Regioselectivity in the Diels–Alder Reaction of 1-Trimethylsilylbutadiene

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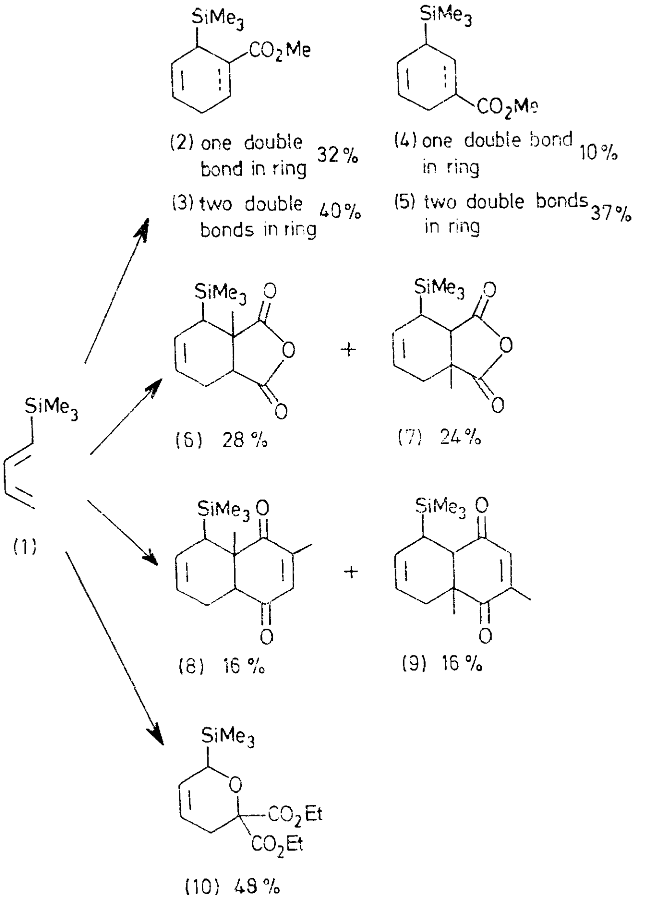
Summary 1-Trimethylsilylbutadiene (**1**) reacts with some simple unsymmetrical dienophiles to give mixtures of regioisomers with the '*ortho*' adducts generally predominating.

In the preceding communication,[1] we demonstrated the potential uses in organic synthesis of some allyl silanes obtained from the Diels–Alder reaction of 1-trimethylsilylbutadiene (**1**) with maleic anhydride. In order to plan further syntheses based on these ideas, we needed to know something of the regioselectivity this diene would show when it reacted with unsymmetrical dienophiles.† '*ortho*' Adducts [*e.g.* (**2**)] may be expected on electronic grounds,[2] but '*meta*' adducts [*e.g.* (**4**)] on steric grounds. Our observations indicate that these factors are indeed in opposition; mixtures of isomers were obtained.

Thus, methyl acrylate, methyl propiolate, and citraconic anhydride gave more '*ortho*' adduct (**2**), (**3**) and (**6**), than '*meta*' (**4**), (**5**), and (**7**), and 2,6-dimethylbenzoquinone gave equal amounts of the regioisomers (**8**) and (**9**). The degree of regioselectivity is evidently small. When steric and electronic factors are in the same direction, a single adduct can be obtained; the reaction of (**1**) with diethyl oxomalonate[3] gave the adduct (**10**) in 48% yield.

In the presence of boron trifluoride, the reactions were mostly faster, as expected,[4] but yields were not always better. Thus citraconic anhydride gave the same adducts (**6**) and (**7**) in 34 and 31% yield, respectively, but methyl acrylate, surprisingly, gave a low yield (19%) of a mixture of equal amounts of (**2**) and (**4**). Methyl propiolate gave a 20% yield of (**3**) alone. [We did not observe any of the products from desilylation of (**5**).] 2,6-Dimethylbenzoquinone gave a 43% yield of a single adduct (**9**), as expected.

The yields in all these reactions, although not optimal, are still disappointing; the probable reason is that 1-trimethylsilylbutadiene (**1**) is not a very reactive diene. Thus we find that it reacts with dienophiles more slowly than butadiene; judging by the reaction conditions reported for the latter,[6] the rates differ approximately by factors between 5 and 100, depending upon the dienophile.



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† The only published work in this field (S. I. Sadykh-Zade and A. D. Petrov, *Zhur. obschei Khim.*, 1958, **28**, 1591), assigns, without evidence, the structure (**4**) to the adduct of (**1**) with methyl acrylate, and analogous structures to the adducts with acrylonitrile and acrolein.

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