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Abstract

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ADDITION OF TRIPHENYLMETHYL RADICALS TO ENYNE HYDROCARBONS AND SILICON HYDROCARBONS

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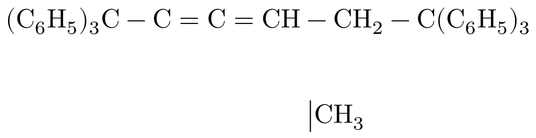
The direct addition of stable free radicals to enyne hydrocarbons has been described in only one example. It was shown that isopropenylacetylene adds triphenylmethyl radicals in the 1,4-position (^{1}).

We have established that other enyne hydrocarbons also add triphenylmethyl radicals in the 1,4-position, with the formation of allene hydrocarbons. Thus, when vinylmethylacetylene (I) was treated with triphenylchloromethane and metallic mercury, a crystalline adduct of composition $C_{43}H_{36}$ was obtained, in the IR spectrum of which there was a rather intense band of the allene grouping at about 1960 cm^{-1} (Fig. 1, 1), and the bands characteristic of acetylene and vinyl groups were absent. On the basis of these data the following structure was assigned to the adduct:



$$(C_6H_5)_3C - C = C = CH - CH_2 - C(C_6H_5)_3$$

$$|CH_3$$

In an analogous manner, a 1,4-adduct is also formed as a result of the addition of triphenylmethyl radicals to vinyltriethynylbutylacetylene (II), but we were unable to isolate it in analytically pure form. The infrared spectrum of this adduct is shown in Fig. 1, 2.

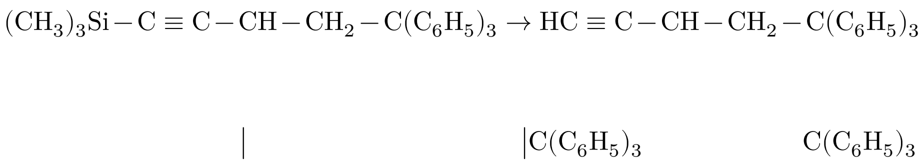
In contrast to vinylacetylene hydrocarbons, silicon-containing enynes add triphenylmethyl radicals in different ways depending on their structure.

Vinyltrimethylsilylacetylene (1-trimethylsilylbut-3-yn-1) (III) adds predominantly at the double bond. In the IR spectrum of the adduct there is an intense band of the triple bond at 2168 cm^{-1} and a weak band in the region of 1945 cm^{-1}, where allene compounds usually absorb (Fig. 1, 3).*

Fig. 1. Infrared transmission spectra

Figure 1: Fig. 1. Infrared transmission spectra

The structure of the adduct was also confirmed by a chemical method. As a result of hydrolytic cleavage of the substance, a hydrocarbon with a terminal acetylene grouping was obtained according to the scheme:

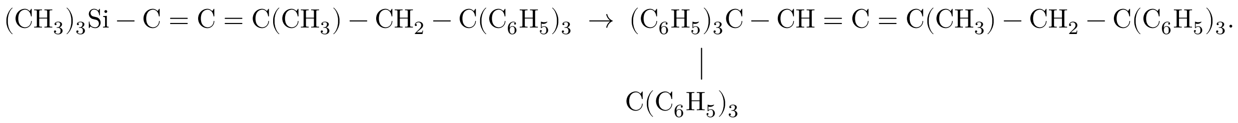


$$(CH_3)_3Si-C\equiv C-CH-CH_2-C(C_6H_5)_3 \rightarrow HC\equiv C-CH-CH_2-C(C_6H_5)_3$$

$$| \qquad |C(C_6H_5)_3 \qquad C(C_6H_5)_3$$

The structure of the hydrocarbon was proved by argentometric titration and by the IR spectrum: an intense frequency of the terminal acetylene grouping was found at 3315 cm^{-1} (Fig. 1, 5). In its structure this hydrocarbon is an isomer of the 1,4-adduct of triphenylmethyl radicals to vinylacetylene and differs from it by a higher melting point. Isopropenyltrimethylsilylacetylene (1-trimethylsilyl-3-methylbut-3-yn-1) (IV) adds triphenylmethyl radicals in the 1,4-position, i.e., in the same direction as enyne hydrocarbons. In this case, triphenylmethane is formed as a by-product.

In the IR spectrum of the adduct there is an intense band of an allene grouping (1930 cm^{-1}) and the band of an acetylenic bond is absent (Fig. 1, 4). On hydrolytic cleavage it gives the allene hydrocarbon described in the literature, a hydrocarbon previously obtained by addition of triphenylmethyl radicals to isopropenylacetylene (1):



$$(CH_3)_3Si-C=C=C(CH_3)-CH_2-C(C_6H_5)_3 \rightarrow (C_6H_5)_3C-\underset{\underset{C(C_6H_5)_3}{|}}{CH}=C=C(CH_3)-CH_2-C(C_6H_5)_3.$$

Fig. 1. Infrared transmission spectra (solutions in CCl_4):
1—2-methyl-1,1,1,6,6,6-hexaphenylhexadiene-2,3;
2—2-tert-butyl-1,1,1,6,6,6-hexaphenylhexadiene-2,3;
3—1-trimethylsilyl-3-triphenylmethyl-5,5,5-triphenylpentyne-1;
4—3-methyl-2-trimethylsilyl-1,1,1,6,6,6-hexaphenylhexadiene-2,3;
5—3-triphenylmethyl-5,5,5-triphenylpentyne-1;
6—4-methyl-1,1,1,6,6,6-hexaphenylhexadiene-2,3.

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* It should be noted that detection of the acetylene adduct is facilitated by the high intensity of the stretching vibration frequency of the triple bond adjacent to the silicon atom.

The structure of the adduct of triphenylmethyl radicals to propenyltrimethylsilylacetylene (1-trimethylsilylpent-3-yne-1) (V) has not yet been established with certainty. Apparently, it has a 1,3-diene structure, since in its IR spectrum there are no frequencies of allene or acetylenic groupings, while the frequencies of the 1,3-diene grouping in the spectrum of a compound with six phenyl nuclei are difficult to detect.

The difference in the order of addition of triphenylmethyl radicals to the analogously constructed hydrocarbon (II) and silicon hydrocarbon (III) can be explained by the increase in steric hindrance at the acetylenic bond on going from quaternary carbon to quaternary silicon—

tion. In the case of silicon hydrocarbons (IV) and (V), steric hindrance also arises at the double bond, as a result of which 1,4-addition becomes more favorable. The lower yield of adducts and the presence of a side process—the formation of triphenylmethane—indicate a lower rate of the addition reaction in this case.

Experimental Part

Enyne hydrocarbons were prepared by alkylation of vinylacetylene ([2])*; silicon hydrocarbons, by the action of trimethylchlorosilane on the organomagnesium derivatives of the corresponding enynes ([3]).

Experiments on the addition of triphenylmethyl radicals were carried out under the following conditions. A mixture of triphenylchloromethane (m.p. 108–112°), the enyne compound (excess), benzene, and metallic mercury (10-fold excess) was shaken in a hermetically sealed bottle in an atmosphere of inert gas for several days. Then the excess enyne compound and solvent were distilled off from the reaction products. The residue was extracted with ether. The oil remaining after distillation of the ether crystallized more or less rapidly on standing. Recrystallization of the adducts was carried out from petroleum ether or acetone. All adducts are poorly soluble in ether, petroleum ether, acetone, and carbon tetrachloride, and are practically insoluble in alcohol. The adduct obtained from silicon hydrocarbon (V) is characterized by especially poor solubility. Constants and analytical data for all the adducts obtained are given in Table 1.

Table 1

Substance	M.p., °C	Yield, %	Found, % C	Found, % H	Found, % Si	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % Si
$(C_6H_5)_3C-C=C=CH-CH_2-C(C_6H_5)_3$	193-194	40	93.8593.4	64786.96	—	$C_{48}H_{38}$	93.48	6.48	–
	|	CH_3							
$(C_6H_5)_3C-C\equiv C-CH-CH_2-C(C_6H_5)_3$	150	53	91.4291.3	71637.63	—	$C_{46}H_{42}$	92.93	7.07	–
	|	$C(CH_3)_3$							
$(CH_3)_3Si-C\equiv C-CH-CH_2-C(C_6H_5)_3$	178	62	88.5388.2	71006.87	4.534.27	$C_{45}H_{42}$	88.59	6.88	4.59
			|		$C(C_6H_5)_3$				
$(CH_3)_3Si-C=C=C(CH_3)-CH_2-C(C_6H_5)_3$	128-130	27	88.5988.3	79247.17	4.544.67	$C_{46}H_{44}$	88.41	7.09	4.49
		|	$C(C_6H_5)_3$						
$(CH_3)_3Si-C=CH-CH=C(CH_3)-C(C_6H_5)_3$ (?)	161-161.5	50	88.6588.5	77307.29	4.584.67	$C_{46}H_{44}$	88.41	7.09	4.49
		|	$C(C_6H_5)_3$						
$HC\equiv C-CH-CH_2-C(C_6H_5)_3$	221	–	93.8593.4	63666.58	—	$C_{42}H_{34}$	93.57	6.43	–
		|	$C(C_6H_5)_3$						
$(C_6H_5)_3C-CH=C=C-CH_2-C(C_6H_5)_3$	184	–	–	–	–	$C_{43}H_{36}$	–	–	–
			|		CH_3				

In experiments with silicon hydrocarbons (IV) and (V), in addition to the adducts, triphenylmethane was isolated from the residue after evaporation of the ether in yields of about 17 and 6%, respectively. It differs from the adducts by its considerably better solubility in acetone and petroleum ether. M.p. 93.5° (from petroleum ether). It gives no depression of the melting point with an authentic sample.

$C_{19}H_{16}$. Found %: C 93.48; 93.67; H 6.73; 6.90
Calculated %: C 93.44; H 6.55

Hydrolysis of adducts of triphenylmethyl radicals to silicon hydrocarbons (III) and (IV) was carried out by boiling for 35 h with alcoholic

* Vinyltretylbutylacetylene was prepared by I. A. Maretina.

with a KOH solution (25-fold excess). The hydrocarbons obtained were recrystallized from acetone or petroleum ether. The constants and analytical data are given in Table 1.

In the hydrocarbon obtained by hydrolysis of the adduct from the silicon hydrocarbon (III), argentometric titration [1] found 98.0; 97.5% of the compound with a terminal acetylene group.

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References Cited

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[1] S. Weibel, *Identification of Organic Compounds*, IL, 1957.