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ADDITION, SUBSTITUTION, AND TELOMERIZATION REACTIONS OF OLEFINS IN THE PRESENCE OF METAL CARBONYLS OR COLLOIDAL IRON*

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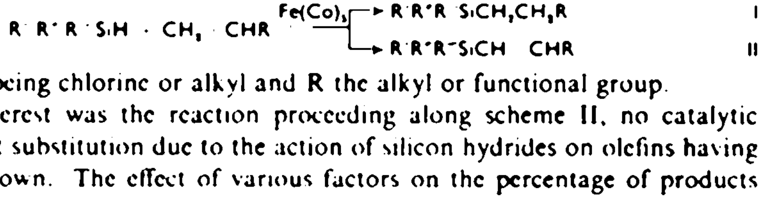
THERE are about fifty reactions known to be catalysed by metal carbonyls,[1] those for olefins being mainly of three types such as carbonylation, hydrogenation and isomerization. They are essentially effected in the presence of carbon monoxide and metal carbonyls under 400 atm and up to 300°. Reactions that seem to be similar to those catalysed by metal carbonyls also proceed on the surface of the catalysing metal in the presence of carbon monoxide.[1]

We suggest now several new ways to apply metal carbonyls as catalysts. The reactions under study proved to be specific in running without carbon monoxide usually used to regenerate metal carbonyls.

We have found[2] silicon hydrides to react with olefins with small amounts of iron pentacarbonyl at 100–140° in two directions according to schemes I and II to form saturated or unsaturated silanes



$$R'R''R'''SiH + CH_2{=}CHR \xrightarrow{Fe(CO)_5} \begin{cases} R'R''R'''SiCH_2CH_2R & \text{I} \\ R'R''R'''SiCH{=}CHR & \text{II} \end{cases}$$

with R', R'', R''' being chlorine or alkyl and R the alkyl or functional group.

Of special interest was the reaction proceeding along scheme II, no catalytic reactions of direct substitution due to the action of silicon hydrides on olefins having been formerly known. The effect of various factors on the percentage of products obtained following schemes I or II is not always clear. In some cases an excess of silicon hydride favours the formation of saturated compounds along scheme I and an excess of olefins that of unsaturated products via scheme II. See Table 1.

The direction of addition following scheme I was determined by structural study of the saturated addition product of methyldichlorosilane to propylene. The compounds were methylated with Grignard reagent, the products isolated were treated with conc sulphuric acid to dissolve unsaturated silanes and the saturated remainder was conventionally purified identified by its constants, analysis and Raman spectra as n-propyltrimethylsilane[2]. The direction of addition proved thus to be the same as when carrying the reaction in the presence of platinum or peroxides.

Instanced by the reaction of methyldichlorosilane and decene-1 the process was shown to be catalysed only by iron pentacarbonyl without any co-catalysts, unlike the reaction of methyldichlorosilane with acrylonitrile described below.[3] Indeed methyldichlorosilane and decene-1 react in the presence of iron pentacarbonyl

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* Translated by A. L. Pumpiansky, Moscow.

[1] H. W. Sternberg, R. Markby and J. Wender *Chem. & Ind.* 42, 41 (1960)

[2] R. Kh. Freidlina, E. C. Chukovskaya, J. Tsao and A. N. Nesmeyanov, *Dokl. Akad. Nauk. SSSR* 132, 374 (1960)

TABLE 1. REACTION OF SILICON HYDRIDES AND OLEFINS IN THE PRESENCE OF IRON PENTACARBONYL OR COLLOIDAL IRON

N N	Silicon hydride	Olefin	Silicon hydride / Olefin (mole)	Structure of resulting products	Conversion of silan accounted for by the charget silan (%)	Overall yield of I and II	Relative yield (%) I	Relative yield (%) II
				$Fe(CO)_5$				
1	$(C_2H_5)_3SiH$	$CH_2{=}CH_2$	3:1†	$(C_2H_5)_4Si$‡ I	100	79	100	—
2	$(C_2H_5)_3SiH$	$CH_2{=}CH_2$	1:5	$(C_2H_5)_3SiCH{=}CH_2$ II	73	92	—	100
3	CH_3SiCl_2H	$CH_2{=}CH_2$	1:7	$CH_3SiCl_2C_2H_5$ I	57	89	100	—
4	$SiCl_3H$	$CH_3CH{=}CH_2$	1:3	$Cl_3SiC_3H_7$ I $Cl_3SiC_3H_5$ II	34	85	50	50
5	$SiCl_3H$	$CH_3CH{=}CH_2$	2:1†	$Cl_3SiC_3H_7$ I $Cl_3SiC_3H_5$ II	48	83	60	40
6*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	3:1†	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	49	79	75	25
7*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:4	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	67	73	25	75
8*	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:8	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	66	83	5	95
9	CH_3SiCl_2H	$C_8H_{17}CH{=}CH_2$	1,25:1	$CH_3SiCl_2C_{10}H_{21}$ I $CH_3SiCl_2C_{10}H_{19}$ II	39	94	20-30	70-80
10	CH_3SiCl_2H	$C_8H_{17}CH{=}CH_2$	5:1†	$CH_3SiCl_2C_{10}H_{21}$ I $CH_3SiCl_2C_{10}H_{19}$ II	39	91	20-30	70-80
11	$(C_2H_5)_3SiH$	$CH_2{=}CHOC_2H_5$	1:1,5	$(C_2H_5)_3SiOC_2H_5$ I $(C_2H_5)_3SiCH{=}CHOC_2H_5$ II	52	100	52,5	47,5
				Colloidal iron				
12	CH_3SiCl_2H	$CH_2{=}CH_2$	1:4	$C_2H_5SiCl_2CH_3$ I	44	90	100	—
13	CH_3SiCl_2H	$CH_3CH{=}CH_2$	1:3	$CH_3SiCl_2C_3H_7$ I $CH_3SiCl_2C_3H_5$ II	24	80	20	80

* These runs gave rise to a considerable amount of solid polypropylene

† Conversion in these runs was estimated in percentage to 1 mole of silane charget

‡ The reaction also led to 4 per cent yield of $(C_2H_5)_3SiCH_2CH_2Si(C_2H_5)_3$.

in nitrogen both in sealed glass ampoules and autoclave to form the same products in similar yields. This reaction allowed us to establish that during the formation of unsaturated silanes following scheme II it is decene that is acting as hydrogen acceptor to be thereby hydrated to n-decane.

The Raman spectra of the mixture of trimethyl derivatives obtained after methylation with Grignard reagent of the sum of products formed in the reaction between methyldichlorosilane and decene-1 revealed in the $C=C$ range two bands, one at 1615 cm^{-1} and the other at 1662-1670 cm^{-1} split into two components. This allows to deduce that the mixture contained both a vinyl compound $(CH_3)_3SiCH=CHC_8H_{17}$ and allylic *cis-trans*-isomers $(CH_3)_3SiCH_2CH{-}CHC_7H_{15}$ (*cf.*[3,4,5]).

To elucidate the possibility of applying these reactions to unsaturated compounds involving reactive groups we have investigated the reaction of triethylsilane with vinylethyl ether and that of methyldichlorosilane and triethylsilane with acrylonitrile.[2,6,7] With vinylethyl ether the reaction yielded β-triethylsylylvinylethyl ether $(C_2H_6)_3SiCH=CHOC_2H_5$, whose structure was proved by acid hydrolysis to give acetaldehyde and hexaethyldisyloxane as well as by the absence in the infra-red spectrum 3000 and 3060 cm^{-1} of frequencies assigned to the terminal CH_2 group.

The infra-red spectra in the $C=C$ range revealed a double bond line, split into two components at 1597 and 1609 cm^{-1}, such a split being characteristic of vinyl ethers observed before.[8-10]

Ethoxytriethylsilane was also isolated. Its formation seems possibly to be due to β-decomposition of an intermediate saturated β-triethylsilyldiethyl ether $(C_2H_6)_3SiCH_2{-}CH_2OC_2H_6$ produced following scheme I.

It is to be particularly noted that in no instances mentioned above did a large excess of olefins or ethylene with its large excess up to the pressure of 500 atm give rise to telomer homologues.

Some of the described reactions when carried out in the presence of colloidal iron led to results similar to those obtained with iron pentacarbonyl. Thus, methyldichlorosilane and ethylene in the presence of colloidal iron gave methyldichlorosilane, and with propylene produced correspondingly a mixture of saturated and unsaturated silanes (see Table 1).

The investigation of the reaction of silicon hydrides and acrylonitrile gave different results. The reaction was carried out in a stainless steel autoclave or sealed glass ampoules at 120–150° with no catalyst or with iron pentacarbonyl, nickel chloride or their mixture. The results had been reported in detail[6] and can be summarized here as follows. In the absence of catalysts or in the presence of nickel chloride alone there is no reaction. Triethylsilane fails to react with acrylonitrile in the presence of iron pentacarbonyl or colloidal iron in an autoclave. Methyldichlorosilane does not react with acrylonitrile in the presence of iron pentacarbonyl in a sealed glass ampoule, but under the same experimental conditions in an autoclave an adduct is formed whose yield increases with increasing excess acrylonitrile. These data permitted to suggest

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[3] A. D. Petrov, Yu. P. Yegorov, *et al. Izv. Akad. Nauk, SSSR, Otdel Khim. Nauk* 50 (1956).

[4] Yu. P. Yegorov, *Izv. Akad. Nauk. SSSR, Otdel Khim. Nauk* 124 (1957).

[5] A. D. Petrov, S. I. Sadikh-Zade, *et al., Zh. Obsch Khim.* 24, 2479 (1957).

[6] R. Kh. Freidlina, I. Tsao and E. C. Chukovskaya, *Dokl. Akad. Nauk SSSR* 132, 149 (1960).

[7] R. Kh. Freidlina, E. C. Chukovskaya and I. Tsao *Dokl. Akad. Nauk SSSR* 127, 352 (1959).

[8] M. I. Batuyev, E. N. Prilezhaeva and M. F. Shostakovsky, *Izv. Akad. Nauk Otdel. Khim. Nauk SSSR,* 123 (1947).

[9] A. Kirrmann, P. Chancel, *Bull. Soc. Chim. Fr* 1388 (1954).

[10] P. P. Shorygin, T. N. Shkurina, *et al., Izv. Akad. Nauk SSSR, Otdel Chim. Nauk* In press.

that the reaction takes place because the mixture contains, in addition to iron carbonyl, traces of heavy metal salts formed on the autoclave walls under the action of chlorosilanes.

A similar effect of traces of heavy metal salts was observed when cyanoethylating silicochloroform in autoclaves in the presence of pyridine.[11] Indeed, when iron pentacarbonyl and nickel chloride are both present in small amounts acrylonitrile adds both methyldichlorosilane and triethylsilane. The reactions proceed equally well in an autoclave and in sealed ampoules, addition giving rise to α-methyldichlorosilylpropionitrile $CH_3SiCl_2CH(CH_3)CN$ with methyldichlorosilane or α-triethylsilylpropionitrile $(C_2H_5)_3SiCH(CH_3)CN$ with triethylsilane.

TABLE 2. REACTION OF $C_2H_5OCO(CH_2)_4SH$ WITH UNSATURATED COMPOUNDS

Unsaturated compound	Molar ratio mercaptan – unsat. comp.	Initiator	Temp(°C)	Time(hr)	Adduct yield (% of theory)
$CH_2=CHCO_2CH_3$	3	without initiator	175–200	7.5	20
$CH_2=CHCO_2CH_3$	3	$Fe(CO)_5$	130–150	4	85
$CH_2=CHCO_2CH_3$	3	Bz_2O_2	80–85	3.5	31*
$CH_2=CHCN$	4	without initiator	140–150	5	41
$CH_2=CHCN$	4	$Fe(CO)_5$	140–150	5	85
$CH_2=CHCN$	4	Bz_2O_2	80–85	3.5	76
$CH_2=CHCN$	4	colloidal iron	140–150	2.5	91

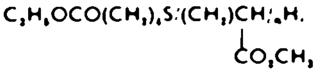
* Accounted for by the mercaptoester that had reacted. In addition to the adduct, such telomers as $C_2H_5OCO(CH_2)_4S(CH_2CHR)_nH$ were isolated, where $n = 2$ and 3, in 15.3 and 16.5 per cent yield, respectively.

We have further found iron pentacarbonyl and colloidal iron to catalyse mercaptane addition to acryl compounds and succeeded in effecting reactions between ethyl δ-mercaptovalerate and acrylonitrile and methylacrylate (see Table 2). The reaction gave high yields at 130–150° following scheme III:

$$C_2H_5OCO(CH_2)_4SH + CH_2=CHR \rightarrow C_2H_5OCO(CH_2)_4SCH_2CH_2R$$

with R = CN, CO_2CH_3.

The reactions could also be effected without any catalyst but at higher temperatures and in substantially decreased yields (see Table 2). The reaction of mercaptane in the presence of iron carbonyl, even with a high excess of methylacrylate or acrylonitrile, does not lead to telomer homologues. In the presence of benzoyl peroxide, methylacrylate is telomerized by ethyl δ-mercaptovalerate to form a mixture of telomer homologues



$$C_2H_5OCO(CH_2)_4S[CH_2CH(CO_2CH_3)]_nH,$$

from which were isolated compounds with $n = 1, 2, 3$.

With acrylonitrile, and in the presence of benzoyl peroxide only, a corresponding adduct was formed. Those obtained using iron pentacarbonyl, colloidal iron, benzoyl peroxide, or by heating in the absence of catalysts proved to be identical and appeared to have the structure $C_2H_5OCO(CH_2)_4SCH_2CH_2R$ with R being CO_2CH_3, CN.

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[11] S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan* **29**, 323, 326 (1956).

Considering the fact that in the presence of iron pentacarbonyl it is possible to add smoothly to olefins and their derivatives various compounds containing a labile hydrogen-element bond, and that these reactions are not affected by telomerization, it was thought of interest to study the reaction of ethylene and chloroform as well as other chloromethanes in the presence of metal carbonyls. Iron pentacarbonyl, as well as chromium, molybdenum, and tungsten hexacarbonyls were found to initiate the ethylene telomerization reaction by chloroform or carbon tetrachloride*[12,13] and iron pentacarbonyl by ethyltrichloroacetate. The most useful metal carbonyls investigated proved to be iron pentacarbonyl and chromium hexacarbonyl whose presence allowed us to obtain at 100–130° the same products as with benzoyl peroxide. A close similarity was observed in the extent of conversion of polychloromethanes and the yields of telomer homologues, under comparable conditions, but using as a catalyst iron pentacarbonyl or benzoyl peroxide.

Molybdenum and tungsten hexacarbonyls proved, under much the same conditions, less effective not only due to a lower conversion but also the formation of a complex mixture of by-products when ethylene was telomerized by chloroform or carbon tetrachloride (see Table 3).

There are not yet enough data to judge on the mechanism of the reactions under study. It seems, however, rather difficult to envisage them as proceeding along a single mechanism.

The reactions under discussion can be divided into two classes. The first class involves silicon hydride and mercaptan additions to unsaturated compounds and telomerization of ethylene by polychloromethane. Iron pentacarbonyl or colloidal iron may be supposed to form with unsaturated compounds π-complexes that actually catalyse these reactions. The second class comprises the addition of silicon hydrides to acrylo nitrile in the presence of iron pentacarbonyl and nickel chloride.

It is to be noted that the conditions leading to optimum conversion in the reactions in question were not studies. Therefore we did not deem it possible to discuss the relationship between the structure of starting compounds and the extent of the conversion observed.

EXPERIMENTAL

1. *The reaction of triethylsilane and ethylene*

The reaction was carried out with excess ethylene to obtain triethylvinylsilane. A stainless steel (500 cm) autoclave was charged with $(C_2H_5)_3SiH$ (34 g) and $Fe(CO)_5$ (0.5 ml). The air was substituted by nitrogen and ethylene fed up to 45 atm. After heating for 5 hr at 130 pressure was allowed to drop from 70 to 35 atm. Overall yield: 39.5 g with 27 g of triethylvinylsilane isolated. After repeated distillation: b.p. 144.5; n_D^{20} 1.4330; d_4^{20} 0.7718 (Found: Mr, 47.92. Calc. for $C_8H_{18}Si$†, 48.26), lit.[16] (Found: C, 67.27, 67.39; H, 12.96, 13.18. $C_8H_{18}Si$ requires C, 67.57; H, 12.75%).

Raman spectrum‡ is in agreement with that reported for triethylvinyl silane.[18] The product was

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* Shortly after the publication of our paper[12] we got to know that a British Patent[14] also mentioned the possibility of using iron pentacarbonyl and iron to initiate the telomerization of ethylene by CCl_4 and $CHCl_3$.

† The calculation here and further on was made using increments of groups suggested by Mirinov and Nikishin[19].

‡ Spectra referred to in this paper were all taken and interpreted by L. A. Leites (Institute of Chemistry of the U.S.S.R. Academy of Sciences).

[12] R. Kh. Freidlina and A. B. Belyavsky, *Dokl. Akad. Nauk SSSR* **127**, 1027 (1959).

[13] R. Kh. Freidlina and A. B. Belyavsky, *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk* 177 (1961).

[14] Brit. Pat. 803,463, *Chem. Abstr.* 11222c (1959).

[16] K. A. Andrianov, *Organo-Silicon Compounds* p. 113. Moscow (1955).

[17] K. A. Andrianov, *Organo-Silicon Compounds* p. 414. Moscow (1955).

[18] Yu. P. Yegorov and P. A. Bazhulin, *Dokl. Akad. Nauk SSSR* **88**, 647 (1953).

[19] V. P. Mironov and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1080 (1958).

completely soluble in conc. H_2SO_4, on dilution only hexaethyldisiloxane was isolated, b.p. 233°, n_D^{20} 1·4328, d_4^{20} 0·8448.

(Found: Mr, 75·85. Calc. for $C_{12}H_{30}Si_2O$ 76·08), lit.[17]

Repeating the experiment under initial ethylene pressure of 5 atm with a pressure drop in the course of the reaction from 20 to 10 atm at 130° gave $(C_2H_5)_4Si$ in 73% yield (theory), accounted for by the triethyl silane that had reacted and hexaethyldisilylethane in 4% yield.

2. *The reaction of propylene and methyldichlorosilane*

(a) *In the presence of iron pentacarbonyl.* A stainless steel autoclave (500 cm³) was charged with 57 g of CH_3SiCl_2H (0·5 mole), 1 ml of $Fe(CO)_5$ and 108 g of C_3H_6 (2·5 moles). It was heated at 130–140° for 4 hr. Overall yield: 70 g. After separation of unreacted CH_3SiCl_2H, 42 g of a fraction, b.p. 124–127°, n_D^{20} 1·4395, d_4^{20} 1·0593, were produced (*cf.* a similar experiment in ref. 2).

Methylation with Grignard reagent gave a fraction b.p. 85–87°, n_D^{20} 1·4065, d_4^{20} 0·7186.

Below are given comparative literature data for trimethylalkenylsilanes and trimethylpropyl silane[19,20]

	b.p.	n_D^{20}	d_4^{20}
$(CH_3)_3SiCH{=}CHCH_3$	86–87	1·4086	0·7167
$(CH_3)_3SiCH_2CH{=}CH_2$	84·9	1·4074	0·7193
$(CH_3)_3Si{-}\underset{\underset{CH_2}{\Vert}}{C}{-}CH_3$	82·8–83	1·4070	0·7186
$(CH_3)_3SiC_3H_7$-*n*	90	1·3918	0·7020

The Raman spectra substantiated that the product obtained was indeed mostly $(CH_3)_3SiCH{=}CHCH_3$. 1 ml of this fraction was treated with 4 ml of conc. H_2SO_4 resulting in a violent reaction accompanied by strong heating and dissolution of the whole product to leave a minute organic layer ~0·08 mm thick.

(b) *In the presence of colloidal iron.* The experiment was conducted as above. An autoclave was charged with 119 g (1·05 moles) of CH_3SiCl_2H, 132 g of C_3H_6 (3 moles) and 2 ml of colloidal iron solution prepared as reported[21] to yield 30 g of a fraction, b.p. 115–130° (boiling mainly at 124–127°), n_D^{20} 1·4370, d_4^{20} 1·0537. Methylation with Grignard reagent led to a substance, b.p. 86–87·5°, n_D^{20} 1·4050, d_4^{20} 0·7181. (Found: C, 62·25, 62·31; H, 12·97, 13·17. $C_6H_{14}Si$ requires: C, 63·08; H, 12·35; Si, 24·57. $C_6H_{16}Si$ requires: C, 61·98; H, 13·87; Si, 24·15%.)

On treatment of 1 ml of the substance with 4 ml of conc. H_2SO_4 0·8 ml of the substance dissolved to leave 0·2 ml of undissolved organic layer.

Raman spectra revealed bands assigned to $(CH_3)_3SiCH{=}CHCH_3$ and $(CH_3)_3SiC_3H_7$—n.

3. *Cyanoethylation of silicon hydrides*

(a) *Reaction with methyldichlorosilane.* A stainless steel autoclave was charged with 115 g (1 mole) of CH_3SiCl_2H, 160 g (3 moles) of $CH_2{=}CHCN$, 1 ml of $Fe(CO)_5$ and 0·15 g of $NiCl_2$. The air was substituted by nitrogen and then nitrogen was fed up to 30 atm. After heating for 5 hr at 120–130° the reaction mixture was fractionated *in vacuo* to give 120 g (72% of theory) of α-methyldichlorosilylpropionitrile, b.p. 59–60°/1 mm, n_D^{20} 1·4490, d_4^{20} 1·1635. (Found: Mr, 38·74. Calc. for $C_4H_7SiCl_2N$: 38·62) (Found: Si, 17·21, 16·88. Calc.: Si, 16·71%). Titration of 0·1 N NaOH gave: Cl, 42·49, 42·41. $C_4H_7SiCl_2N$ requires: Cl, 43·17%.)

The structure of the adduct was proved as usual.[9,11] α-Methyldichlorosilyl propionotrile was methylated with methylmagnesiumiodide to give α-trimethyl silyl propionitrile. Yield 80%, b.p. 71·5°/20 mm, n_D^{20} 1·4245, d_4^{20} 0·8303. (Found: Mr, 39·14. Calc. for $C_6H_{13}SiN$: 39·09), lit.[11]: n_D^{25} 1·4232, d_4^{25} 0·8254. (Found: C, 56·64, 56·55; H, 10·47, 10·37; Si, 22·08, 22·39. $C_6H_{13}SiN$ requires: C, 56·63; H, 10·30; Si, 22·05%.)

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[20] A. D. Petrov and G. I. Nikishin, *Zh. Obshchei Khim.* 26, 1233 (1956).

[21] C. L. Sims and E. W. S. Mardles, *Trans. Faraday Soc.* 22, 364 (1926).

TABLE 3

Run	Carbonyl	Telogen	Amount of telogen (g)	Pressure change at 115–120	Telogen conversion (%)	Telomer homologues obtained (g): $CCl_3(CH_2CH_2)_nX$ (X = H,Cl)* or $Cl(CH_2CH_2)_nCCl_2CO_2C_2H_5$				
						$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n > 4$
1	$Cr(CO)_6$	$CHCl_3$	223	110–75	27	(7)	20	12	5	(22)
2	$Cr(CO)_6$	CCl_4	240	100 60	52	(20)	84	30	10	(15)
3	$Cr(CO)_6$	CCl_4	240	35–5	—	33	(18)			
4	$Mo(CO)_6$	CCl_4	240	115–80	23		13		(6)	
5	$W(CO)_6$	CCl_4	240	110–95	20	(8)	27	7		
6	$Fe(CO)_5$	CCl_4	236	130–100†	70	(8)	53	36	11	(23)
7	$Fe(CO)_5$	$HCCl_3$	440	230–140‡	41	(17)	32	21	15	(56)
8	$Fe(CO)_5$	$CCl_3CO_2C_2H_5$	125		72	34	42	6	(63)§	

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* Figures not included in brackets indicate the weight of individual compounds produced. Those in brackets denote the weight of the product obtained as a broad fraction.

† At reaction temperature 100–105°.

‡ At reaction temperature 130–135°.

§ The weight of the fraction $n > 3$.

(b) *Reaction with triethylsilane* The experiment was conducted as with methyldichlorosilane. 87 g (0·73 mole) of triethylsilane, 132 g (2·5 moles) of acrylonitrile, 0·5 ml of $Fe(CO)_5$ and 0·2 g of $NiCl_2$ yielded 92 g (73% of theory) of a substance, b.p. 97-98/8 mm. Repeated distillation resulted in n_D^{20} 1·4535, d_4^{20} 0·8534 (Found: Mr, 52·95. Calc. for $C_9H_{19}SiN$: 52·88) (Found: C, 63·77, 63·49; H, 11·38, 11·33; Si, 16·83, 16·85. $C_9H_{19}SiN$ requires: C, 63·85; H, 11·31; Si, 16·57%.)

The infra-red spectrum of this compound reveals a band 2205 ± 10 cm^{-1} assigned to α-nitriles.

4. *Reaction of ethyl δ-mercaptovalerate with acrylonitrile*

(a) *In the presence of iron pentacarbonyl.* A mixture of ethyl mercaptovalerate (20 g, 0·12 mole), acrylonitrile (25 g, 0·47 mole) and iron pentacarbonyl (0·3 ml) was heated for 5 hr, in an autoclave after substitution of nitrogen for air at 140-150

The polymeric precipitate of acrylonitrile was filtered off and washed with chloroform, the filtrate and chloroform extract were poured together, the solvent separated and the residue distilled *in vacuo*. Yield of addition product: 22·6 g (85% of theory), b.p. 158-160/3 mm, n_D^{20} 1·4790, d_4^{20} 1·0599. (Found: Mr, 57·52. Calc. for $C_{10}H_{17}O_2SN$: 57·73). (Found: C, 55·66, 55·59; H, 7·95, 8·00; S, 14·33, 14·28. Calc.: C, 55·81; H, 7·90; S, 14·88%.)

The sulphide produced was saponified with alkali to 4-carboxybutyl-2-carboxyethyl sulphide, m.p. 78·5-79 (Found: C, 46·29, 46·22; H, 6·76, 6·78; S, 15·67, 15·75. $C_8H_{14}O_4S$ requires: C, 46·60; H, 6·79; S, 15·53%.) The mixed melting point with the sample produced on hydrolysis of 4-carbetoxybutyl-2-carbometoxyethyl sulphide showed no depression.

(b) *In the presence of colloidal iron* The experiment was conducted as above.

Twenty grammes (0·12 mole) of mercaptoester and 25 g (0·47 mole) of acrylonitrile and colloidal iron produced from 1 ml of iron pentacarbonyl yielded 24·5 g (91% of theory) of pure adduct. Its hydrolysis led to 4-carboxybutyl-2-cathoxyethyl sulphide, m.p. 78-79° whose mixed melting point with the sample obtained as in the previous experiment showed no depression.

5. *Reaction of ethyl δ-mercaptovalerate with methylacrylate in the presence of iron pentacarbonyl*

The experiment was conducted as above.

Ethyl δ-mercaptovalerate (15·5 g, 0·09 mole) methylacrylate (26·3 g, 0·3 mole) and iron pentacarbonyl (0·3 ml) were charged in an autoclave and after substitution of nitrogen for air heated at 130-150° for 4 hr. Distillation of the reaction mass over the column gave 4-carbethoxybutyl-2-carbomethoxyethylsulphide. Yield: 20·1 g (85% of theory), b.p. 146/1 mm, n_D^{20} 1·4708, d_4^{20} 1·0803 (Found: Mr, 64·14. Calc. for $C_{11}H_{20}O_4S$: 64·30) (Found: C, 53·10, 52·92; H, 8·29, 8·15; S, 13·32, 13·16. Calc.: C, 53·22; H, 8·06; S, 12·90%.)

Eight grammes of the sulphide were saponified to yield 5·7 g (85% of theory) of 4-carboxybutyl-2-carboxyethylsulphide, m.p. 78-79° (from water). The mixed melting point with samples from the previous experiments and those obtained by hydrolysing products produced thermally and in the presence of benzoyl peroxide showed no depression.

6. *Telomerization of ethylene in the presence of metal carbonyls*

The experiments were conducted in a rocking stainless steel autoclave (500 ml) charged with carbon tetrachloride, chloroform or ethyltrichloroacetate, the respective metal hexacarbonyl (0·1 g) or iron pentacarbonyl (0·5 ml). The air was substituted by nitrogen and ethylene introduced. The reaction mixture was heated for 4-5 hr at 100-130 and the products fractionated *in vacuo*, the results being listed in Table 3.

[13] A. D. Petrov and M. V. Vdovin, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1490 (1957).