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(1*E*)-1,3-DIMETHOXY-1,3-BUTADIENE

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Abstract Reaction of 1,1-dimethoxy-2-butyne (II) with sodium methoxide in dimethyl sulfoxide at 100° yields (1*E*)-1,3-dimethoxybutadiene (III) (20-30%) The diene III undergoes ready Diels-Alder reaction with maleic anhydride, N-phenyltriazolinedione and dimethyl acetylenedicarboxylate

The utility of the 1,3-dioxygenated butadienes has been demonstrated by the recent accomplishments of Danishefsky and his coworkers,[1] who have explored (1*E*)-1-methoxy-3-trimethylsilyloxybutadiene (I), as well as a number of other electron-rich dienes, in a variety of synthetic applications.

We recently encountered an instance in which the anticipated Diels-Alder reaction of I with thiolene-2-one was circumvented by a competing intermolecular trimethylsilyl group transfer reaction yielding 2-trimethylsilyloxythiophene and 4-methoxybut-3-ene-2-one

For this reason, it seemed worthwhile to explore the 1,3-dialkoxybutadienes (i) for those rare instances in which silyl group transfer diverts the normal course of the Diels-Alder reaction, and (ii) because in spite of the considerable interest recently generated in this area,[1] the 1,3-dialkyloxybutadienes are a rarity and their preparation has remained obscure [1,2]

We have now found that heating a mixture of 1,1-dimethoxy-2-butyne (II) with sodium methoxide in dimethyl sulfoxide at 100° for 2.75 hours, yields directly (1*E*) 1 3-dimethoxybuta-1,3-diene (III)[3] in 20-30% yield after workup and distillation as a colorless liquid bp 53-58°/22 mm Although the yield is modest, the reaction is simple and isolation of the product is straightforward We view this reaction, tentatively as an S_N2' displacement of methoxide by methoxide followed by isomerization of the resulting intermediate allene to the product diene The normal course of such a reaction, in which the butyne II is heated with sodium methoxide in methanol, results in addition to the triple bond yielding 1,1,3-trimethoxybut-2-ene.[4]

The diene III readily yields adducts with maleic anhydride, N-phenyltriazolinedione and dimethyl acetylenedicarboxylate.[5]

We found the Danishefsky diene[1] much easier to handle than the new diene III The latter is subject to discoloration and polymerization on heating and it was found to be advantageous to include a small amount of BHT in the preparation and distillation of III

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References and Notes

(1) S Danishefsky, T Kitahara, C F Yan, and J. Morris, J. Am Chem Soc , 101 6996 (1979); S Danishefsky, Accts. Chem Res., 14, 400 (1981)

(2) O. A. Shavrygina and S M Makin, Khim Farm. Zh , 3, 17 (1969)

(3) The 300 MHz nmr spectrum showed a vinyl AB quartet at δ 6.93 and 5.32 with J_{AB}=12 53 Hz, indicative of the E configuration, a terminal vinyl AB quartet at δ 3.93 and 3.91 with J_{AB}=1 82 Hz together with a pair of methoxy singlets at δ 3.59 and 3 61 ppm. The nmr spectrum also revealed a persistent small impurity with peaks near 3.60 ppm which was diminished but not completely removed in two conventional short-path distillations

(4) L Claisen, Chem. Ber , 44, 1165 (1911), J C Lunt and F Sondheimer J Am Chem Soc., 72, 3361 (1950), L Crombie, S. H Harber and R J D Smith J. Chem. Soc , 2754 (1956)

(5) Dimethyl acetylenedicarboxylate yielded both dimethyl 4-methoxyphthalate (44%) and dimethyl 3-methoxyphthalate (19%), whose properties compared favorably with those reported Cf H Neunhoeffer and G. Werner, Ann , 1955 (1973), and J. A Profitt, T Jones, and D S. Watt, Syn Comm , 457 (1975).

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