

Regioselectivity in the Diels–Alder Reactions of 3- and 4-Substituted 1-Trimethylsilylbutadienes†

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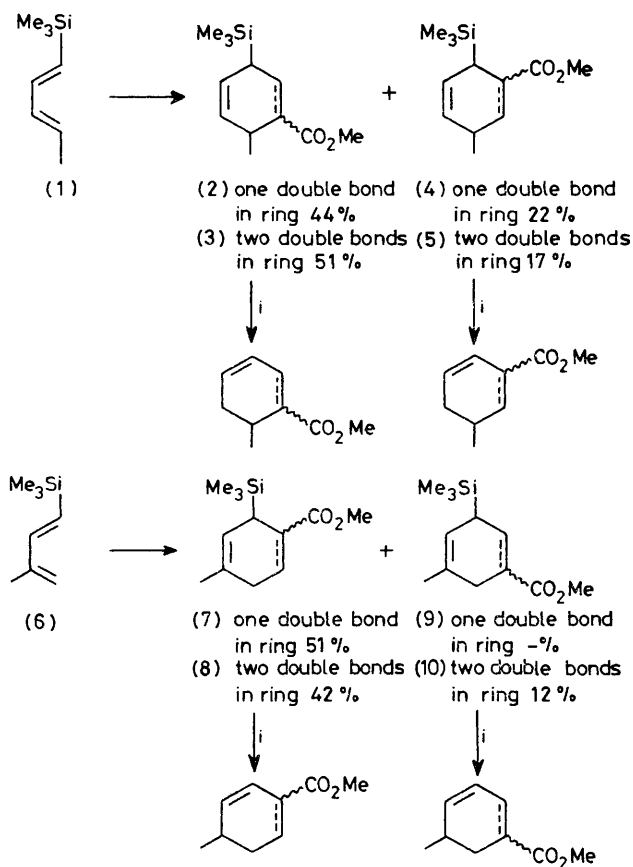
Summary 1-Trimethylsilylbutadienes with a substituent in the 3- or 4- position undergo Diels–Alder reactions in which the regioselectivity is controlled by the 3- or 4- substituent rather than by the trimethylsilyl group.

WE reported earlier¹ that 1-trimethylsilylbutadiene shows little regioselectivity in its reactions with unsymmetrical dienophiles. We have also observed² that 2-trimethylsilylcyclopentadiene³ shows little regioselectivity in its

† Reprints of this paper will not be available.

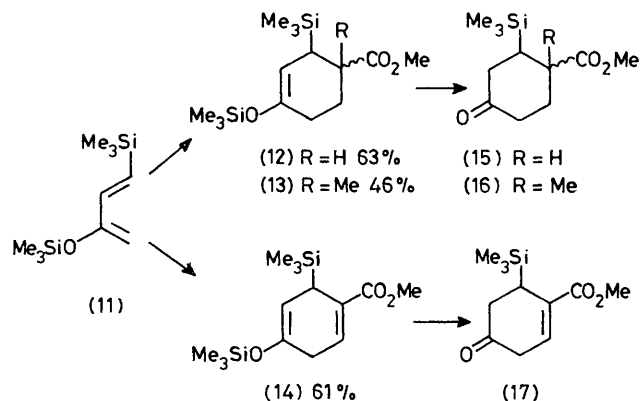
reaction with methyl acrylate. Although these results might be deemed disappointing for any application of simple silylated dienes in synthesis, they do have a useful aspect: since the trimethylsilyl group evidently exerts little directing effect, any other substituent on the diene should exert its directing effect more or less unimpeded. The regioselectivity shown by substituted dienes in Diels-Alder reactions is rather well understood, which means that it should be easy to predict what the regioselectivity will be for the corresponding silylated diene. We now report that this is indeed so.

regioselectivity induced by the methyl group in (6) and to hamper the regioselectivity induced by the methyl group in (1). The regioselectivity in these reactions was proved by high-yielding protodesilylations (Scheme 1) followed by easy aromatisation with dichlorodicyanobenzoquinone. In the presence of a powerful directing group, such as the silyloxy group in the diene (11), regioselectivity is essentially complete; this diene reacted with methyl acrylate, methyl methacrylate, and methyl propiolate to give only the adducts (12), (13), and (14), respectively.

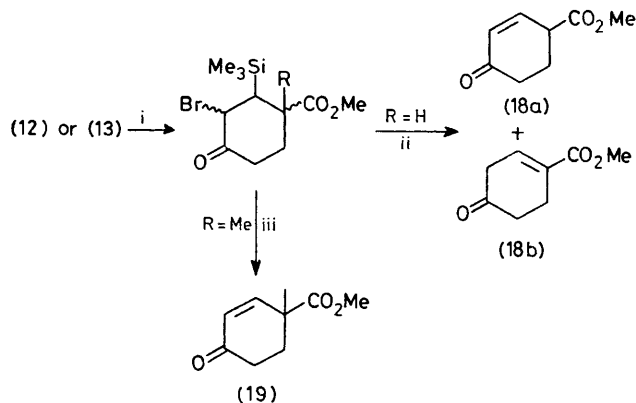


SCHEME 1.† Reagent: i, $\text{TsOH}-\text{C}_6\text{H}_6$ -reflux.

1-Trimethylsilylpenta-1,3-diene (1) and methyl acrylate gave the adducts (2) and (4) in a ratio of 2:1. With methyl propiolate, the ratio of (3) to (5) was 3:1. 3-Methyl-1-trimethylsilylbuta-1,3-diene (6) and methyl acrylate gave the adduct (7) as a mixture of stereoisomers, but the regioisomer (9) was not observed and could only have been a very minor product. With methyl propiolate, both regioisomers (8) and (10) were observed in a ratio of 4:1. The greater regioselectivity in the case of the diene (6) compared to the diene (1) is in agreement with our observations with 1-trimethylsilylbutadiene:¹ what little regioselectivity that compound showed was such as to boost the



These compounds were easily hydrolysed to the corresponding β -silyl ketones (15), (16), and (17). As described in the preceding papers,⁴ such compounds are masked $\alpha\beta$ -unsaturated ketones, and this connection with the work described in those papers is demonstrated by the conversion (Scheme 2) of the adduct (12) into the mixture of unsaturated ketones (18a) and (18b) (78%), and of the



SCHEME 2.† Reagents: i, N -bromosuccinimide-tetrahydrofuran; ii, CsF -dimethylformamide; iii, Me_3SO .

adduct (13) into the unsaturated ketone (19) (82%). The formation of products like (18) and (19) has also been achieved by Danishefsky and Kitahara⁵ and by Ibuka and

† The wavy lines indicate mixtures of stereoisomers of the acrylate adducts.

his co-workers,⁶ who used 1,3-dioxygenated dienes. In their case, the elimination of the β -oxygen substituent was more or less unavoidable. The advantage of our method is that the intermediate ketones, such as (15) and (16), are

available for further manipulation before the $\alpha\beta$ -unsaturation is introduced by bromination.

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¹ I. Fleming and A. Percival, *J.C.S. Chem. Comm.*, 1976, 681.

² I. Fleming and B. W. Au-Yeung, unpublished results; compare ref. 3, where some regioselectivity was reported for the corresponding reaction with ethyl trimethylsilylpropiolate.

³ C. S. Kraihanzel and M. L. Losee, *J. Amer. Chem. Soc.*, 1968, **90**, 4701.

⁴ I. Fleming and J. Goldhill, *J.C.S. Chem. Comm.*, 1978, 176 and D. J. Ager and I. Fleming, *ibid.*, 177 (preceding communication).

⁵ S. Danishefsky and T. Kitahara, *J. Amer. Chem. Soc.*, 1974, **96**, 7807.

⁶ T. Ibuka, Y. Mori, and Y. Inubushi, *Tetrahedron Letters*, 1976, 3169.