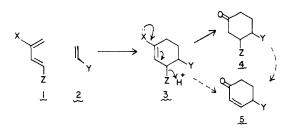# Communications to the Editor

A Useful Diene for the Diels–Alder Reaction

Sir:

The range of variations, in terms of functionality and oxidation level, which has been developed for Diels–Alder dienophiles has not been paralleled for the dienic components.[1] The major structural modification for the dienes has been realized by manipulation of their alkylation level (*cf.* 1,3-butadiene, alkylated butadienes, cycloalkadienes, anthracenes, etc.). Also, the 1- and 3-alkoxydiene derivatives are very important in that they are more reactive than 1,3-butadiene itself and also allow for the introduction of oxygen into the resultant product.

In connection with a variety of synthetic objectives it would be useful to realize transformations of the type generalized below.[2,3]
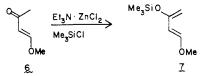
The nature of X and Z should be such as to confer high reactivity and high orientational specificity on diene **1** in its reactions with unsymmetrical dienophiles of the type **2**, where Y is an election withdrawing group such as carbonyl, cyano, etc.[4] The character of X should allow for facile conversion of the XC=C type of enol derivative in **3** into the ketone found in **4** and **5**. The function Z should be amenable to β-elimination, thus allowing for the transformation of **4 → 5**. Indeed, the direct transformation of **3 → 5** (*cf.* arrows) may also be possible.[5] Alternatively, the Z group in **4** may be maintained for purposes of protection of a latent enone or, possibly, for its own functionality. Finally, of course, the diene **1** should be readily available.

A 1,3-dialkoxybutadiene, in principle, meets all the above stated structural specifications. Such systems have been generated and used in the cyclohexadiene series.[6,7] However, there is only one recorded example of the preparation and use of a parent 1,3-dialkoxybutadiene. The preparation of this type of compound is beset by severe difficulties. The primary route to enol ethers involves acetal formation[9] followed by pyrolytic dealcoholysis. The difficulties associated with this rather cumbersome process are compounded when the objective is the formation of enol ethers of the alkoxybutadiene type. This generally involves the twofold elimination of alcohol from a β-alkoxyacetal system.[10] In our laboratory attempts at the formation of the parent compound, 1,3-dimethoxy-1,3-butadiene, (*cf.* ref 7) by pyrolysis of 1,1,3,3-tetramethoxybutane under several catalytic conditions were uniformly unsuccessful and were invariably attended by the formation of intractible tars.[11]

In contrast, the formation of silyl enol ethers by direct silylation of aldehydes and ketones is considerably more straightforward. In general, two procedures have been successfully employed. The ketone may be silylated using tri-

ethylamine–trimethylchlorosilane.[12] Alternatively an enolate, generated in an experimentally distinct step, is silylated using trimethylchlorosilane.[13]

With these considerations in mind, we studied the feasibility of silylating the readily (and commercially) available *trans*-4-methoxybutene-2-one (**6**). It will be noted that the carbonyl group of **6** is a vinylogous ester. Accordingly, it was perhaps not surprising[14] to find that attempted silylation of **6** by the trimethylamine method gave only the faintest indication of success. However, reaction of **6** with trimethylchlorosilane in the presence of triethylamine–zinc chloride[15] gave a 68% yield of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**7**) as an easily distillable liquid. A procedure for the preparation of 58 g of this compound is given.[16] Below we describe the facile cycloaddition reactions[17] of **7** with dienophiles and the subsequent unraveling of the adducts so produced. This chemistry, coupled with the ready availability of compound **7**, mark this diene as a reagent of considerable possibilities in synthesis. Moreover, the strategy implicit in the formation and reactions of **7** may be extendable to the incorporation of still more elaborate functionality, though this remains to be demonstrated.
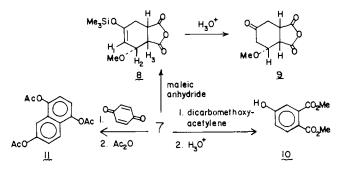

Addition of maleic anhydride (1 equiv) to compound **7** (2 eq) at room temperature in neat form results in an exothermic reaction leading to a homogeneous solution. The nmr spectrum of the solution indicates the formation of adduct **8**. Work-up with HCl (0.1 *N*)–THF at room temperature for 10 min gives a 93% yield of the crystalline methoxyketoanhydride **9**, mp 97–98° (ether–chloroform): $\nu_{max}^{CHCl_3}$ 1852, 1786, 1720 cm^{-1}; nmr δ (CDCl$_3$) 3.25 (s, 3 H, OCH$_3$), 4.1–4.3 (m, 1 H, CH$_3$OCHR$_2$).

The stereochemical assignment for **9** follows from the nmr spectrum of its precursor, **8**, wherein J_{H_1} (δ 5.02)$_{-H_2}$ (δ 4.16) = 6.0 Hz and $J_{H_2-H_3}$ = 3.6 Hz are easily seen. The assignment is also in accord with the usual precept of endo addition.[4a]

A different pathway is followed during the reaction of **7** (1.5 equiv) with dimethyl acetylenedicarboxylate (1 equiv). In benzene under reflux, cycloaddition is accompanied by 1,4-elimination of methanol. The crude phenyl silyl ether, so produced, is hydrolyzed with dilute acid to give the known dimethyl 4-hydroxy-*o*-phthalate (**10**), mp 105.5–106.5, lit.[18] 107–108°, in 79% overall yield.
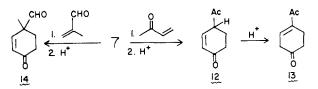
Compound **7** may also be used in a one-step synthesis of oxygenated naphthalenes. Treatment with *p*-benzoquinone results in an exothermic reaction. It was found most advantageous to acetylate the product so produced (acetic anhydride–pyridine, room temperature) whereupon an 87% yield of 1,4,6-triacetoxynaphthalene (**11**), mp 92–95° (lit.[19] 94–95°), was obtained.

We return to the applications of compound **7** to alicyclic synthesis. Compound **7** (1.5 equiv) was heated with methyl vinyl ketone (1 equiv) at 95° for 20 hr. The adduct was then subjected to rapid acidic work-up. At this stage a mixture of

types of cyclohexenones, see F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 4474 (1972).

(4) (a) J. Sauer, *Angew Chem., Int. Ed. Engl.*, **6**, 23 (1967); (b) K. N. Houk, *J. Amer. Chem. Soc.*, **95**, 4092 (1973).

(5) *Cf.* M. Stiles and A. L. Longroy, *J. Org. Chem.*, **32**, 1095 (1967).

(6) I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and W. Kernick, *Tetrahedron*, **26**, 201 (1970).

(7) For the generation, *in situ*, of 1,3-diacetoxycyclohexa-1,3-diene and its use as a Diels–Alder diene, see J. Wolinsky and R. B. Login, *J. Org. Chem.*, **35**, 1987 (1970).

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

(9) S. A. Patwardhan and S. Dev, *Synthesis*, 348 (1974).

(10) For the complexities involved in the preparation of 2-methoxybutadiene by pyrolysis, see L. J. Dolby and K. Marshall, *Org. Prep. Proced.*, **1**, 229 (1969).

(11) S. Mazza, private communication.

(12) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(13) (a) C. R. Kruger and E. G. Rochow, *J. Organometal. Chem.* **1**, 476 (1964); (b) R. Bouchis and E. Frainnet, *Bull. Soc. Chim. Fr.* 3552 (1967); (c) G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462 (1968).

(14) The triethylamine method[12] has not been successfully used in the case of esters. For silylation of esters *via* preformed enolates, see M. W. Rathke and D. F. Sullivan, *Syn. Commun.*, **3**, 67 (1973).

(15) *Cf* A. Bozouin, J. Dunogues, and M. Le Fort, French Patent Rhone-Poulenc 1,436,568 (1966); *Chem Abstr.*, **65**, 5487d (1966); **66**, 18764z (1967).

(16) Anhydrous powdered zinc chloride (2.0 g) was added to triethylamine (115 g, 1.1 mol). The mixture was stirred for 1 hr at room temperature until the salt was suspended in the amine. To this was added a solution of compound 6 (50 g, 0.5 mol) in 150 ml of benzene followed by (108.5 g, 1 mol) of trimethychlorosilane. An exothermic reaction was noted. After 30 min, the temperature was raised to 40° and stirring continued overnight. After cooling, the reaction mixture was added to 1 l. of ether and filtered. The filtrate and combined ether washings were concentrated *in vacuo* to give a brown oil. Distillation through a Vigreux column gave 58.2 g (68%) of compound 7 in a middle cut, 54–55° (5 mm): $\nu_{max}^{CHCl_3}$ 1656, 1618, 1597, 1567, 1538 (sh), 1300, 1234, 1010, 950 cm^{-1}; nmr δ (CDCl₃) 0.23 (s, 9 H), 3.57 (s, 3 H), 4.03–4.17 (broadened d, 2 H), 5.36 (d, *J* = 12 Hz, 1 H), 6.81 (d, *J* = 12 Hz, 1 H); *m/e* 172 (P), 173 (P + 1). Although the presence of ca 1% of 6 was indicated by the nmr spectrum, the material so produced afforded excellent combustion data. (Calcd C, 55.77; H, 9.36. Found: C, 55.57; H, 9.21%).

(17) For previous involvement of siloxy derivatives in bond reorganization reactions see (a) siloxy Cope rearrangement, R. W. Thies, M. T. Wills, A. W. Chim, L. E. Schick, and E. S. Walton, *J. Amer. Chem. Soc.*, **95**, 5281 (1973); (b) siloxy Claisen rearrangement, R. E. Ireland and R. H. Mueller, *ibid.*, **94**, 6190 (1972); (c) disiloxycyclobutene → disiloxybutadiene, T. Mori, R. Nakahara, and H. Nozaki, *Can. J. Chem.*, **47**, 3266 (1969); (d) siloxyvinylcyclopropane → siloxycyclopentene, B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 289 (1973); (e) cycloadditions, P. Cazeau and E. Frainnet, *Bull. Soc. Chim. Fr.*, 1658 (1972).

(18) W. H. Bentley and C. Weizmann, *J. Chem. Soc.*, **91**, 98 (1907).

(19) O. Fischer and C. Bauer, *J. Prakt. Chem.*, **94**, 1 (1916).

(20) R. M. Acheson, *J. Chem. Soc.*, 3415 (1952).

(21) A. A. Petrov, *J. Gen. Chem. USSR*, **17**, 538 (1947).

(22) *Cf.* Prephenic acid and trisporic acid, D. M. Thomas and T. W. Goodwin, *Phytochemistry*, **6**, 355 (1972).

(23) In the reactions of 7 with the unsymmetrical dienophiles, methyl vinyl ketones, and methacrolein, tlc analysis of the mixtures after acidic work-up indicated the presence of the products described (12, 13, and 14) plus nonmobile residue (presumably polymerized dienophile). Chromatography easily separates the product from the polymer. There is no indication for the formation of regioisomers. Nevertheless the incomplete accounting of material prevents us from ruling out the possibility of their formation in small quantities.

enediones, 12 and 13 (*ca.* 1:1), resulted. Neither was obtained in pure form but the presence of each component could be ascertained by nmr analysis. When this mixture was exposed to the action of 0.1 *N* HCl–THF for 1 hr at room temperature, an 86% overall yield of 13 ($\nu_{max}^{CHCl_3}$ 1727, 1684, 1647 cm^{-1}; nmr δ (CDCl₃) 2.30 (s, 3 H), 2.10–2.80 (m, 4 H), 3.03 (d, xt, *J* = 4 Hz, J = 2 Hz, 2 H), 6.73 (t, *J* = 4 Hz, 1 H)) contaminated by *ca.* 5% of 12 was isolated. The 2 H multiplet centered at δ 3.03 is assigned to the allylic methylene protons at C₂ adjacent to the cyclic ketone. Compound 13 was reduced (5% Pd–C–EtOH) to the known[20] 4-acetylcyclohexanone. Since the 2,4-DNP derivative produced from this material had a melting point (EtOAC) of 218–218.5°, while it has been reported from 200°[20] to 207°,[21] our compound was submitted to combustion analysis. *Anal.* Calcd for bis(2,4-DNP: C, 48.00; H, 4.02; N, 22.39. Found: C, 48.07; H, 3.95; N, 22.15. While we have not established the point with certainty, we believe 12 to be the principal kinetic product from unraveling of the Diels–Alder adduct. This would, of course, be the expected product if the enone is produced without involvement of an intermediate β-methoxy ketone. (*cf.* 3 → 5 and ref 5).

The reaction of compound 7 with methacrolein (benzene, reflux, 20 hr) is indicative of its possibilities for the one-step synthesis of 4,4-disubstituted cyclohexenones.[22] The adduct, upon gentle acidic hydrolysis, gave a 72% yield of 4-methyl-4-formylcyclohex-2-ene-1-one (14).[23] Compound 14 ($\nu_{max}^{CHCl_3}$ 2732, 1720, 1765, 1594, 874 cm^{-1}; δ (CDCl₃ 1.31 (s, 3 H), 1.70–2.27 (m, 4 H); 5.94 (d, *J* = 10 Hz), 6.62 (d, *J* = 10 Hz, 1 H), 9.40 (s, 1 H)) was characterized as its bis(2,4-DNP), mp (EtOAC–EtOH) 136–136.5°. The AB pattern of the vinylic protons in the nmr spectrum rules out the alternative regioisomer 5-methyl-5-formylcyclohex-2-ene-1-one. The latter would be expected to exhibit a multiplet for the proton on the β-carbon.

Further applications of siloxydienes to organic synthesis are currently under investigation.

References and Notes

(1) A. S. Onishchenko, Diene Synthesis, Israel Program of Scientific Translations, Daniel Davy & Co., New York, N.Y., 1964.

(2) An ingenious sequence due to D. A. Evans accomplishes the overall transformation of 2 to the allylic alcohol equivalent of 5 for the case where Y is electron donating, X = H, and Z = phenyl sulfinyl. See D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Amer. Chem. Soc.*, **94**, 2891 (1972).

(3) For the application of vinylketene thioacetals to the synthesis of certain

S. Danishefsky,* T. Kitahara

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received August 24, 1974

Reactions of (Diphenylcarbene)pentacarbonyltungsten(0) with Alkenes. Role of Metal-Carbene Complexes in Cyclopropanation and Olefin Metathesis Reactions

Sir:

Stable transition metal–carbene complexes[1] are potentially useful model systems for the study of catalytic reactions such as cyclopropanation and olefin metathesis[2] which are postulated to involve metal–carbene complexes as transient intermediates.[3] Heteroatom-substituted carbene complexes have proven to be somewhat too thermally stable and unreactive as methylene transfer agents toward simple alk-