HYDROSILYLATION OF 1-HEXENE IN THE PRESENCE OF $Re_2(CO)_{10}$ AND $Mn_2(CO)_{10}$

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We were the first to detect the capacity of $Fe(CO)_5$ to catalyze hydrosilylation with the formation of both saturated and unsaturated silicohydrocarbons (SH) [1]. Further development of these reactions was carried out by Schroeder and Wrighton [2]. The use of binuclear metal carbonyls in hydrosilylation reactions was explored largely for $Co_2(CO)_8$, and a mechanism has been proposed for such reactions [3]. The reaction of Et_3SiH with olefins in the presence of $Mn_2(CO)_{10}$ has also been described [4].

In the present work, we studied the possibility of using $Re_2(CO)_{10}$ for the initiation of the hydrosilylation of α-olefins and compared the properties of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ in such reactions. We previously studied the reduction of $RCCl_2X$ (X = H, Cl, Alk) by Et_3SiH initiated by $Re_2(CO)_{10}$ [5].

We studied the hydrosilylation of 1-hexene by Et_3SiH in the presence of $M_2(CO)_{10}$ (M = Mn and Re). In the case of $Re_2(CO)_{10}$, triethylhexylsilane (I) is formed under the conditions studied in 60-81% yield. Special experiments showed that an increase in the $Re_2(CO)_{10}$ concentration from 1 to 5 mole % (relative to C_6H_{12}) does not affect the product yields. The structure of (I) was supported by ^{13}C NMR and PMR spectroscopy. The ^{13}C NMR spectrum corresponds to that of a sample obtained by an independent pathway [6]. Gas–liquid chromatographic analysis showed the presence of traces of alkenylsilane (II). This impurity gives weak signals in the ^{13}C NMR spectrum in the C_{sp^2} region only upon prolonged accumulation. The formation of 4-9% hexane was also noted.

$$C_4H_9CH{=}CH_2 + HSiEt_3 \xrightarrow{Re_2(CO)_{10}} \underset{(I)}{Et_3SiC_6H_{13}} + C_6H_{14}$$

Carrying out the reaction with the same reagent ratio but in the presence of $Mn_2(CO)_{10}$ leads to different results. Gas–liquid chromatographic analysis shows formation of a mixture of adduct (I) with (II) and (III) which are $Et_3SiC_6H_{11}$ isomers differing in the position of the double bond. Indeed, the ^{13}C NMR spectrum of mixture (I)-(III) has signals for four C_{sp^2} atoms. In addition, about 1% hexaethyldisiloxane was identified in the mixture. A mixture of saturated and unsaturated SH and hexane is formed. The (I):(II):(III) ratio depends on the $Mn_2(CO)_{10}$ concentration. Thus, the relative yield of (II) and (III) increases with increasing $Mn_2(CO)_{10}$ concentration (Table 1, experiments 1 and 2). For the same $Mn_2(CO)_{10}$ concentration, the content of the unsaturated SH depends on the $[C_6H_{12}]:[Et_3SiH]$ ratio (see Table 1, experiments 2 and 3). An analogous effect of excess olefin leading to an increase in the relative yield of unsaturated SH was observed previously in the case of $Fe(CO)_5$ [7].

$$C_4H_9CH{=}CH_2 + HSiEt_3 \xrightarrow{Mn_2(CO)_{10}} (I) + \underset{(II)}{Et_3SiCH{=}CHC_4H_9} + \underset{(III)}{Et_3SiCH_2CH{=}CHC_3H_7} + C_6H_{14}$$

The presence of unsaturated adduct (I) and the unsaturated SH in the reaction mixture was indicated by ^{13}C and ^1H NMR spectroscopy. Table 2 gives the ^{13}C NMR spectral parameters for (I)-(III) for pure (I) and for the mixture of (I)-(III).

EXPERIMENTAL

The gas–liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a katharometer detector using helium as the gas carrier on A) a 2 m × 3 mm column packed

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TABLE 1. Reaction of Et_3SiH (8 mmoles) with 1-Hexene (4 mmoles) in the Presence of $Mn_2(CO)_{10}$ at 145°C for 5 h

Experiment No.	$Mn_2(CO)_{10}$, mole % rel. to 1-hexane	Conversion of C_6H_{12}	Yield, %		(I):(II):(III) Ratio by PMR
			C_6H_{14}	Mixture of (I)-(III)	
1	5	61	24	31	33 : 26 : 41
2	1	38	19	22	65 : 19 : 16
3*	1	–	52 †	28	33 : 33 : 33

*$[Et_3SiH]:[C_6H_{12}]$ = 1:3.

†Relative to C_6H_{12} consumed.

TABLE 2. ^{13}C NMR Spectra for Silicohydrocarbons (I)-(III)

Compound*	^{13}C NMR (δ, ppm)						$J_{C_\alpha-H}$, Hz
	C^1	C^2	C^3	C^4	C^5	C^6	
$Et_3Si\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$ (I)	11,3	23,6	33,4	31,4	22,4	13,9	116
$Et_3SiCH{=}CHCH_2CH_2CH_2CH_3$ (II)	125,4	148,2	34,8	30,8	22,8	13,7	142
$Et_3SiCH_2CH{=}CHCH_2CH_2CH_3$ (III)	17,1	125,8	128,4	36,5	22,0	13,4	120

*The regions of the poorly resolved signals for Et_3Si from (I)-(III) are: δCH_2 3.05 ppm and δCH_3 7.10-7.20 ppm.

with 6% β,β-hydroxydipropionitrile and C) a 2 m × 3 mm column packed with 15% SKTFT. The solid support was Chromaton N-AW-HMDS (0.16-0.20 mm). The yields of SH (I)-(III) were determined relative to internal standard $Et_3SiC_3H_7$. The temperature was programmed from 100 to 220°C at a rate of 12 deg/min. Hexane was identified relative to authentic samples, while hexaethylsiloxane was identified according to authentic samples on columns A and C. Separation of $Et_3SiC_6H_{13}$ and $Et_3SiC_6H_{11}$ was achieved on column B.

The ^{13}C NMR spectra both with and without suppression of C–H coupling and using the DEPT technique were obtained on a Bruker WP-200 spectrometer at 200 MHz using CCl_4 or $CHCl_3$ as the standards. The PMR spectra were taken on the same instrument for CCl_4 solutions using TMS as the standard. The ratios of the integral intensities were in accord with the predicted values. The relative contents of $Et_3SiC_6H_{13}$ and $Et_3SiC_6H_{11}$ were determined using the integral intensities of the CH_2 group protons.

The experiments shown in Table 1 and those with $Re_2(CO)_{10}$ were carried out in glass ampules filled in an argon atmosphere using the freeze–thaw technique. Residual $M_2(CO)_{10}$ was found in the experiments with 5% $M_2(CO)_{10}$ (M = Re and Mn). After separation of the residual $M_2(CO)_{10}$, the conversion of the initial reagents and the product yields were determined by gas–liquid chromatography.

Hydrosilylation of 1-Hexane. a) In the presence of $Re_2(CO)_{10}$. A mixture of 8 mmoles Et_3SiH, 4 mmoles 1-hexane, and 0.2 mmole $Re_2(CO)_{10}$ was heated for 5 h at 145°C. After separation of the precipitate and distillation of the unreacted starting reagents in vacuum, a residue was obtained which, according to gas–liquid chromatography, consisted of pure $(C_2H_5)_3SiC_6H_{13}$. The ^{13}C NMR spectral parameters are given in Table 2. PMR spectrum (δ, ppm): 0.53 q (4 CH_2) 0.95 t (4 CH_3), 1.36 m (4 CH_2) [8].

b) In the presence of $Mn_2(CO)_{10}$. Analogously, the reaction mixtures of experiments 1-3 (Table 1) gave fractions of SH (I)-(III). The ^{13}C and ^1H NMR spectra were obtained for these fractions.

CONCLUSIONS

1. This is the first report that $Re_2(CO)_{10}$ may be used as a catalyst for the hydrosilylation of α-olefins.

2. The reaction of 1-hexene with Et_3SiH in the presence of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ under comparable conditions leads to different reaction products. Triethylhexylsilane is formed in

the case of $Re_2(CO)_{10}$, while a mixture of saturated and unsaturated silicohydrocarbons was formed in the case of $Mn_2(CO)_{10}$.

LITERATURE CITED

1. R. Kh. Freidlina, E. Ts. Chukovskaya, and I. Tsao, Dokl. Akad. Nauk SSSR, 127, 352 (1959).
2. M. A. Schroeder and M. S. Wrighton, J. Organomet. Chem., 128, 345 (1977).
3. J. F. Harrod and A. J. Chalk, in: Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley-Interscience, New York (1977), p. 690.
4. A. B. Terent'ev, M. A. Moskalenko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim.. 2825 (1984).
5. R. G. Gasanov, L. V. Ivanova, N. A. Kuz'mina, and E. Ts. Chukovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2062 (1985).
6. R. Kh. Freidlina, Yu. P. Egorov, E. Ts. Chukovskaya, I. Tsao, and E. D. Lubuzh. Izv. Akad. Nauk SSSR, Ser. Khim., 1256 (1961).
7. E. Ts. Chukovskaya, N. A. Kuz'mina, and M. A. Rozhkova, Zh. Obshch. Khim., 36, 2170 (1966).
8. A. Millan, E. Towns, and P. M. Maitlis, J. Chem. Soc., Chem. Commun., 673 (1981).

OXIDATION OF ISOPRENE BY MOLECULAR OXYGEN IN THE PRESENCE OF THE TETRAPHENYLPORPHIN COMPLEX OF DIVALENT MANGANESE

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The tetraphenylporphinate $(TPP)Mn^{II}Cl$ obtained by the reduction of the corresponding Mn^{III} complex activates O_2 and thereby catalyzes the oxidation of olefins with different extents of substitution into ketones and alcohols [1-3]. The kinetics was studied, and a reaction mechanism was proposed [3, 4]. In the present work, we studied the regioselectivity of the oxidation of isoprene and 2-methylpentene in the presence of this catalytic system.

The oxidation of isoprene by O_2 in the presence of a system consisting of $TPPMn^{III}Cl$ and sodium borohydride gave only 3-methyl-2-buten-1-ol whose structure was supported bv IR spectroscopy. gas–liquid chromatography, and ozonization. Comparison of the data for the oxidation of isoprene and 2-methyl-2-pentene (Table 1) shows that the oxidation in both cases proceeds regioselectivity. The rate of the oxidation of isoprene is about five times greater than that for 2-methyl-2-pentene, while the yields of the oxidation products differ correspondingly by a factor of 2-3.

TABLE 1. Oxidation of Isoprene and 2-Methyl-2-pentene by Atmospheric Oxygen in the Presence of $TPPMn^{III}Cl–NaBH_4$

Olefin	Reaction products	$k_{ef}\cdot 10^{-4}$,* sec^{-1}	Reaction product yield relative to olefin, %	Reaction product yield yield relative to catalyst, %
2-Methyl-2-pentene	2-Methyl-2-pentanol	2,5	20	$4\cdot 10^3$
Isoprene	2-Methyl-2-buten-1-ol	15	50	$12\cdot 10^3$

*The value for k_{ef} was found using the initial slope of the experimental curves.

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