Chemistry

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Abstract

Full Text

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Addition of Trichlorobromomethane to Compounds of the Structure $R(C_6H_5)_2ECH = CH_2$ (where $R = C_6H_5, CH_3;\ E = Sn, Si, C$)

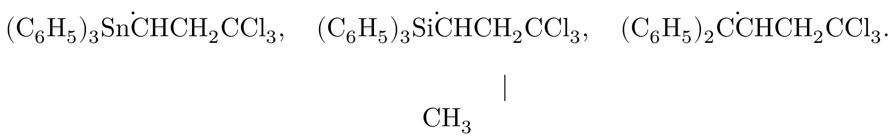
In recent years, radical rearrangements in solution with 1,2-migration of phenyl from one carbon atom to another have been studied in detail (see, for example, (^{1})) according to the scheme

$$C_6H_5CR_1R_2\dot{C}HR_3 \rightarrow \dot{C}R_1R_2CHR_3C_6H_5,$$

$$R_1 = CH_3,\ Ar;\ R_2 = CH_3,\ Ar;\ R_3 = H,\ CH_3.$$

An analogous rearrangement with 1,2-migration of phenyl from a metal atom to a carbon atom is unknown.

The present work is devoted to studying the capacity for rearrangement in solution of radicals of the structure



$$(C_6H_5)_3Sn\dot{C}HCH_2CCl_3, \quad (C_6H_5)_3Si\dot{C}HCH_2CCl_3, \quad (C_6H_5)_2\underset{CH_3}{C}\dot{C}HCH_2CCl_3.$$

For this purpose we studied the addition of trichlorobromomethane to vinyltriphenylstannane*, vinyltriphenylsilane**, and 3,3-diphenylbutene-1***. 3,3-Diphenylbutene-1 was chosen for the investigation because of its greater availability compared with vinyltriphenylmethane.

The addition of trichlorobromomethane to vinyltriphenylstannane and vinyltriphenylsilane proceeds very readily, and the unrearranged addition products are formed in almost quantitative yield according to the scheme

$$(C_6H_5)_3ECH = CH_2 + BrCCl_3 \xrightarrow{Bz_2O_2} (C_6H_5)_3ECHBrCH_2CCl_3.$$

The structure of the compounds obtained is confirmed by the absence of an E—Br bond**** (negative test with $AgNO_3$, etc.), and also by the behavior of the adducts obtained toward alcoholic alkali. The organotin compound is not hydrolyzed, but undergoes dehydrobromination according to the scheme

$$(C_6H_5)_3SnCHBrCH_2CCl_3 \xrightarrow{\text{KOH}} (C_6H_5)_3SnCH = CHCCl_3.$$

The organosilicon compound, as was to be expected for an α-haloalkylsilane (5), is inert to the action of alcoholic alkali at room temperature.

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* It was briefly reported (2) that a product of addition of trichlorobromomethane to vinyltriethylstannane had been obtained; the structure of the adduct was not investigated.

** The addition of chloroform and carbon tetrachloride to vinyltriphenylsilane has been described (3); compounds of the structures $(C_6H_5)_3Si(CH_2)_2CCl_3$ and $(C_6H_5)_3SiCHClCH_2CCl_3$ were obtained.

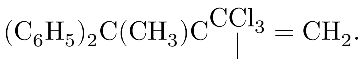
*** Homolytic addition of *n*-butyl mercaptan and thioacetic acid to 3,3-diphenylbutene-1 leads to unrearranged products; addition of *n*-butyraldehyde proceeds with rearrangement in the intermediately formed radical with 1,2-migration of phenyl (4).

**** In the event of rearrangement, one could have expected the formation of compounds of the structure $(C_6H_5)_2EBrCH(C_6H_5)CH_2CCl_3$.

The addition of trichlorobromomethane to 3,3-diphenylbutene-1 proceeds with difficulty. After 20 hours of boiling of the reaction mixture with repeated addition of peroxide, 66% of the initial diphenylbutene was recovered unchanged. The main reaction product is an unsaturated compound of composition $C_{17}H_{15}Cl_3$. On ozonolysis of this compound, formaldehyde and a ketone of composition $C_{16}H_{13}Cl_3O$ were obtained, the latter giving a 2,4-dinitrophenylhydrazone of composition $C_{22}H_{17}Cl_3N_4O_4$. If the reaction under study proceeds without rearrangement, the formation of an unsaturated compound of structure I or II may be expected:

$$(C_6H_5)_2C(CH_3)CH = CHCCl_3,$$

I



$$(C_6H_5)_2C(CH_3)\overset{CCl_3}{\overset{|}{C}} = CH_2.$$

II

If the reaction proceeds with rearrangement, the formation of compounds III or IV may be expected:

$$CH_2 = C(C_6H_5)CH(C_6H_5)CH_2CCl_3, \quad CH_3 - C = C - CH_2 - CCl_3$$

$C_6H_5 \quad C_6H_5$

III IV

The data presented above, characterizing the compound obtained, are compatible only with formula III.

Compounds I and IV cannot account for the formation of formaldehyde and the indicated ketone upon ozonolysis. The formation of compound II is extremely unlikely, since it would require addition of the CCl_3 radical contrary to the known rules of orientation. Moreover, compound II, although capable of forming formaldehyde and a ketone of composition $C_{16}H_{13}Cl_3O$ upon ozonolysis, would in this case give a ketone of structure $(C_6H_5)_2C(CH_3)COCCl_3$ and, consequently, could not give a 2,4-dinitrophenylhydrazone of composition $C_{22}H_{17}Cl_3N_4O_4$, since it is known⁽⁶⁾ that carbonyl compounds containing the grouping

$$CCl_3C = O,$$

on treatment with dinitrophenylhydrazine in the presence of sulfuric acid, give hydrazones that do not contain chlorine.

The formation of substance III in the course of the reaction under study may be described by the scheme

$$CH_3C(C_6H_5)_2CH = CH_2 + \dot{C}Cl_3 \rightarrow CH_3C(C_6H_5)_2\dot{C}HCH_2CCl_3$$

$$\uparrow$$

$$\dot{C}Cl_3 + HBr + CH_2 = C(C_6H_5)CH(C_6H_5)CH_2CCl_3 \xleftarrow{BrCCl_3} CH_3\dot{C}(C_6H_5)CH(C_6H_5)CH_2CCl_3$$

$\}$ rearrangement

Simultaneously with substance III, a saturated adduct was obtained in small yield, the structure of which was not investigated. Thus, under comparable conditions, radicals of structure $(C_6H_5)_3E\dot{C}HCH_2CCl_3$ ($E = \text{Sn, Si}$) did not rearrange, whereas radicals of structure $(C_6H_5)_2C(CH_3)\dot{C}HCH_2CCl_3$ did rearrange. A possible reason for this difference may be either the lower stability of radicals of the type $(C_6H_5)_2\dot{E}CH(C_6H_5)CH_2CCl_3$ in comparison with the initial radicals $(C_6H_5)_3\dot{E}CHCH_2CCl_3$, or the tin and silicon atoms are less capable of transmitting the influence produced by the presence of an unpaired electron at the neighboring carbon atom to the phenyl group.

Experimental Part

Addition of trichlorobromomethane to vinyltriphenylstannane in the presence of benzoyl peroxide

A solution of 9.42 g (0.025 mole) of vinyltriphenylstannane (prepared according to(7)), 10 g of trichlorobromomethane, and 0.15 g of benzoyl peroxide was heated on a water bath at 80° for 7 h. During this time, to the reac-

···an additional 0.15 g of benzoyl peroxide in 10 g of trichlorobromomethane was added to the reaction solution. After removal of the excess trichlorobromomethane by distillation, 14.3 g of a viscous oil remained; from it, by dissolution in absolute alcohol and cooling to −40°, γ,γ,γ-trichloro-α-bromopropyltriphenylstannane was isolated as crystals with m.p. 58–60°; yield 13.5 g (94% of theory); after recrystallization from alcohol, m.p. 61–62°.

$C_{21}H_{18}SnCl_3Br$. Found, %: C 43.76; 43.58; H 3.15; 3.20
Calculated, %: C 44.02; H 3.15

The compound obtained does not react with potassium fluoride or silver nitrate, nor does it form a complex compound with pyridine.

Reaction of γ,γ,γ-trichloro-α-bromopropyltriphenylstannane with alkali. To a solution of 4.80 g (0.008 mole) of γ,γ,γ-trichloro-α-bromopropyltriphenylstannane in 120 ml of ethyl alcohol, cooled to 0°, 0.45 g (0.008 mole) of caustic potash in 16 ml of ethyl alcohol was added. The reaction mixture was left overnight at room temperature. Complete neutralization occurred. Crystals of γ,γ,γ-trichloropropen-1-yltriphenylstannane separated; after two recrystallizations from alcohol they had m.p. 132°. Yield 3.35 g (80% of theory).

$C_{21}H_{17}SnCl_3$. Found, %: C 50.33; 50.31; H 3.41; 3.41; Sn 23.73; 23.72
Calculated, %: C 50.90; H 3.44; Sn 24.00

Addition of trichlorobromomethane to vinyltriphenylsilane in the presence of benzoyl peroxide. A solution of 7.15 g (0.025 mole) of vinyltriphenylsilane (prepared according to (8)), 10 g of trichlorobromomethane, and 0.15 g of benzoyl peroxide was heated on a water bath at 80° for 7 h. During this time, an additional 0.15 g of benzoyl peroxide in 10 g of trichlorobromomethane was added to the reaction solution.

After removal of the excess trichlorobromomethane by distillation, 11.9 g of an oil was obtained, which dissolved readily in ether and benzene. After crystallization from alcohol, 11.3 g (94.1% of theory) of γ,γ,γ-trichloro-α-bromopropyltriphenylsilane was obtained, m.p. 98–102°. After a second recrystallization from alcohol, m.p. 102–103°.

$C_{21}H_{18}SiCl_3Br$. Found, %: C 52.09; 52.00; H 3.72; 3.71; Si 5.87; 5.72; Hal 38.43; 38.69
Calculated, %: C 52.03; H 3.74; Si 5.74; Hal 38.39

The compound obtained does not react with a solution of silver nitrate, and also remains unchanged under the action of alcoholic alkali for 20 h at room temperature.

3,3-Diphenylbutene-1. The synthesis was carried out according to the known procedure (4).* The product had the following constants: b.p. 92–94° at 1 mm, n_D^{25} 1.5770; n_D^{20} 1.5790; d_4^{20} 1.0106. Found MR 68.49. Calculated for $C_6H_{16}F_7$, MR 68.42. Literature data (4): b.p. 111–115° at 1.5 mm, n_D^{25} 1.5780. A solution of 2.5 g of 3,3-diphenylbutene-1 in 100 g of carbon tetrachloride, while cooled with ice, was saturated with 6% ozone for 3 h. After addition of water, the carbon tetrachloride was distilled off in vacuo, after which the ozonide was decomposed by heating on a boiling water bath. Extraction with ether gave 2.1 g (84% of theory) of α,α-diphenylpropionaldehyde with b.p. 111–113° at 1 mm, n_D^{20} 1.5820; d_4^{20} 1.0810. Found MR 64.85. Calculated for $C_{15}H_{14}OF_6$, MR 64.25. According to literature data (9), the b.p. of α,α-diphenylpropionaldehyde is 111–113° at 1 mm, n_D^{20} 1.5800. From the aqueous layer a dimedone derivative was obtained with m.p. 189°, which did not depress the melting point··· melting point in admixture with the dimedone derivative of formaldehyde. This confirms the structure of the original 3,3-diphenylbutene-1.

Reaction of trichlorobromomethane with 3,3-diphenylbutene-1 in the presence of benzoyl peroxide. A solution of 25 g (0.12 mole) of 3,3-diphenylbutene-1, 100 g of trichlorobromomethane, and 0.4 g of benzoyl peroxide was boiled for 20 hr; every 3 hr 0.4 g of benzoyl peroxide was added. In all, 3 g of peroxide was added over 20 hr. After 15-20 min from the start of heating, evolution of hydrogen bromide began. After completion of the reaction, the mixture was washed with soda solution, then with water, and dried over magnesium sulfate; the excess trichlorobromomethane was distilled off. Distillation of the residue gave:

I fraction, 92-94° (1 mm), 15 g, n_D^{25} 1.5770 (starting material).
II fraction, 94-180° (1 mm), 10.5 g.
Residue, 3 g.

After redistillation of fraction II at 1 mm, the following were obtained:
I fraction, 92-95°, 1.5 g, n_D^{25} 1.5770.
II fraction, 95-142°, 0.5 g.

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* In contrast to the procedure, the product obtained after decomposition of the xanthate was subjected, without preliminary distillation, to heating with 5% aqueous alkali for 2 h. After distillation of the product, the alkali-treatment operation was repeated; this gave 3,3-diphenylbutene-1 in 72.5% yield of theory (50.7% of theory according to the procedure).

III fraction, 142–150°, 6.5 g.
IV fraction, 160–170°, 1 g.
Residue, 1 g.

After redistillation of fraction III, 4.5 g of 5,5,5-trichloro-2,3-diphenylpentene-1 was obtained, b.p. 142–142.5° at 1 mm, n_D^{20} 1.5935; d_4^{20} 1.2437. Found MR 88.74. Calculated for $C_{17}H_{15}Cl_3F_7$ MR 87.64.

As analysis showed, the substance obtained contains a small impurity of the saturated bromide.

Found %:	C 61.50; H 4.65; Hal 34.04
$C_{17}H_{15}Cl_3$. Calculated %:	C 62.69; H 4.64; Hal 32.66

A solution of 2.6 g of 5,5,5-trichloro-2,3-diphenylpentene-1 in 100 g of carbon tetrachloride, while cooled with ice, was saturated with 6% ozone for 4 hr. After addition of water, the CCl_4 was distilled off in vacuo. The ozonide was decomposed by heating on a boiling water bath. Extraction with ether gave 2.3 g (88.5% of theory) of white crystals with m.p. 103°.

Found %:	C 58.77; 58.42; H 4.06; 4.09; Cl 32.67; 32.77
$C_{16}H_{13}Cl_3O$. Calculated %:	C 58.65; H 4.00; Cl 32.47

These crystals with 2,4-dinitrophenylhydrazine form a 2,4-dinitrophenylhydrazone with m.p. 161° (from alcohol).

Found %:	C 51.71; 51.94; H 3.55; 3.65; N 10.72; 10.77
$C_{22}H_{17}N_4Cl_3O_4$. Calculated %:	C 52.03; H 3.38; N 11.03

From the aqueous layer, the dimedone derivative with m.p. 189° was obtained, which gave no depression of the melting point in admixture with the dimedone derivative of formaldehyde.

From fraction IV, by dissolution in a small amount of ether and cooling, crystals of the saturated addition product with m.p. 108° were obtained.

Found %:	C 50.60; 50.36; H 4.02; 4.04; Hal 45.85; 45.73
$C_{17}H_{16}Cl_3Br$. Calculated %:	C 50.22; H 3.96; Hal 45.83

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CITED LITERATURE

1. D. Y. Curtin, M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).
2. D. Seyferth, *J. Org. Chem. Soc.*, **22**, 1252 (1957).
3. R. A. Benkeser, E. W. Bennet, R. A. Huckner, *J. Am. Chem. Soc.*, **79**, 6253 (1957).
4. J. Weinstock, S. H. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1947).
5. S. N. Ushakov, A. M. Itenberg, *ZhOKh*, **7**, No. 19, 2495 (1937).
6. F. D. Chattaway, R. Bennett, *J. Chem. Soc.*, **1927**, 2850.
7. S. D. Rosenberg, A. J. Gibbons et al., *J. Am. Chem. Soc.*, **79**, 2137 (1957).
8. L. F. Cason, H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).
9. F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955).

Note: Figure translations are in progress. See original paper for figures.