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REACTION OF OXYGEN-CONTAINING MONOMERS WITH TRIETHYLSILANE IN THE PRESENCE OF IRON, MANGANESE, AND RHENIUM CARBONYLS

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A study was carried out on the reaction of triethylsilane (TES) with acrolein, the diethyl acetal of acrolein, and allyl alcohol in the presence of $Fe(CO)_5$*,* $Mn_2(CO)_{10}$*, and* $Re_2(CO)_{10}$*. Acrolein reacts with TES in the presence of* $Fe(CO)_5$ *to give the 1,4-addition product in high yield. The reaction of the diethyl acetal of acrolein largely features cleavage of the C–O bond and formation of* Et_3SiOEt*. Allyl alcohol reacts with TES in the presence of* $Fe(CO)_5$*,* $Mn_2(CO)_{10}$*, and* $Re_2(CO)_{10}$ *to give the dehydrocondensation product, namely, triethylallyloxysilane, which undergoes hydrogenation and hydroxylation to give triethylpropyloxysilane and* γ*-(triethylsilyloxy)propyltriethylsilane, respectively. The yields of these products depend on the metal carbonyl used.*

The nature of the substituent at the double bond has been shown to have a significant effect in the hydrosilylation of $CH_2{=}CHX$ compounds (X = H, Alk, OEt, and CO_2Me) in the presence of Fe, Mn, and Re carbonyls [1-3].

In the present work, we clarified the possibility of using Fe, Mn, and Re carbonyls for the hydrosilylation of acrolein (I), the diethyl acetal of acrolein (II), and allyl alcohol (III) by TES.

The reaction of TES with (I) in the presence of $Fe(CO)_5$ gives the 1,4-addition product, namely, 1-triethylsilyloxy-1-propene [4, 5]:

$$CH_2 = \underset{(I)}{CHCHO} + Et_3SiH \rightarrow CH_3CH = \underset{(IV)}{CHOSiEt_3}$$

The yield of (IV) increases with increasing $Fe(CO)_5$ concentration and decreasing [TES]:[(I)] ratio (Table 1). In the presence of Mn and Re carbonyls, a mixture of products is formed, one of which is $(Et_3Si)_2O$.

The hydrosilylation of (II) in the presence of $Fe(CO)_5$ and $Mn_2(CO)_{10}$

$$CH_2 = CHCH(OEt)_2 + Et_3SiH \rightarrow \underset{(V)}{Et_3SiCH_2CH_2CH(OEt)_2}$$

proceeds with a low yield of the hydrosilylation product, namely, γ,γ-diethoxypropyltriethylsilane (V) (see Table 1). The predominant process in this case is the cleavage of (II) by the action of TES to give Et_3SiOEt (VI); the yield of (VI) in the presence of $Mn_2(CO)_{10}$ is 80%. This shows that the splitting of the C–O bond in acetals by triethylsilane in the presence of metal carbonyls proceeds much more readily than in ethers (under comparable conditions) [2].

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TABLE 1. Reaction of Triethylsilane (TES) with Unsaturated Compounds (UC) in the Presence of Metal Carbonyls (MC) at 140°C over 4 h

UC	[TES] / [UC]	MC, mole %	Product yields, %
$CH_2{=}CHCHO$ (I)	2	$Fe(CO)_5$, 1	(IV), 68
(I)	2	$Fe(CO)_5$, 4	(IV), 82
(I)	0.5	$Fe(CO)_5$, 4	(IV), 95
$CH_2{=}CHCH(OEt)_2$ (II)	2	$Fe(CO)_5$, 1	(V), 14 (VI), 27
(II)	2	$Mn_2(CO)_{10}$, 1	(V), 5 (VI), 80

TABLE 2. Reaction of Allyl Alcohol (III) with TES in the Presence of 1 mole % MC at 140°C over 4 h

$\frac{[TES]}{[(III)]}$	MC	Yield of reaction products, %†		
		(VII)	(VIII)	(IX)
2	$Fe(CO)_5$	26	32	–
0,5	$Fe(CO)_5$	24	14	–
2	$Mn_2(CO)_{10}$	60	10	19
0,5	$Mn_2(CO)_{10}$	91	8	1
3	$Mn_2(CO)_{10}$	47	17	23
2	$Re_2(CO)_{10}$*	18	23	5

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*Experiment carried out at 150°C.

†Yield calculated in % of the starting compound taken in insufficient amounts.

TABLE 3. NMR Spectral Parameters

Compound*		^{13}C (δ, ppm)			PMR (δ, ppm)		
		C^1	C^2	C^3	H^1	H^2	H^3
$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2OSiEt_3$	(VIII)	10,12	25,87	63,98	0,9 (m)	1,50 (m)	3,50 (t)
$CH_2{=}CHCH_2OSiEt_3$	(VII)	113,27	137,23	63,29	5,0–5,3 (m)	5.8–6,0 (m)	4.05 (m)
$CH_3CH{=}CHOSiEt_3$	(IV)	8,43	138,59	104,56	1,55 (m)	4.40 (m)	6,15 (m)
$Et_3Si\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2OSiEt_3$	(XI)	4,44	27,20	65,44	0,6 (q)	1,4–1,6 (m)	4,5 (t)
$Et_3Si\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H(OEt)_2$ †	(V)	6.22	28,30	59,40	0,6 (q)	2,20 (m)	4,05
$Et_3SiO\overset{1}{C}H_2\overset{2}{C}H_3$	(VI)	58,96	14,55	–	3,65 (q)	1,25 (t)	–

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* $SiCH_2CH_3$ (δ, ppm) ^{13}C 3,04—4,41, 6,52—7,30; ^1H: CH_2 0,4—0,6; CH_3: 0,8—1,0.
† OCH_2CH_3 (δ, ppm) ^{13}C: 28,3, 14,29; ^1H: 4,05 q, 1,25 t.

Allyl alcohol (III) reacts with TES in the presence of Fe, Mn, and Re carbonyls largely to give triethylallyloxysilane (VII), which then participates in two parallel reactions, namely, hydrogenation and hydrosilylation:

$$Et_3SiH + \underset{(III)}{CH_2{=}CHCH_2OH} \rightarrow \underset{(VII)}{CH_2{=}CHCH_2OSiEt_3} + H_2$$

$$(VII) + H_2 \rightarrow \underset{(VIII)}{CH_3CH_2CH_2OSiEt_3}$$

$$(VII) + Et_3SiH \rightarrow \underset{(IX)}{Et_3SiCH_2CH_2CH_2OSiEt_3}$$

Product (VIII) may also be formed by hydrogenation of (III) with subsequent dehydrocondensation:

$$CH_2{=}CHCH_2OH \xrightarrow{H_2} CH_3CH_2CH_2OH \xrightarrow{Et_3SiH} (VIII)$$

However, 1-propanol was not detected in the reaction mixtures by gas-liquid chromatography.

In the presence of $Fe(CO)_5$ and $Re_2(CO)_{10}$, dehydrocondensation and hydrogenation proceed with similar yields (Table 2). Dehydrocondensation predominates in the presence of $Mn_2(CO)_{10}$. In the case of excess TES, hydrosilylation product (IX) is formed in 19-23% yield in the presence of $Mn_2(CO)_{10}$.

The reaction of (III) and TES in the presence of $H_2PtCl_6 \cdot 6H_2O$ largely leads to dehydrocondensation products [6]. The use of $Rh(acac)_3$ gives only $(Et_3Si)_2O$ [7].

The structures of all the compounds synthesized were supported by the NMR spectral data given in Table 3 [8].

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph using a katharometer detector, helium gas carrier, and a 2 m × 3 mm column packed with 15% SKTFT-50 on Chromaton N-AW-HMDS (0.15-0.2 mm). In order to separate the products by preparative gas-liquid chromatography, a 0.8 m × 8 mm column was used packed with 15% E-301 on Chromaton N-AW (0.20-0.25 mm). The NMR spectra were obtained on a Bruker P-200SY spectrometer. The PMR spectra were taken for 20-50% solutions in CCl_4 with TMS as the internal standard. The ^{13}C NMR spectra were taken in the Imodecho mode and without suppression of the spin-spin coupling with protons for solutions in CCl_4.

The hydrosilylation of (I)-(III) in the presence of metal carbonyls (Tables 1 and 2) was carried out in glass ampuls sealed in an argon atmosphere by the freeze-thaw method. The product yields were determined by gas-liquid chromatography using an internal standard with temperature programming from 50 to 250°C at a rate of 8 deg/min.

Preparative gas-liquid chromatography was used to separate cis- and trans-1-triethylsilyloxy-1-propenes (IV), γ-diethoxypropyltriethylsilane (V), and triethylethoxysilane (VI), the mixture of triethylallyloxysilane (VII) and triethylpropyloxysilane (VIII) as well as γ-(triethylsilyloxy)propyltriethylsilane (IX) (n_D^{20} 1.4489 and d_4^{20} 0.8523). Authentic samples of (VII) and (VIII) were synthesized according to a patent procedure [9] and used for identification.

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