RADIATION-CHEMICAL HYDROGERMYLATION AND HYDROSTANNATION

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The hydrogermylation and hydrostannation of unsaturated compounds are realized by heating a mixture of the olefin and a Ge or Sn hydride, as well as by reacting them in the presence of Pt catalysts or radical-forming initiators [1]. A common shortcoming of these methods is their restricted range of application. These reactions can also be initiated by ^{60}Co γ radiation [2, 3], which significantly alters the rate of the reaction and the composition of the products obtained. In the present work we studied the main laws governing hydrogermylation and hydrostannation reactions initiated by ^{60}Co γ radiation in the example cases of the olefins listed in Tables 1 and 2 and Ge and Sn hydride. Irradiation of a mixture of a hydride and an olefin at ~25° initiates the smooth hydrometallation of the olefin, practically without the formation of by-products (see Tables 1 and 2). The detailed mechanism of the radiation-chemical hydrometallation was not investigated in this work. However, the high values of the radiation-chemical yields ($G \simeq 10^3$ molecules/100 eV) for all the reaction systems indicate that it has a chain character. A step involving the radiolysis of the hydride is probably responsible for the initiation of this reaction, and the hydrometallation process as a whole may be represented by the scheme:

$$R_3MH \xrightarrow{\gamma} R_3M^{\cdot} + H^{\cdot} \tag{1}$$

$$CH_2 = CHR' + R_3M^{\cdot} \rightarrow R_3MCH_2\dot{C}HR' \tag{2}$$

$$R_3MCH_2\dot{C}HR' + R_3MH \rightarrow R_3MCH_2CH_2R' + R_3M^{\cdot} \tag{3}$$

$$R_3MCH_2\dot{C}HR' + CH_2 = CHR' \rightarrow R_3MCH_2\underset{\displaystyle R'}{\underset{|}{C}}HCH_2\dot{C}HR' \tag{4}$$

The absence of high-molecular-weight organometallic compounds in the reaction products shows that telomerization step (4), which is characteristic of reactions involving radiation-induced addition across a C = C bond, is not realized in this case.

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*Deceased.

TABLE 1. Hydrogermylation of Olefins Initiated by γ Radiation

Olefin	Hydrides	Dose, Mrad	Reaction product	Yield, %	G, molecules/100 eV
$CH_2{=}CHC_4H_9$	$(C_4H_9)_3GeH$	7	$(C_4H_9)_3GeC_6H_{13}$	98	400
$CH_2{=}CHC_4H_9$	$(C_6H_5)_3GeH$	3	$(C_6H_5)_3GeC_6H_{13}$	82	700
$CH_2{=}CHC_4H_9$	$(C_4H_9)_3GeH$	7	$(C_4H_9)_3GeC_8H_{17}$	64	250
$CH_2{=}CHC_6H_{13}$	$(C_6H_5)_3GeH$	5	$(C_6H_5)_3GeC_8H_{17}$	81	650
$C_6H_5CH{=}CH_2$	$(C_4H_9)_3GeH$	20	$(C_4H_9)_3GeCH_2CH_2C_6H_5$	46	24
cyclo-C_6H_{10}	$(C_4H_9)_3GeH$	20	$(C_4H_9)_3GeC_6H_{11}$	75	100
cyclo-C_6H_{10}	$(C_6H_5)_3GeH$	3	$(C_6H_5)_3GeC_6H_{11}$	76	650
$C_6H_5C{\equiv}CH$	$(C_4H_9)_3GeH$	3	$(C_4H_9)_3GeCH{=}CHC_6H_5$	51	500
$CH_2{=}CHCH_2OH$	$(C_4H_9)_3GeH$	30	$(C_4H_9)_3GeCH_2CH_2CH_2OH$	76	100
$CH_2{=}CHCH_2OH$	$(C_6H_5)_3GeH$	5	$(C_6H_5)_3GeCH_2CH_2CH_2OH$	94	800
$CH_2{=}CHOC_4H_9$	$(C_4H_9)_3GeH$	7	$(C_4H_9)_3GeCH_2CH_2OC_4H_9$	94	500
$CH{\equiv}CCH_2OH$	$(C_4H_9)_3GeH$	20	$(C_4H_9)_3GeCH{=}CHCH_2OH$	60	70
$CH_2{=}CHCOOCH_3$	$(C_4H_9)_3GeH$	7	$(C_4H_9)_3GeCH_2CH_2COOCH_3$	92	400
$CH_2{=}C(CH_3)COOCH_3$	$(C_4H_9)_3GeH$	7	$(C_4H_9)_3GeCH_2CH(CH_3)COOCH_3$	92	400
$CH_2{=}CHCONH_2$	$(C_6H_5)_3GeH$	5	$(C_6H_5)_3GeCH_2CH_2CONH_2$	82	450
$CH_2{=}CHCN$	$(C_4H_9)_3GeH$	20	$(C_4H_9)_3GeCH_2CH_2CN$	65	100
$CH_2{=}CHCN$	$(C_6H_5)_3GeH$	5	$(C_6H_5)_3GeCH_2CH_2CN$	98	550
$CH_2{=}CHCH_2NH_2$	$(C_4H_9)_3GeH$	50	$(C_4H_9)_3GeCH_2CH_2CH_2NH_2$	80	50
$CH_2{=}CHCH_2NH_2$	$(C_6H_5)_3GeH$	3	$(C_6H_5)_3GeCH_2CH_2CH_2NH_2$	95	1000

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TABLE 2. Hydrostannation of Olefins Initiated by γ Radiation

Olefin	Hydride	Dose, Mrad	Reaction product	Yield, %	G, molecules/100 eV
$CH_2{=}CHC_5H_{11}$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnC_7H_{15}$	86	960
$CH_2{=}CHC_5H_{11}$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnC_7H_{15}$	74	1000
$CH_2{=}CHC_6H_{13}$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnC_8H_{17}$	77	1000
$CH_2{=}CHC_6H_{13}$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnC_8H_{17}$	70	750
$CH_2{=}CHC_6H_{13}$	$(C_6H_5)_3SnH$	2	$(C_6H_5)_3SnC_8H_{17}$	74	700
$CH_2{=}CHC_7H_{15}$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnC_9H_{19}$	86	1200
$CH_2{=}CHC_7H_{15}$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnC_9H_{19}$	87	1200
$CH_2{=}CHC_8H_{17}$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnC_{10}H_{21}$	86	1200
$CH_2{=}CHC_8H_{17}$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnC_{10}H_{21}$	96	1000
$CH_2{=}CHC_6H_5$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH_2CH_2C_6H_5$	50	700
$CH_2{=}CHC_6H_5$	$(C_4H_9)_3SnH$	1	$(C_4H_9)_3SnCH_2CH_2C_6H_5$	97	2100
$C_6H_5C{\equiv}CH$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH{=}CHC_6H_5$	70	800
$C_6H_5C{\equiv}CC_6H_5$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3Sn(C_6H_5)C{=}CHC_6H_5$	70	800
$C_6H_5C{\equiv}CC_6H_5$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3Sn(C_6H_5)C{=}CHC_6H_5$	80	720
$CH_2{=}CHCH_2OH$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH_2CH_2CH_2OH$	93	1500
$CH_2{=}CHCH_2OH$	$(C_4H_9)_3SnH$	1	$(C_4H_9)_3SnCH_2CH_2CH_2OH$	81	2000
$CH_2{=}CHCH_2OH$	$(C_4H_9)_2SnH_2$	2	$(C_4H_9)_2Sn(CH_2CH_2CH_2OH)_2$	86	1000
$CH_2{=}CHCH_2OH$	$(C_6H_5)_3SnH$	2	$(C_6H_5)_3SnCH_2CH_2CH_2OH$	80	1200
$CH_2{=}CHOC_2H_5$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH_2CH_2OC_2H_5$	80	1300
$CH_2{=}CHOC_2H_5$	$(C_4H_9)_3SnH$	3	$(C_4H_9)_3SnCH_2CH_2OC_2H_5$	92	1300
$CH_2{=}CHOC_4H_9$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH_2CH_2OC_4H_9$	88	1300
$CH_2{=}CHOC_4H_9$	$(C_4H_9)_3SnH$	3	$(C_4H_9)_3SnCH_2CH_2OC_4H_9$	99	1100
$CH_2{=}CHCOOCH_3$	$(C_2H_5)_3SnH$	2	$(C_2H_5)_3SnCH_2CH_2COOCH_3$	74	1200
$CH_2{=}C(CH_3)COOCH_3$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnCH_2CH(CH_3)COOCH_3$	91	1000
$CH_2{=}CHCONH_2$	$(C_4H_9)_3SnH$	2	$(C_4H_9)_3SnCH_2CH_2CONH_2$	75	950

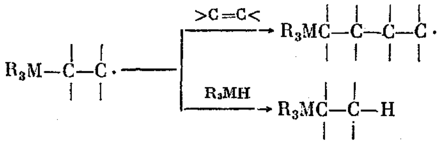
The difference between the radiation-chemical variant of hydrometallation and the thermal variant is graphically displayed in the reactions of the hydrides with the α-olefins. According to the data in [4], when triphenylgermane is heated (115°C, 360 h) with 1-octene, the extent of addition is only 29%. Hydrides of the aliphatic series are not added to α-olefins upon heating without a catalyst. In a field of γ radiation with a dose equal to 2 Mrad triethyl- and tributylstannane are quantitatively added to 1-hexene, 1-octene, and 1-decene, the radiation-chemical yield being $G \simeq 10^3$ molecules/100 eV:

$$CH_3(CH_2)_nCH = CH_2 + R_3SnH \rightarrow CH_3(CH_2)_nCH_2CH_2CH_2SnR_3, \text{ where } n = 3,\ 5,\ 7$$

The organogermanium hydrides require irradiation with a dose equal to 7 Mrad ($G \simeq 10^2$ molecules/100 eV).

The smooth course of the reaction with relatively unreactive olefins indicates that the rate-limiting step of the hydrometallation process is probably the decomposition of the hydride molecule, as was previously postulated for hydrides in [5].

An important feature of radiation-chemical hydrometallation is the inhibition of the polymerization of the original olefin in the presence of a hydride. Apparently, at 25°C the radical adducts (A) are added to the new olefin molecule more slowly than they eliminate an H atom from the hydride:



The hydrometallation of acetylene compounds is regioselective. For example, the irradiation (3 Mrad) of a mixture of phenylacetylene and tributylgermane results in the formation of β-tributylgermylstyrene (51% yield). Further irradiation does not increase the yield of the latter and does not cause its hydrogermylation, as observed when tributylgermane is heated with tributylgermylstyrene.

The structure of the original reactants significantly alters the rate of hydrometallation. The nature of the metal atom in the hydride has the strongest influence. The Ge hydrides are less reactive than are the Sn hydrides (Fig. 1). This is apparently due to the greater strength of the Ge–H bond than of the Sn–H bond (69 and 35-50 kcal/mole, respectively) and the features of the absorption of the radiation energy by the Ge and Sn atoms. A comparison of the data obtained with the data on radiation-chemical hydrosilylation [5, 6] shows that the effects of γ irradiation on the hydrometallation of olefins by hydrides of the group-IVB elements decrease along the series Sn > Ge > Si. The structure of the organic radical in the Sn hydrides has almost no influence on the rate of hydrostanation. In the case of the less reactive Ge hydrides, the replacement of the aliphatic substituents by aromatic substituents significantly accelerates the reaction (Fig. 2).

The influence of the functional group in the olefin on the course of the reaction can be clearly traced in the example of the Ge hydrides. In the series of α olefins the reaction is slowed as the length of the hydro-

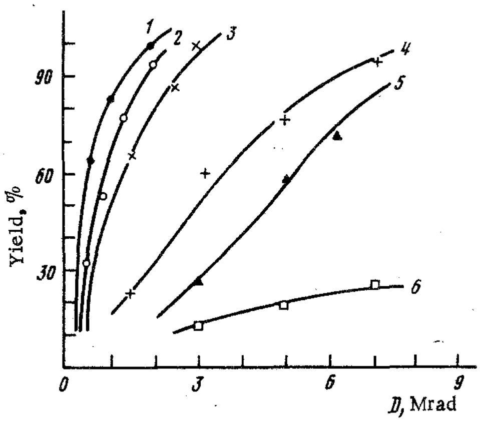


Fig. 1. Influence of the nature of the metal atom on the radiation-chemical hydrometallation of allyl alcohol (1, 6), methyl acrylate (2, 5), and methyl methacrylate (3, 4) by tributylstannane (1-3) and tributylgermane (4-6).

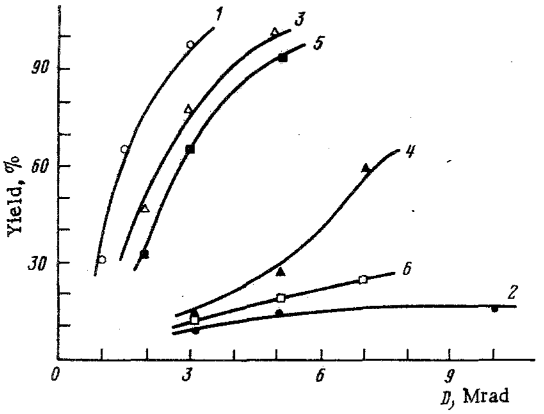


Fig. 2

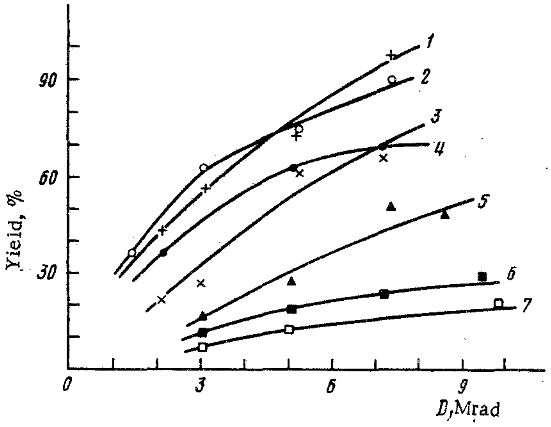


Fig. 3

Fig. 2. Influence of the nature of the organic substituents on Ge on the radiation-chemical hydrogermylation of allylamine (1, 2), acrylonitrile (3, 4), and allyl alcohol (5, 6) by triphenyl- (1, 3, 5) and tributylgermane (2, 4, 6).

Fig. 3. Variation in the yields of the products of the hydrogermylation of functionally substituted olefins by tributylgermane as a function of the nature of the substituent: 1) 1-hexene; 2) butyl vinyl ether; 3) methyl methacrylate; 4) methyl acrylate; 5) acrylonitrile; 6) allyl alcohol; 7) allylamine.

carbon chain is increased. The olefins with an internal location for the C = C bonds are more inert than the α-alkenes. Thus, with a dose of 7 Mrad 1-hexene is completely consumed, while the extent of reaction of cyclohexene is only 65%. The results of the experiments on the hydrogermylation of unsaturated compounds with different functional groups show that there is a correlation between the rate of addition and the value of the electron density in the double bond. The data obtained are consistent with the idea that the germyl and stannyl radicals are electrophilic. As we see in Fig. 3, the α-olefins are the most reactive. The introduction of electron-acceptor substituents lowers the reaction rate: Methyl methacrylate and acrylonitrile react more slowly than does 1-hexene. Allyl alcohol and allylamine do not fit into this series (curves 6 and 7), and this is attributed to the inertness of radicals of the allyl type.

EXPERIMENTAL

A freshly distilled unsaturated compound and a Ge or Sn hydride in a 1 : 1 or 1.5 : 1 mole ratio were placed in a glass ampul with a ground-glass stopper, which had been blown through with argon. The ampul was placed in a field of ^{60}Co γ irradiation. In the case of high dose rates, which are associated with the evolution of heat, the temperature was held close to 25°C with the aid of water cooling. The reaction product was analyzed by GLC, the liquids were vacuum-distilled, and the solid compounds were recrystallized.

The analysis of the organotin compounds was carried out on a Tsvet-4 chromatograph with a katharometer in a stream of helium (60-80 ml/min). The column was 2 m × 4 mm and contained 10% Apiezon on Chromosorb W (80-100 mesh). The quantitative determinations were carried out relative to an internal reference, viz., hexadecane. The analysis of the organogermanium compounds was carried out on an AG K-6 chromatograph with a katharometer in a stream of helium (80 ml/min). The column was 3 m × 4 mm and contained 5% SE-30 on Chromaton N, which was treated with dimethyldichlorosilane. The analysis was carried out with programming of the temperature from 100 to 270°C and from 170 to 270°C at the rate of 20 deg/min. The internal reference was tetradecane.

CONCLUSIONS

1. The hydrostannation and hydrogermylation of olefins is efficiently initiated by ^{60}Co γ radiation.

2. The addition of Ge and Sn hydrides to olefins initiated by γ radiation is consistent with the main laws governing radical chain reactions in the liquid phase.

3. The radiation effects in the hydrometallation reaction decrease upon the transition from Sn hydrides to Ge hydrides and from hydrides of the aromatic series to the aliphatic series.

4. The rate of the radiation-chemical hydrometallation increases with increasing electron density in the double bond; the introduction of electron-acceptor substituents lowers the reaction rate.

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REACTIONS OF SEVERAL α-ENONES WITH TRIMETHYL PHOSPHITE

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It is known [1-3] that the reaction of trialkyl phosphites with α,β-unsaturated ketones containing electron-acceptor groups proceeds with the formation in the first step of an adduct of bipolar structure and its subsequent stabilization in the form of a cyclic phosphorane or enol ester. We have previously [4-6] demonstrated the possibility of the formation of Δ^4-oxaphospholenes in reactions of trialkyl phosphites with α-enones in which there are no electron-acceptor substituents, but which offer the possibility of the stabilization of the bipolar ion by means of a resonance interaction between the anionic center and the benzylidene group or an aromatic ring.

As a continuation of these investigations we studied the reaction of 2,5-dibenzylidenecyclopentanone (I) and 3,3-diphenyl-2-benzylidenehydrindone (II) with trimethyl phosphite (III). In analogy to 2,6-dibenzylidenecyclohexanone [4] and 2-benzylidenetetralone [6], in the case of I and II we postulated the formation of bipolar ions IV and V, which subsequently yield cyclic phosphoranes VI and VII:

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