and not equimolar amounts of the initiator are used and a compound of iron with higher valence is formed at the initiation stage and then oxidizes the radical A (Scheme 1, stage b), giving tetrahydronaphthalene and a compound of iron with lower valence, which continues the chain [5].

The aim of the present work was to extend the region of application of the process and to answer the question as to whether other metal carbonyls (MC) and their complexes can take part in redox initiation and then redox cyclization like $\text{Fe}(\text{CO})_5$. As a new example we took the simplest representative of phenyl-containing trichloromethyl compounds, i.e., 1,1,1-trichloro-2-phenylethane (I). The reactions of (I) with 2-chloropropene (CP) and 1-hexene (HX), which differ in their polar characteristics, were studied. As transition-metal compounds we took the metal carbonyls and their complexes with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) [where dppe = 1,2-bis(diphenylphosphino)ethane], i.e., $\text{Mo}(\text{CO})_6$, $\text{Mo}(\text{CO})_2(\text{dppe})_2$, $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ and $\text{Fe}(\text{CO})_5$.

It is known that $\text{Mo}(\text{CO})_6$ is effective in the initiation of reactions involving the homolytic removal of Cl from the CCl_3 group [6, 7]. The cyclization of arylbutyl radicals in the presence of molybdenum compounds has not been described.

The reaction of (I) with CP or HX is realized according to Scheme 2.

In addition to the formation of the products from the cyclization of the arylbutyl radical C (stages c and d), the formation of linear reaction products as a result of the removal of the Cl atom from the donor (ACl) (stage e) is also possible. The initial radical B can also take part in competing reactions, i.e., the abstraction of H from the molecules of the medium (AH) or oxidation (stages f and g).

TABLE 1. Reaction of $\text{PhCH}_2\text{CCl}_3$ (3 mmole) with $\text{CH}_2=\text{CClCH}_3$ (3 mmole), Initiated by MC (0.3 mmole) with Additions (0.9 mmole) in Acetonitrile (6 mmole) at 140°C for 3 h

Expt. No.	Initiator	Additions	Conversion of $\text{PhCH}_2\text{CCl}_3$, %	Product yield, %		
				(IV), (V)	(VI)	(IIIa)
1 ^b	$\text{Fe}(\text{CO})_5$	DMFA	48	2	29	2
2 ^{b,c}	$\text{Fe}(\text{CO})_5$	HMPTA	73	2	39	4
3	$\text{Fe}(\text{CO})_5$	PPh_3	95	(IV), 20	55	—
4	$\text{Mo}(\text{CO})_6$	None	38	2	18	—
5 ^d	$\text{Mo}(\text{CO})_6$	PPh_3	45	5	38	—
6 ^d	<i>trans</i> - $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$	None	44	7	29	1

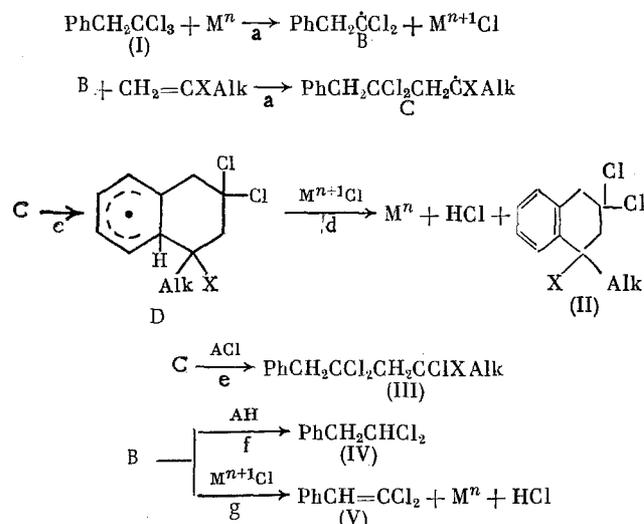
^aExperiments 2 and 3 were also carried out on a preparative scale, see the experimental section.

^bThe experiments were carried out in the absence of acetonitrile.

^cThe realization of this experiment at 120°C leads to a decrease in the degree of conversion of (I) and the yield of (VI).

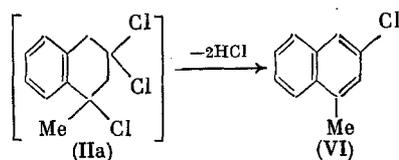
^dIncrease in the heating time to 9.5 h leads to an increase in the resinification of the reaction products.

Scheme 2



$\text{M} = \text{Fe, Mo}; \text{X} = \text{Cl, Alk} = \text{Me (a)}; \text{X} = \text{H, Alk} = \text{Bu (b)}$.

In the reaction of (I) with CP the main product is 2-chloro-4-methylnaphthalene (VI), which is formed during the dehydrochlorination of (IIa) under the experimental conditions:



The results from the investigation of the reaction of (I) with CP in the presence of the metal carbonyl (MC) and various additions are given in Table 1. As seen from Table 1, in all cases the main reaction product is the disubstituted naphthalene (VI), and its yields amount to 18–55%. This compound was obtained both with systems based on $\text{Fe}(\text{CO})_5$ and in the presence of $\text{Mo}(\text{CO})_6$ and its complexes (experiments 4–6). This demonstrates the ability of molybdenum compounds to initiate the reaction (see Scheme 2, stage a) and oxidize the radical D (stage d) to the substituted tetrahydronaphthalene. In the presence of $\text{Fe}(\text{CO})_5$, however, the conversion of (I) and the yields of (VI) are somewhat higher (cf. experiments 1–3 and 4–6). The yields of the linear adduct (IIIa) are insignificant (1–4%). The adduct (IIIa) was only obtained in experiments 1, 2, and 6. Of the systems based on $\text{Fe}(\text{CO})_5$ the $\text{Fe}(\text{CO})_5 + \text{PPh}_3$ system

TABLE 2.^a Reaction of PhCH₂CCl₃ (3 mmole) with CH₂=CHBu (3 mmole) in the Presence of MC (0.3 mmole) and Acetonitrile (6 mole) at 140°C for 3 h

Expt. No.	Initiator	Conversion of (I), %	Product yields, %					
			dichlorides (IV), (V)	cyclic		linear		
				(VII), (VIII)	(II b)	(X)	(IX)	(IIIb)
1b	Fe(CO) ₅ + PPh ₃	99	15	14	18	3	6	26
2b	Mo(CO) ₆ + PPh ₃	50	9	7	19	2	None	None
3	Mo(CO) ₆	49	9	19	3	None	None	None
4	trans-Mo(N ₂) ₂ (dppe) ₂	70	9	5	15	None	8	22

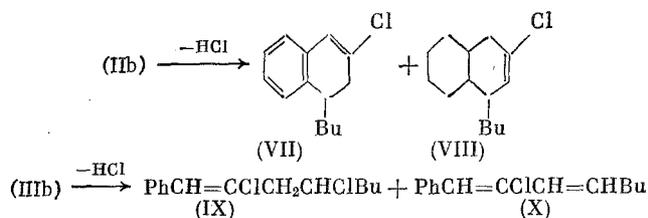
^aExperiments 1 and 4 were also carried out on a preparative scale.

^b0.9 mmole of triphenylphosphine was used.

proved most effective (experiment 3). Systems involving molybdenum compounds (experiments 4-6) and also Mo(CO)₆ + DMFA and cis-Mo(CO)₂(dppe)₂ were tested. It was shown that the Mo(CO)₆ + DMFA system is not effective, while cis-Mo(CO)₂(dppe)₂ has low effectiveness. In the case of Mo(CO)₆ without additions, appreciable resinification of the reaction mixture occurred, and the yield of (VI) amounted to 18% (experiment 4). The use of Mo(CO)₆ + PPh₃ or trans-Mo(N₂)₂(dppe)₂ gave similar results; the yields of (VI) were 30-38% (experiments 5 and 6). Thus, the presence of phosphine ligands in the initiating molybdenum complex helps to increase the yields of the products. In all cases the formation of the dichlorides (IV) and (V) as side products with yields of 2-7% was observed. Compound (IV) was only formed with an appreciable yield in the presence of the Fe(CO)₅ + PPh₃ (IV) system (experiment 3). By special tests it was shown that variation of the conditions (increase in the heating time, decrease in the reaction temperature, decrease in the concentration of the metal carbonyl) does not lead to an increase in the yield of (VI). Thus, the radical-adduct C (see Scheme 2) is largely stabilized by cyclization followed by oxidation (stages c and d, Scheme 2). Chain transfer to the telogen, which leads to the adduct (IIIa) (stage e), only takes place to a small degree.

The cyclization of arylbutyl radicals in the presence of iron or molybdenum compounds was also studied for the case of the reaction of the addend (I) with HX. Earlier, for a different example it was shown that the reaction of AlkCCl₃ with HX in the presence of the discussed systems takes place more readily than the reaction with CP [7]. This may be due to the more favorable polar effects.

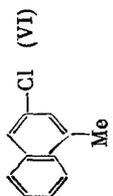
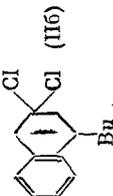
A feature of this reaction is the thermal instability of the high-boiling products, i.e., tetrahydronaphthalene (IIb) and the adduct (IIIb), which are dehydrochlorinated according to the following scheme:



The isomeric dihydronaphthalenes (VII) and (VIII) [mostly (VII)] and also the alkene (IX) and diene (X) are therefore formed during distillation and GLC analysis. This makes it difficult to isolate the individual compounds and to analyze the reaction mixtures. The results are given in Table 2.

As seen from Table 2, all the investigated systems based on molybdenum and also the Fe(CO)₅ + PPh₃ system lead to the production of the cyclic product (IIb) or its dehydrochlorination products. The yields of (IIb), (VII), and (VIII) amount to 20-32% with 50-99% conversion of the initial (I). It was shown that the adduct (IIIb) and its dehydrochlorination products (IX) and (X) are also formed with appreciable yields in experiments 1 and 4. Thus, only the cyclic products are formed with Mo(CO)₆ and Mo(CO)₆ + PPh₃ in the reaction of (I) with HX, while the formation of the linear adduct (IIIb) begins to play an appreciable role with trans-Mo(N₂)₂(dppe)₂ or Fe(CO)₂ + PPh₃. The yield of (IIIb) and its dehydrochlorination products (IX) and (X) reaches 25-35% in experiments 1 and 4 (Table 2).

TABLE 3. Parameters of the PMR Spectra

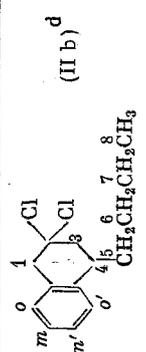
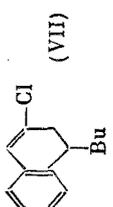
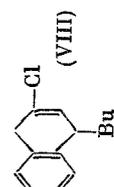
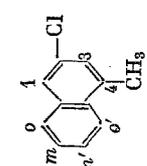
Compound	δ , ppm						
	Ph	α -CH ₂	γ -CH ₂	CHCl, CHCl ₂	CH ₂	Me	
$\text{PhCH}_2\text{CHCl}_2$ (IV)	7.41 s	3.22 d	—	5.58 t	—	—	
$\text{PhCH}_2\text{CCl}_2\text{CH}_2\text{CCl}_2\text{Me}$ (IIIa) ^a	7.28 s	3.40 s	3.20 s	—	—	2.30 s	
$\text{PhCH}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_2\text{Pr}$ (IIIb) ^b	7.06–7.47 m	3.45 q	2.68 m	4.27 m	1.82m 1.34 m	0.91 t	
$\text{PhCH}=\text{CClCH}_2\text{CHClCH}_2\text{Pr}$ (IX) ^{b, c}	7.43–7.45 m	—	2.75 d	4.22m	1.69 m 1.30m	0.91 t	
$\text{PhCH}=\text{CClCH}=\text{CHCH}_2\text{Pr}$ (X) ^c	7.43–7.45 m	—	—	—	1.30 m	0.92 t	
 (VI)	6.95–7.80 m	—	—	—	—	2.40 s	
 (II6)	6.85–7.54 m	3.52 s	2.69 s	—	1.30 m	0.92 t	

^aFor the $\text{AlkCH}_2\text{CCl}_2\text{CH}_2\text{CCl}_2\text{Me}$ fragment, cf. [4, 8].

^bcf. for $\text{C}_4\text{H}_9\text{CHClCH}_2\text{CCl}_2\text{Et}$ (δ , ppm): 4.19 m (CHCl), 2.73 d and 2.31 q (CH₂) [9].

^c δ , ppm 6.48 s (CH=).

TABLE 4. ^{13}C NMR Spectra (δ , ppm)

Compound	Aromatic					Other groups				
	C_{key}	o^-	m^-	p^-		C^1	C^2	C^3	C^4	C^5
$\text{PhCH}_2\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (IIIa)	133.6	131.4	128.0	127.6		57.7	86.3	62.4	88.0	37.4
$\text{PhCH}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_7$ (IIIb)	134.2	131.4	128.0	127.6		53.8	94.5	55.6	58.5	39.2
$\text{PhCH}=\text{CClCH}_2\text{CHClCH}_2\text{C}_6\text{H}_7$ (IX)	134.6	[129.0]	[128.0]	[127.5]		[126.3]	[126.4]	49.9	59.0	37.0
$\text{PhCH}=\text{CClCH}=\text{CHCH}_2\text{C}_6\text{H}_7$ (X)	135.1	[129.4]	[128.0]	[127.5]		[128.4]	[130.0]	[127.7]	[134.7]	[34.8] c
Compound	C_{key}	C_{key}	o, o'	m, m'		C^1	C^2	C^3	C^4	C^5
 (II b) d	132.5	136.9	128.4	127.5		[48.29]	88.0	[50.41]	37.22	34.6
 (VII)	132.8	137.2	127.0 125.9	124.5 126.5		128.9	132.7	36.8	38.9	34.2
 (VIII)	134.6	138.0	128.0	127.1		45.7	[125.8]	[128.2]	41.2	34.9
 (VI) e	133.8	130.5	127.3 123.6	126.2 125.5		124.6	130.7	126.7	136.4	—

^aThe spectrum of the individual cyclic product (VI) and the spectrum of the mixture of (VI) and (IIIa) were obtained; the spectrum of the crude fraction (IIIb) (85-90% of the main substance) and the spectrum of the mixture of (IIb) and (IIIb) (50:50) were obtained; the spectra of the mixture of (IX) and (X) and also (VII) and (VIII) (ratio 80:20) were obtained.

^bFor $\text{CH}_3\text{CH}_2\text{CH}_2$ (δ , ppm): 28.1-29.1 (C^6), 21.9-22.7 (C^7), 13.5-13.7 (C^8).

^cFor $\text{CH}_2\text{CH}_2\text{CH}_3$ (δ , ppm): 31.2 (C^6), 22.1 (C^7); 13.8 (C^8), (cf. for 3-octene [10]).

^dThe assignment of the signals for C^1 and C^3 was made by comparison with data for Tetralin [10] and alkylcyclohexane [11] with allowance for the β effect of the CCl_2 group.

^e $\delta\text{CH}_3 = 18.7$ ppm. The same values ± 0.5 ppm were obtained by the additive method on the basis of data for 2-chloronaphthalene [12] and 1-methylnaphthalene [13].

The results given in Tables 1 and 2 indicate that the systems based on molybdenum compounds can be used for the initiation of the reaction and for the oxidation of the intermediate cyclohexadienyl radicals to substituted tetrahydronaphthalenes. Under the compared conditions (without optimization of the process) the product yields and the conversion of the initial (I) are higher with the systems based on $\text{Fe}(\text{CO})_5$ than with molybdenum compounds.

The structures of the products (I-X) were confirmed by the ^1H and ^{13}C NMR spectra (Tables 3 and 4), which were obtained for the individual compounds, for the fractions enriched in one component, or for mixtures of the two compounds, one of which was present in the individual form. The structure of (X) was also confirmed by comparison of its UV spectrum with the spectrum of 1-phenyl-1,3-pentadiene [14].

The PMR spectra of the individual compounds (IIIa, IIIb, IV, VI, X) and also of mixtures of (IIb) with (IIIb), and of (IX) with (X) were obtained (Table 3). The assignment of the signals was made from the multiplicity and on the basis of analogies with published data [4, 8, 9]. The assignment of the signals for the vinyl protons and the C_6H_5 group in the diene (X) was not made. The ^{13}C NMR spectra of compounds (I)-(X) were also obtained. The spectra of (IIb), (IIIa, b), and (VII-X) are given in Table 4. The assignment of the C^1 and C^3 signals for (IIIa) was made by analogy with $\text{PhCH}_2\text{CCl}_2\text{CH}_2\text{CCl}_3$ [4] and $\text{ClCH}_2\text{CH}_2\text{CCl}_2\text{CH}_2\text{CHClBu}$ [15]. The assignment of the signals from CH and the key carbons was made by the method of polarization transfer to intensify the signals without distortion (the DEPT method).

EXPERIMENTAL

The GLC analysis was performed on an LKhM-8MD chromatograph [katharometer, helium, steel columns, Chromaton N-AW-DMCS, 0.16-0.20 mm, 1 m \times 3 mm with 5% SE-30 (a), 2 m \times 3 mm with 15% SKTFT (b), 1 m \times 3 mm with 15% Carbowax 20 M (c), 1 m \times 3 mm with 7% FS-1265 (d)]. The degrees of conversion of the initial compound (I) and the yields of the reaction products were calculated against 1,1,1-trichloro-2-(p-methylphenyl)ethane (XI) as internal standard (IS). For the preparation of (I) and (XI), see [4]. The products were isolated by preparative GLC on a Tsvet 3-66 instrument with a preparative attachment (55 cm \times 8 mm steel column, Chromaton N-AW, 0.315-0.400, 10% SE-301). The PMR spectra were obtained on a Perkin-Elmer R-12 instrument at 60 MHz and a Bruker WP-200 instrument at 200 MHz for 30-50% solutions in carbon tetrachloride with TMS and HMDS as internal standards and D_2O as external standard.

The ^{13}C NMR spectra with suppression of the CH coupling and by the DEPT procedure were obtained on a Bruker WP-200 spectrometer at 200 MHz with chloroform or carbon tetrachloride as standards. The IR spectra were obtained on a UR-20 spectrophotometer. The electronic spectra were obtained on a Specord M-40 instrument in ethanol in quartz cuvettes (0.1-1 cm).

The experiments (Tables 1 and 2) were carried out in glass tubes which had been sealed in an atmosphere of nitrogen by the freezing-evacuation-thawing procedure. The ampuls were heated with agitation by rotation. The reaction products from the experiments with $\text{Fe}(\text{CO})_5$ were diluted with chloroform and washed with 10% hydrochloric acid. The products from the experiments with the molybdenum complexes were filtered through paper filter (Table 1) or through a layer of silica gel L100/160 with a thickness of 1.5-2 cm, covered with filter paper (Table 2). Powdered colored precipitates of the molybdenum compounds remained on the filter. The silica gel was washed with 10-15 ml of carbon tetrachloride. The compositions of the mixtures (by comparison of the retention times with the samples obtained as described below) and the products yields were determined in the filtrate by GLC.

1. Reaction of 1,1,1-Trichloro-2-phenylethane with 2-Chloropropene. The reaction was initiated by the $\text{Fe}(\text{CO})_5$ + DMFA system. A mixture of 12.6 g (60 mmole) of $\text{PhCH}_2\text{CCl}_3$, 4.5 g (60 mmole) of $\text{CH}_2=\text{CClCH}_3$, 1.18 g (6 mmole) of $\text{Fe}(\text{CO})_5$, and 3.2 g (18 mmole) of HMPTA was heated in a sealed tube at 140°C for 3 h. The following fractions were obtained: I) 65-99°C (5 mm Hg), 4.6 g; II) 100-109°C (5 mm Hg), 2.8 g; III) 130-140°C (5 mm Hg), 1.8 g. The solid residue weighed 1.8 g. The yields of (IIIa), (IV)-(VI) and the degrees of conversion of (I) were determined by GLC (column a, temperature programming between 130 and 220°C, $v = 8$ deg/min) (Table 1, expt. 2). From fraction II by repeated distillation (bp 102-103° at 5 mm Hg) and purification by preparative GLC (column temperature 180°C) we obtained 2-chloro-4-methylnaphthalene (VI). Found, %: C 74.48; H 5.19; Cl 20.25. $\text{C}_{11}\text{H}_9\text{Cl}$. Calculated, %: C 74.79; H 5.10; Cl 20.07%. n_D^{20} 1.6221. Fraction III contained 65% of (VI) and 35% of (IIIa) (calculated from the integral intensity ratios of the singlets for the Me groups in the PMR spectrum). For fraction III, found, %: C 62.20; H 5.03; Cl 32.89. For the mixture of 65% of $\text{C}_{11}\text{H}_9\text{Cl}$ and 35% of $\text{C}_{11}\text{H}_{12}\text{Cl}_4$, calculated, %: C 62.64; H 4.75; Cl 32.60. For the ^1H and ^{13}C NMR spectra of (IIIa, IV, VI), see Tables 3 and 4.

2. Reaction of 1,1,1-Trichloro-2-phenylethane with 1-Hexene. a) The reaction was initiated by the $\text{Fe}(\text{CO})_5 + \text{PPh}_3$ system in acetonitrile. From a mixture of 12.6 g (60 mmole) of $\text{PhCH}_2\text{-CCl}_3$, 5.04 g (60 mmole) of 1-hexene, 1.18 g (6 mmole) of $\text{Fe}(\text{CO})_5$, 4.72 g (18 mmole) of triphenylphosphine, and 4.69 g (115 mmole) of acetonitrile, similarly to expt. 1, we obtained the following fractions: I) 76–82°C (5 mm Hg), 2.1 g; II) 125–146°C (5 mm Hg), 3.4 g; III) 147–152°C (5 mm Hg), 6.6 g; IV) 154–172°C (5 mm Hg), 2.4 g. The residue was 9.0 g of a solid resin. By repeated distillation of the combined fractions II and III followed by purification by preparative GLC (column temperature 190°C) we obtained a mixture of isomeric dihydronaphthalenes (VII) and (VIII) (ratio 80:20, column b, temperature programming from 130 to 200°C). Found, %: C 76.47; H 7.93; Cl 15.64. Calculated, %: C 76.17; H 7.76; Cl 16.16. We also isolated 2-chloro-1-phenyl-1,3-octadiene (X). Found, %: C 76.56; H 7.44; Cl 15.64. $\text{C}_{14}\text{H}_{17}\text{Cl}$. Calculated, %: C 76.17; H 7.76; Cl 16.16. We also obtained a mixture of the diene (X) and the octene (IX) in the ratio (X):(IX) = 45:55 (GLC). Found, %: C 69.91; H 7.51; Cl 22.26. For a mixture of 45% of $\text{C}_{14}\text{H}_{17}\text{Cl}$, and 55% of $\text{C}_{14}\text{H}_{18}\text{Cl}_2$, calculated, %: C 69.88; H 7.35; Cl 22.77. The ^1H and ^{13}C NMR spectra of the products are given in Tables 3 and 4, and the yields of (IIb), (IIIb), (IV), (V), (VII)–(X) are given in Table 3 (expt. 1).

b. The reaction was initiated by the complex $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ in acetonitrile. A mixture of 11.34 g (54 mmole) of $\text{PhCH}_2\text{CCl}_3$, 4.54 g (54 mmole) of 1-hexene, 5.13 g (4 mmole) of $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$, and 4.22 g (103 mmole) of acetonitrile was heated in a tube similarly to expt. 1. The precipitated molybdenum compound (4.4 g) was filtered off, boiled successively with dioxane, acetone, chloroform, and benzene, and dried under vacuum with heat (100°C). The decomposition temperature was 310°C (sealed capillary). Found, %: C 55.68; H 4.65; Cl 17.33; P 10.72; N 1.71; Mo 10.70. $\text{MoCl}_3 \cdot \text{CH}_3\text{CN} \cdot 1.5 \cdot (\text{dppe}) \cdot \text{HCl}$. Calculated, %: C 56.18; H 4.49; Cl 16.18; P 10.61; N 1.60; Mo 10.95. According to the IR spectrum, the precipitate was identical to the precipitate from expt. 6 in Table 1. The spectrum did not contain a band at 1970 cm^{-1} characteristic of $\nu\text{N} \equiv \text{N}$; there were bands for the aromatic rings, bands at 2900 and 2960 cm^{-1} (CH_2 stretching vibrations), and a strong broad band of complex structure at 2200–3600 cm^{-1} , indicating the presence of a strong hydrogen bond. By distillation of the filtrate we obtained the following fractions: I) 71–86°C (3 mm Hg), 2.9 g; II) 130–156°C (3 mm Hg), 5.0 g; III) 156–158°C (3 mm Hg), 0.7 g. The precipitated solid resin amounted to 1.4 g. By repeated distillation of the combined fractions II and III we obtained the following fractions: IV) 136–140°C (3 mm Hg), 1.7 g; V) 141–147°C (3 mm Hg), 2.7 g; VI) 148–152°C (3 mm Hg), 0.2 g. Fraction V consisted mainly of a mixture of the cyclic product (IIb) and the adduct (IIIb), (^{13}C NMR spectrum), and fraction VI contained 85–90% of the adduct (IIIb). The diene (X) and the cyclic product (IIb) were separated on column b (temperature programming from 130 to 200°C). The product yields and the degrees of conversion of (I) are given in Table 2 (expt. 4). The ^1H and ^{13}C NMR spectra are given in Tables 3 and 4.

The $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ was obtained according to the method in [16] and was supplied by V. D. Makhaev, to whom the authors express their gratitude.

CONCLUSIONS

1. 1,1,1-Trichloro-2-phenylethane reacts with 2-chloropropene or 1-hexene with initiation by systems based on iron or molybdenum compounds, giving substituted tetrahydronaphthalenes. The latter are formed by cyclization and subsequent oxidation of the 2,2,4-trichloro-1-phenylbutyl radical.

2. Depending on the initiating system, linear products are formed in addition to the cyclic products during the reaction of 1,1,1-trichloro-2-phenylethane with 1-hexene.

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DETERMINATION OF THE RATE CONSTANT OF HYDROGEN ABSTRACTION FROM
 TRIETHYLSILANE BY $\text{Re}(\text{CO})_5$ RADICALS AND USE OF THE $\text{Re}_2(\text{CO})_{10}$ - Et_3SiH SYSTEM
 FOR THE REDUCTION OF POLYCHLOROALKANES

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The carbonyls of transition metals (MC) of the subgroup of chromium, manganese, and iron in combination with Et_3SiH are more efficient systems for the generation of RCCl_2 radicals from polyhalogen-containing compounds than the MC themselves [1]. The system $\text{Fe}(\text{CO})_5$ - Et_3SiH is more efficient for the reduction of MeCCl_3 than tert-butyl peroxide (TBP) in the presence of Et_3SiH [2]. The availability of kinetic data on the abstraction of hydrogen from Et_3SiH under the action of different MC and the detachment of chlorine by metal carbonyl radicals would allow us firstly to establish which particle participates at the chlorine detachment stage when using the system $\text{MC} + \text{Et}_3\text{SiH}$; secondly, it would allow us to assess which of the MC in combination with the silicon hydride would be the most efficient in the detachment of chlorine. It has been shown in [1, 3] that MC participate in the detachment of hydrogen from Et_3SiH also in the absence of chlorine-containing compounds.

In the present work EPR was used to determine the rate constant of the break-off of hydrogen (k_{br}) from Et_3SiH by $\text{Re}(\text{CO})_5$ radicals (A), formed in the photolysis of $\text{Re}_2(\text{CO})_{10}$



The constant k_{br} was determined by the concurrent kinetics procedure [4]. The stage competing with stage (2), selected for the work, was the addition of radicals A to 2,4,6-tri-tert-butyl-nitrosobenzene (BNB)



$\text{R}^1 = 2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$.

The selection of BNB as the spin trap (ST) was based on the fact that, firstly, this trap allows us to distinguish radicals (I) from radicals (II) [1, 5, 6]

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