tiomers of lactone **4** afforded a 1:1 mixture of the GLC-separable (Carbowax, 150 °C) cis and trans isomers of **1**.[8] Since the methylation sequence has no effect upon the stereochemistry of the configurationally known δ carbon of **4**,[9] the absolute configurations of the four stereoisomers of **1** are established. Even had the absolute configuration of **4** not been previously assigned,[9] it could have been assigned from the elution order of the diastereomeric carbamates **3a** and **3b**.[10] Moreover, the absolute configurations of the enantiomers of *cis*-**1** (and hence the *trans*-**1** as well) are assignable from the sense of the (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol induced NMR spectral nonequivalence.[11] This induced NMR nonequivalence allows facile NMR determination of the enantiomeric purity of *cis*-**1** (and thus *trans*-**1** as well); both enantiomers were enantiomerically pure by this criterion. Lactone **4** recovered by GLC from the methylation reaction mixture was of unchanged specific rotation.[12]

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Supplementary Material Available: the experimental details of this work (4 pages). Ordering information is given on any current masthead.

References and Notes

(1) Although the report[2] of the identification of *cis*-**1** as the major component of the sex attractant contains no chiroptic data, it is reasonable to assume that the natural material is chiral and not racemic. In the absence of such data, we cannot state which enantiomer of *cis*-**1** corresponds to the natural material. Toward this end, samples of the stereoisomers are available for testing.

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(8) Cis–trans assignments were made originally on the basis of low-temperature NMR studies.[2] In the present instance, assignments are based upon previously reported[2] chemical shifts and GLC elution orders.

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(10) From the chromatographic separation model advanced for diastereomeric carbamates in ref 3, the known absolute configuration of the resolving agent, and the knowledge that polar groups such as cyano absorb rather strongly upon silica gel or alumina, one expects **3a** to elute before **3b**.

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(12) Our specific rotations of the enantiomers of **4** are not in close agreement with prior literature values. Note that the prior values are also in disagreement [i.e., (*R*)-(+)-**4**, $[\alpha]^{20}{}_D$ +18.4° (1.7, MeOH);[13] (*S*)-(−)-**4**, $[\alpha]^{19}{}_D$ −51.4° (EtOH)[9a]]. Owing to our use of preparative GLC for purification and subsequent NMR demonstration of enantiomeric purity, we believe our rotational values to be those of the enantiomerically pure enantiomers.

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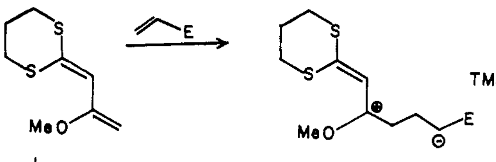
Diels–Alder Reactions of 1,1-Dimethoxy-3-trimethylsilyloxy-1,3-butadiene

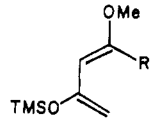
Summary: The title compound has been shown to be a powerful diene in Diels–Alder reactions with electron-deficient dienophiles. In these processes, it functions as a directed synthetic equivalent of $^{+}COCH_2COCH_2^{-}$. The contrast in behavior between this diene and that of 2-(2-methoxy)allylidene-1,3-dithiane, which has a high tendency to afford Michael addition products with highly electrophilic olefins, is particularly striking.

Sir: Recently we investigated the feasibility of cycloaddition reactions of diene **1** with potential dienophiles.[1] We found that the generality of Diels–Alder cycloadditions of **1** was undermined by its tendency to afford simple Michael addition products with highly electrophilic olefins such as benzoquinone and dimethyl acetylenedicarboxylate. Cycloaddition reactions were observed only with less electrophilic olefins such as methyl vinyl ketone.

It seemed likely that strong electrophiles might react with the powerfully nucleophilic **1** via its "s-trans" conformer, thereby affording an intermediate of the type **2**, wherein cyclyzation would be noncompetitive with proton transfer as a means of charge dissipation.



1 2



3 R = OMe
4 R = H

It seemed worthwhile to pursue this line of study. Thus, the general proposition of using heavily functionalized dienes which might endow their Diels–Alder adducts with convenient access points for orderly future elaborations has, potentially, considerable possiblities in the design of synthetic strategy.[2-4] During the course of our studies, addressed to correcting the limitations of diene **1** described above, Brassard and coworkers[5] reported the preparation of diene **3** and homologues thereof by a method similar to that which we used for the preparation of **4**.[6] Of particular interest to us was the finding that compound **3** and its homologues gave cycloaddition products with several naphthoquinones. No other Diels–Alder reactions of **3** were described. Since we had found that reaction of compound **1** with the parent 1,4-benzoquinone afforded a benzofuran which was clearly derived from Michael addition and proton transfer,[1] we have examined the general enophilicity of compound **3**. Below we report that this substance is, in fact, an excellent diene for Diels–Alder reactions and its use allows for the facile elaboration of aromatic and alicyclic systems bearing extensive functionality.

Compound **3** reacted with dimethyl acetylenedicarboxylate in benzene. After 30 min under reflux[7] there was isolated an 89% yield of dimethyl 3-methoxy-5-hydroxyphthalate (**5**), mp 141–143 °C.[8] The unraveling of the presumed adduct **5a** is apparently instantaneous under these conditions. Similarly, compound **3** reacts with 1,4-benzoquinone (C_6H_6; room temperature; 15 min). The crude adduct was treated with pyridine–acetic anhydride (reflux; 12 h), thereby affording a 78% yield of 1-methoxy-3,5,8-triacetoxynaphthalene (**6**),[8] mp 172–173 °C.

It will be recalled that, with these two potential dienophiles, compound **1** gave high yields of products derived from simple 1,4-addition. Diels–Alder reaction of compound **3** with 1,3-dicarbomethoxyallene (C_6H_6; reflux; 1 h) afforded a 72% yield of the differentiated homophthalate derivative, **7**[8] (mp 70–72 °C). Similarly, a 74% yield of methyl 2-methoxy-4-hydroxybenzoate (mp 150–151 °C; lit.[9] 152–153 °C) was obtained after cycloaddition of **3** with methyl propiolate.

Thus, through this methodology, one elaborates in a single step a benzene ring in the form of a resorcinol monomethyl ether. The condition of the process with unsymmetrical dienophiles is that the methoxy group emerges ortho to that function which dominates their regiochemical sense of addition.

Cycloaddition of compound **3** with maleic anhydride occurs essentially instantaneously (neat; 0 °C). Trituration with ether gave a 95% yield of compound **9**,[8] mp 152–153 °C. No acidic

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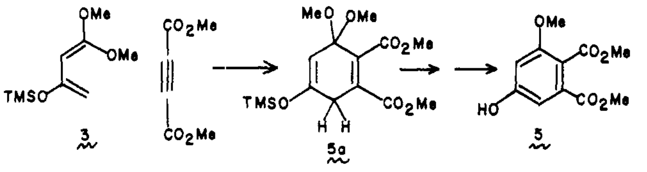
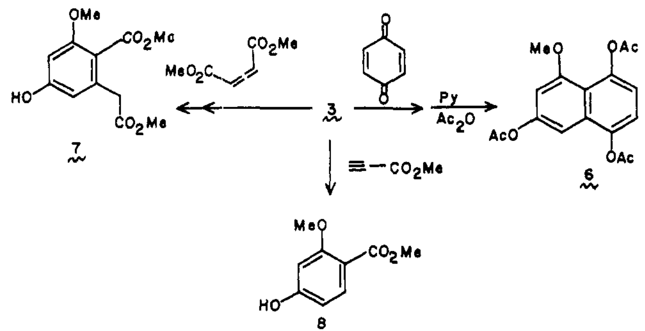
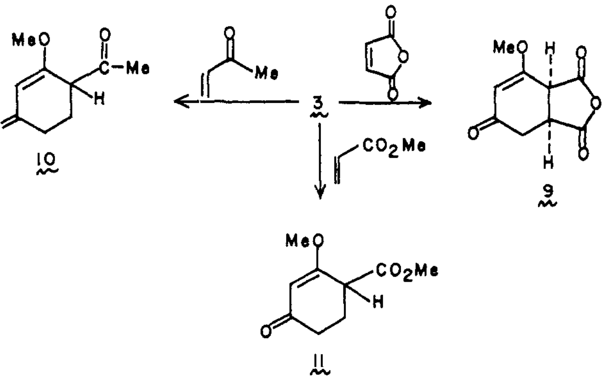
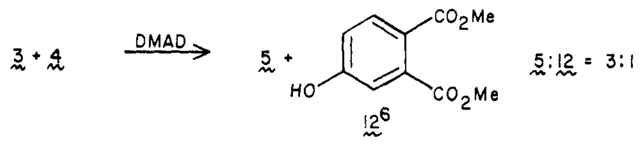


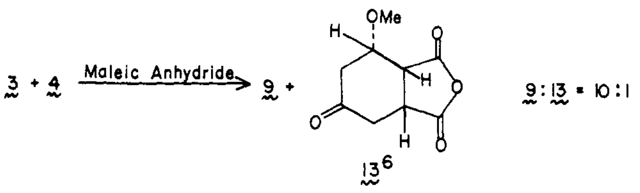


treatment was necessary for unraveling. Cycloaddition of 3 with methyl acrylate (C_6H_6; reflux; 16 h) followed by mild acid hydrolysis afforded a 55% yield of 11.[8] In a similar way, reaction of 3 with methyl vinyl ketone (C_6H_6; 50 °C; 2 h) afforded 10,[8] though the isolated yield of homogeneous product was a disappointing 43%.



We were both pleased and surprised at the extremely mild conditions which sufficed for the cycloadditions of 3, a 1,1-disubstituted butadiene. It was of interest to compare the rate of cycloadditions of 3 with that of parent compound 4,[6] which lacks the (Z)-methoxyl at the 1 position. A direct comparision of these dienes was made as regards their cycloadditions with dimethyl acetylenedicarboxylate and maleic anhydride. In each case, stoichiometric equivalents of 3 and 4 were allowed to compete for 1 equiv of dienophile. The results,[10] described below, indicate that with respect to these dienophiles 3 is a more potent Diels–Alder diene than 4.





Our findings indicate that Diels–Alder reactions between highly "nucleophilic" dienes and highly "electrophilic" dienophiles may proceed effectively even though the 1 position of the diene is disubstituted. Indeed, the indication from this work is that the enhanced nucleophilic character of the diene may override the steric difficulties associated with an additional (Z)-methoxyl function.

In rationalizing the reactivity differences of 1 and 3 with respect to Diels–Alder cyclizations vs. Michael additions, several as yet imponderables await definition. These are: (i) the effect of sulfur (in 1) vs. oxygen (in 3) heteroatoms; (ii) the effect of the ring constraint of the 1,1-heteroatoms (in 1) vs. the conformationally mobile arrangement in 3; and (iii) the effect of the 3-OTMS group of 3[11] relative to the 3-OMe group of 1. For the moment, one must be content with the phenomenological finding, i.e., that diene 1, in many of its reactions, is a functional equivalent of $^-CH_2COCH_2C(O)H$, while diene 3 is a synthetic equivalent of $^-CH_2COCH_2C^+(O)$.

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(11) The possibility that the size of the substituent at position 3 is relevant will be studied, since this could well effect the "s-cis" and "s-trans" conformational populations of the dienes.

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