A New Substitution Reaction of Acetylenic Hydrogen with Silyl Radicals

By HIDEKI SAKURAI* and MINEO YAMAGATA

(*Department of Chemistry, Faculty of Science, Tohoku University, Sendai* 980, *Japan*)

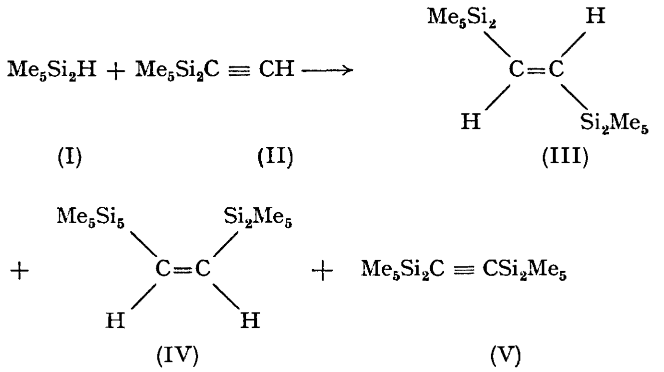
Summary Di-t-butyl peroxide-catalysed reaction of pentamethyldisilane with pentamethyldisilanylacetylene afforded *cis-* and *trans*-bis(pentamethyldisilanyl)ethylene and bis(pentamethyldisilanyl)acetylene, the latter being formed by a novel hydrogen-abstraction process from an intermediate vinyl radical.

IN the course of a study on silyl radicals, di-t-butyl peroxide-catalysed reaction of pentamethyldisilane (I), with pentamethyldisilanylacetylene (II, b.p. 125°, n_D^{20} 1·4435, d_4^{20} 0·7703) was investigated.

A degassed mixture of (I), (II), and di-t-butyl peroxide was heated in an ampoule at 135° for 18 hr. Product studies revealed that in addition to normally expected products, (III) and (IV), bis(pentamethyldisilanyl)acetylene (V) was obtained. (Table).

Reaction of (I) *with* (II) *catalysed by di-t-butyl peroxide at* 135°

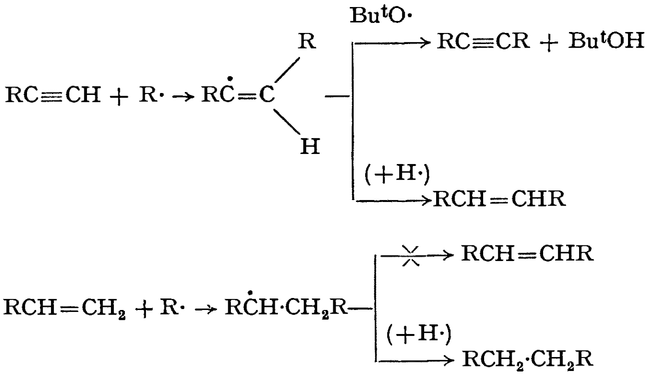
Reactants (mmole)			Products (% yield based on II)		
(I)	(II)	$(Bu^tO)_2$	(III)	(IV)	(V)
2·61	2·55	0·64	28	—	8
2·88	2·74	0·19	19	19	4
3·14	3·02	0·12	12	17	2



Structures of (III) (n_D^{20} 1·4743, d_4^{20} 0·8056), (IV) (n_D^{20} 1·4860, d_4^{20} 0·8285), and (V) (n_D^{20} 1·4692, d_4^{20} 0·8034) were determined by physical constants, elemental analyses, g.l.c., hydrogenation, and i.r. and n.m.r. spectra after separation from the mixture.

In accord with the general view,[1] the *trans*-olefin is seemingly the thermodynamically-controlled product. Now, formation of (V) is quite interesting. That direct reaction of (I) with (II) is not responsible for formation of (V) can be proved from the fact that heating a mixture of (I) and (II) at 135° for 30 hr. with or without diglyme as a solvent afforded no product. In all probability, (V) comes from an intermediate free radical by hydrogen abstraction. It does not conflict with this mechanism that increasing the amount of di-t-butyl peroxide in the reaction mixtures resulted in increasing amounts of (V).

Although the analogous substitution at an aromatic carbon atom is known, it is the first time that a free-radical substitution at an acetylenic carbon atom involving abstraction of a vinylic hydrogen atom has been shown explicitly.



R = $Me_3SiSiMe_2$-

In view of this finding, the analogous reaction of vinylpentamethyldisilane with (I)[2] was re-investigated, but it was confirmed again that no (III) or (IV) was present in the product. Such difference in the behaviour of intermediate radicals may be ascribed to steric requirement in the transition state of hydrogen abstraction from these radicals.

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