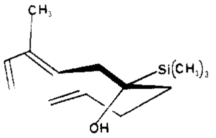
The product **11** has been reported earlier[1a] to undergo intramolecular Diels–Alder reaction leading to a mixture of **12** and **13**. If **10b** is heated at 180 °C for 20 h, cyclization occurs. The product (mainly one isomer) is assigned structure **14** (equatorial Me_3Si) based on the assumption that the bulky Me_3Si group must occupy an equatorial position in the Diels–Alder transition state **15**.[12] When **14** was treated with KH/HMPA, a stereospecific[13] Brook rearrangement[8] led to exclusive axial alcohol **13**.



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In conclusion, we point out that the efficient desilylation of silyl carbinols makes their acyl silane precursors equivalent to aldehydes that are sterically hindered. Two additional advantages are the following: (1) acyl silanes are less prone to self-condensation than aldehydes and thus give higher overall yields and (2) the bulky Me_3Si substituent can be used to control the stereochemistry of subsequent reactions.

Acknowledgment. We thank the National Institues of Health (GM-26039) and the Petroleum Research Fund (11243-ACl) for financial assistance.

Registry No. 1, 51852-87-0; 2 (R_1 = Me; R_2 = H), 75-07-0; 2 ($H_2C=CHCH_2-C_4H_6S_2$; R_2 = H), 75266-68-1; 2 (R_1 = *t*-Bu; R_2 = H), 630-19-3; 2 (R_1 = Me; R_2 = *t*-Bu), 13411-48-8; 3 (R_1 = Me; R_2 = H), 80387-36-6; 3 ($H_2C=CHCH_2-C_4H_6S_2$; R_2 = H), 80387-37-7; 3 (R_1 = *t*-Bu; R_2 = H), 80387-38-8; 3 (R_1 = Me; R_2 = *t*-Bu), 80387-39-9; 4 (R_1 = $H_2C=CHCH_2CH_2$; R_2 = H), 80387-40-2; 4 (R_1 = Me; R_2 = H), 80387-41-3; 4 ($H_2C=CHCH_2-C_4H_6S_2$; R_2 = H), 80387-42-4; 4 (R_1 = *t*-Bu; R_2 = H), 80387-43-5; **6a**, 13411-48-8; **6b**, 80387-44-6; **8**, 80387-45-7; **9**, 2100-17-6; **10a**, 80387-46-8; **10b**, 80387-47-9; **11**, 80387-48-0; **13**, 80433-07-4; **14**, 80387-49-1.

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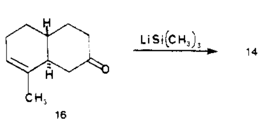
[9] Brook, A. G.; Warner, C. M.; Mcgriskin, M. E. *J. Am. Chem. Soc.* **1959**, *81*, 981–983.

[10] Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* **1979**, 708–709.

[11] Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423–1424.

[12] Additional support for the equatorial disposition of the Me_3Si group comes from the addition of Me_3SiLi[7] to known[1a] ketone **16** which gives **14**.



16

[13] The stereospecificity (retention) of the Brook rearrangement[8] can be rationalized by kinetic equatorial protonation of the anionic intermediate. A related aliphatic Brook rearrangement has also been reported (Hudlick, P., Howard University, personal communcation) to occur with retention.

Bifunctional Cyclopropyl Reagents: Stereocontrolled Approach to Vinyl Sulfides and Chemodifferentiated 1,4-Dicarbonyl Systems

Summary: The use of (*E*)-2-(hydroxymethyl)cyclopropyl phenyl sulfide as a useful conjunctive reagent, particularly in a stereocontrolled synthesis of vinyl sulfides, is reported.

Sir: The immense importance of the carbonyl group in structural elaboration stems from the ability to add nucleophiles to the carbonyl carbon atom and, most importantly, the ability to functionalize at the α carbon atom through the intermediacy of enols or enolates. Stereocontrolled methods for enol or enolate formation, which are generally lacking, would greatly enhance the utility of such synthetic intermediates. Vinyl sulfides not only have the possibility of serving as enol substitutes but, due to a myriad of other reactions involving direct replacement of sulfur or isomerizations to allylic systems, also may provide a much diverse reactivity profile. Thus, stereocontrolled syntheses of vinyl sulfides are particularly important but virtually nonexistent. We report herein that the bifunctional conjunctive reagent, 2-(hydroxymethyl)cyclopropyl phenyl sulfide (**1**),[1] provides a novel stereocontrolled approach to such systems which can greatly enhance the utility of this functionality. Furthermore, it additionally allows transformation into several important building blocks—particularly chemodifferentiated 1,4-dicarbonyl systems.

The reagent **1** (bp 110–111 °C (0.07 torr),[2,3] which has been made on multimole scale, is available in 45% overall yield from thiophenol and γ-butyrolactone as outlined in Scheme I. The pyrrophoric dilithium reagent **2**, which forms readily in contrast to the metalation of 2-methylcyclopropyl phenyl sulfide, forms as a suspension in hexane.[4-6] For synthetic purposes, two volumes of THF are

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[1] For a few recent examples of small ring conjunctive reagents, see: Trost, B. M.; Nishimura, Y.; Yamamoto, K. *J. Am. Chem. Soc.* **1979**, *101*, 1328. Trost, B. M.; Bogdanowicz, M. J.; Frazee, W. J.; Salzmann, T. N. *Ibid.* **1978**, *100*, 5512. Trost, B. M.; Scudder, P. H. *Ibid.* **1977**, *99*, 7601. Trost, B. M.; Frazee, W. J. *Ibid.* **1977**, *99*, 6124. Piers, E.; Nagakura, I.; Morton, H. E. *J. Org. Chem.* **1978**, *43*, 3630. Piers, E.; Lau, C. K. *Synth. Commun.* **1977**, *7*, 495. Danishefsky, S.; Singh, R. K. *J. Am. Chem. Soc.* **1975**, *97*, 3239. Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1979**, 583, 587. Halazy, S.; Lucchetti, J.; Krief, A. *Ibid.* **1978**, 3971. Harms, R.; Schollkopf, U.; Muramatsu, M. *Justus Liebigs Ann. Chem.* **1978**, 1194. Marino, J. P.; Browne, L. J. *Tetrahedron Lett.* **]976**, 3241. Marino, J. P.; Ferro, M. P. *J. Org. Chem.* **1981**, *46*, 1828.

[2] This compound has been characterized by IR, NMR, and mass spectroscopy and elemental composition established by combustion analysis and/or high-resolution mass spectroscopy.

[3] **1**: IR ($CDCl_3$) 3640, 3380, 1590, 1485 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1–7.4 (m, 5 H), 3.70 (dd, J = 11, 6 Hz, 1 H), 3.51 (dd, J = 11, 7 Hz, 1 H), 2.13 (dt, J = 8, 5 Hz, 1 H), 1.41 (m, 1 H), 1.01 (dt, J = 8, 5 Hz, 1 H), 0.91 (dt, J = 9, 5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 139.3, 129.2, 126.9, 125.3, 64.2, 25.7, 17.1, 13.0. **3**: IR ($CDCl_3$) 3590, 3410, 1580, 1480 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.6 (m, 5 H), 5.30 (d, J = 4 Hz, 1 H), 4.12 (dd, J = 8, 3 Hz, 1 H), 3.81 (d, J = 7 Hz, 1 H), 3.74 (d, J = 8 Hz, 1 H), 1.95 (td, J = 7, 3 Hz, 1 H), 1.14 (d, J = 7 Hz, 2 H).

[4] Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080.

[5] For other (1-phenylthiocyclopropyl)lithium reagents, see ref 1 and 4 and the following: Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3088. Cohen, T.; Daniewski, W. M.; Weisenfeld, R. B. *Tetrahedron Lett.* **1978**, 4665. Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311. Tanaka, K.; Uneme, H.; Matsui, S.; Tanikaga, R.; Kaji, A. *Chem. Lett.* **1980**, 287.

[6] For a similar independent observation in a different series, see Klumpp, G. W.; Kool, M.; Schakel, M.; Schmitz, R. F.; Boutkan, C. *J. Am. Chem. Soc.* **1979**, *101*, 7065.

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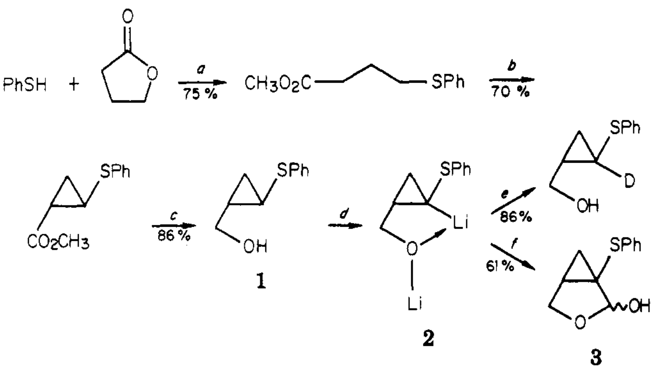
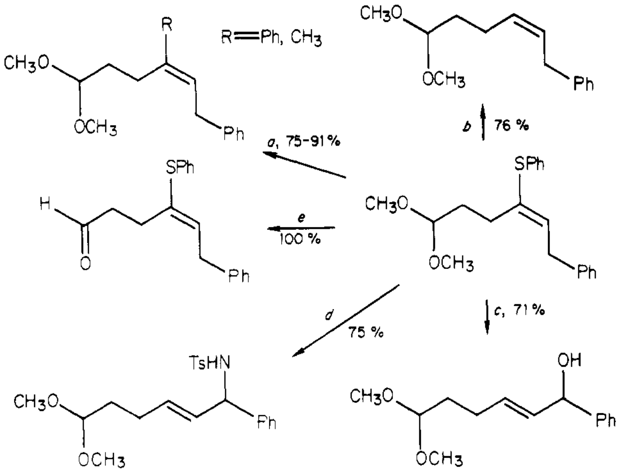
Scheme I. Synthesis and Metalation of 2-(Hydroxymethyl)cyclopropyl Phenyl Sulfide



[a] (i) LiH, THF, HMPA, room temperature; (ii) CH_3OH, H_2SO_4. [b] (i) NCS, CCl_4, reflux; (ii) KOC_4H_9-*t*, THF, −20 °C to room temperature. [c] LAH, ether, reflux. [d] *n*-C_4H_9Li, hexane, room temperature. [e] D_2O, 0°C. [f] DMF, THF, −78 °C.

Scheme II. Selective Reactions of the Vinyl Sulfide[f]

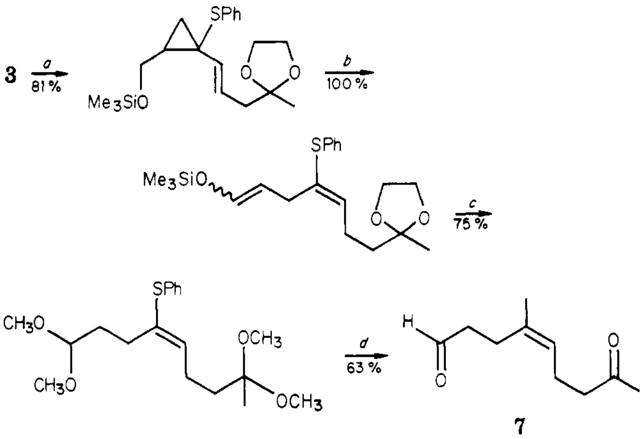


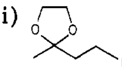
[a] CH_3MgBr or PhMgBr, (dppp)$NiCl_2$, THF–ether, reflux. [b] *i*-C_3H_7MgBr, $(Ph_3P)_2NiCl_2$, THF–ether, 65 °C. [c] (i) MCPBA, CH_2Cl_2, −78 °C; (ii) $NaOC_2H_5$, C_2H_5OH, 60 °C. [d] (i) $C_7H_7SO_2N(Cl)Na$, CH_3OH; (ii) C_2H_5ONa, C_2H_5OH, 60 °C. [e] 10% HCl, CH_3CN, room temperature. [f] See ref 2.

added to the hexane suspension to give a solution of the dianion. Quenching 2 with DMF generates lactol 3[2,3] (mp 98–99.5 °C, recrystallized from 40% ethyl acetate in hexane and carbon tetrachloride), a second valuable conjunctive reagent.

Lactol 3 serves as an intriguing precursor to functionalized 1,4-dienes as shown by eq 1 and summarized in Table I. The vinyl sulfide is generated with 100% *E* stereoselectivity! Transition states arising from conformation I, which correspond to placing a trans double bond in a seven-membered ring, are geometrically precluded. Rearrangement proceeds exclusively via the sterically much more favorable conformation II which produces the *E* vinyl sulfide.[9c] The stereochemistry of the enol silyl ether depends upon reaction via rotamer IIa or IIb. The

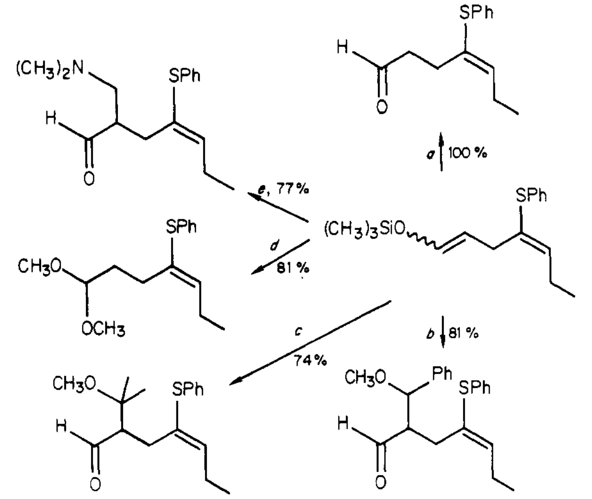
Scheme III. Stereocontrolled Synthesis of Trisporic Acid Side Chain



[a] (i)  , KOC_4H_9-*t*, THF, −20 °C;

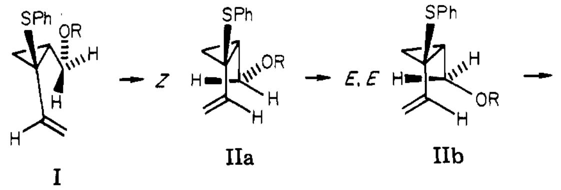
(ii) Me_3SiCl, C_5H_5N, ether. [b] FVP, 650 °C (0.25 torr). [c] CH_3OH, $(CH_3O)_3CH$, HCl. [d] (i) 5 mol % $(dppp)_2NiCl_2$, CH_3MgBr, THF, reflux; (ii) 10% HCl, CH_3CN, H_2O.

Scheme IV. Selective Reactions of the Enol Silyl Ether[f]



[a] KF, H_2O, CH_3CN, room temperature. [b] PhCH-$(OCH_3)_2$, BF_3·ether, CH_2Cl_2, −78 °C. [c] $(CH_3)_2C(OCH_3)_2$, $Me_3SiOSO_2CF_3$, CH_2Cl_2, −78 °C. [d] CH_3OH, $HC(OCH_3)_3$, HCl, room temperature. [e] $(CH_3)_2NCH_2I$, CH_2Cl_2, room temperature. [f] See ref 2.

fact that IIa possesses minimal steric interactions leads to the dominance of the *E* enol silyl ether.



The importance of this novel stereocontrolled approach to vinyl sulfides is highlighted by some of the applications which are summarized in Scheme II.[11-14] Hydrolysis of

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(7) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.

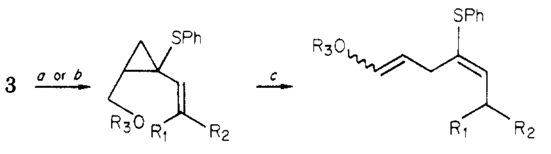
(8) (a) Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 365. (b) Trost, B. M.; Godleski, S. A.; Ippen, J. *J. Org. Chem.* **1978**, *43*, 4559.

(9) (a) Glass, D. S.; Zirner, J.; Winstein, S. *Proc. Chem. Soc.* **1963**, 276. (b) Glass, D. S.; Boikess, R. S. Winstein, S. *Tetrahedron Lett.* **1966**, 999. (c) Frey, H. M.; Solly, R. K. *J. Chem. Soc. B* **1970**, 996.

(10) It is interesting to note the dependence of the olefin stereochemistry on the choice of base in the Wittig reaction. This dependency may be associated with the effect of the lithium cation on the course of the Wittig reaction. See Schlosser, M. *Top. Stereochem.* **1970**, 1.

(11) Okamura, M.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, *20*, 43.

Table I. Synthesis of Functionalized 1,4-Dienes



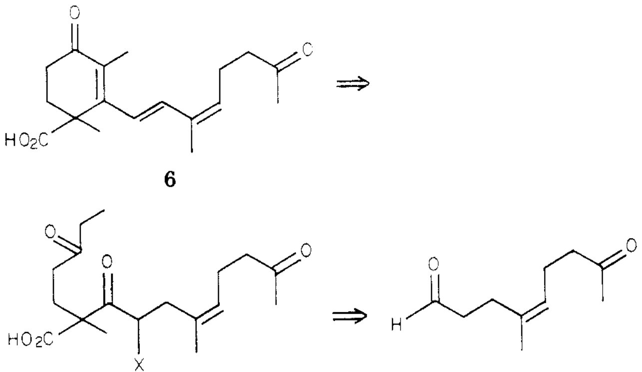
4 5 (1)

entry	R_1	R_2	R_3	4, E/Z^d	5, $E,E/Z,E^e$	overall yield, % of 5
1^f	H	H	t-$BuMe_2Si$		2:1	86
2^f	H	H	Me_3Si		2:1	75
3^f	CH_3	H	t-$BuMe_2Si$	5:95	9:1	96
4^f	CH_3	H	Me_3Si	5:95	4:1	90
5^g	H	CH_3	t-$BuMe_2Si$	91:9	2:1	88
6^f	$CH_3(CH_2)_2$	H	t-$BuMe_2Si$	5:95	8:1	90
7^f	$CH_3(CH_2)_2$	H	Me_3Si	5:95	6:1	89
8^f	$CH_3(CH_2)_3$	H	Me_3Si	5:95	8:1	96
9^f	Ph	H	t-$BuMe_2Si$	5:95	9:1	85
10^f	Ph	H	Me_3Si	5:95	6:1	92
11^f	CH_3	CH_3	t-$BuMe_2Si$		10:1	83
12^h	H	$(CH_2)_2CO_2Et$	t-$BuMe_2Si$	95:5	2:1	75

[a] $Ph_3P^+CHR_1R_2Br^-$, KOC_4H_9-t, THF then R_3SiCl. [b] $CH_2{=}CHMgBr$, THF; R_3SiCl; $(C_2H_5O)_3CCH_3$, $C_2H_5CO_2H$. Reference 7. [c] FVP, 545-650 °C (0.05-0.30 torr). References 8 and 9. [d] By NMR integration of the 270-MHz NMR of the olefin methines. [e] By NMR integration of the bis allylic methylene. [f] KOC_4H_9-t used as base. [g] n-BuLi was the base. Reference 10. [h] See eq 1 and footnote b.

the vinyl sulfide to a ketone is obvious and allows these compounds to serve as 1,4-dicarbonyl synthons. The nickel-catalyzed reactions are particularly noteworthy since the ability to completely control the stereochemistry of the vinyl sulfide translates into stereocontrolled tri- and disubstituted olefin syntheses. The stereochemical homogeneity is established by chromatography and 270-MHz ^1H and 15-MHz ^{13}C NMR spectroscopy.

A simple stereocontrolled approach to the side chain of trisporic acid 6[15,16] emerges as the retrosynthetic analysis summarized in eq 2 illustrates. Furthermore, the fact that the aldehyde is specifically enolized can also facilitate introduction of the X group for the final elimination. The dicarbonyl unit 7 is available in 38% overall unoptimized yield from 3 as summarized in Scheme III.

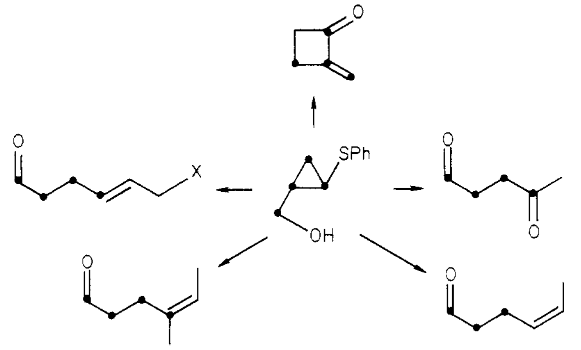


6

7 (2)

While the vinyl sulfide represents a carbonyl equivalent, it allows chemoselective structural elaboration of the other carbonyl equivalent present, the enol silyl ether. Scheme IV summarizes a few of the selective transformations performed.[17-19] The ability to manipulate independently the two functionalities gives special merit to this type of building block.

Scheme V. Synthetic Transformations Derived from 2-(Hydroxymethyl)cyclopropyl Phenyl Sulfide (1)



Small ring bifunctional conjunctive reagents such as 1 and 3 appear to be potentially important new building blocks. From these systems, new syntheses of Z vinyl sulfides, 1,4-dienes, chemodifferentiated 1,4-dicarbonyl systems, and 2-methylenecyclobutanones[20] have emerged as shown in Scheme V. Particularly noteworthy is the rare stereocontrolled synthesis of the vinyl sulfide. Such an entry into this relatively little utilized class of compounds provides a new direction for their utility—stereocontrolled olefin synthesis.[21]

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(12) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463.

(13) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(14) Kakimoto, M.; Yamamoto, T.; Okawara, M. *Tetrahedron Lett.* **1979**, 623.

(15) Bu'Lock, J. D.; Jones, B. E.; Winskill, N. *Pure Appl. Chem.* **1976**, *47*, 191. Sutter, R. P. *Science* **1970**, *168*, 1590. Werkman, T. A.; van den Ende, H. *Arch. Microbiol.* **1973**, *90*, 365.

(16) For a nonstereocontrolled synthesis, see Prisbylla, M. P.; Takabe, K.; White, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 762.

(17) Mukaiyama, T.; Hayashi, M. *Chem. Lett.* **1974**, 15.

(18) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

(19) Danishefsky, S.; Prisbylla, M.; Lipisko, B. *Tetrahedron Lett.* **1980**, *21*, 805. Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715.

(20) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463.

(21) Also see Trost, B. M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4413, 4743.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs. We also thank Ms. Paul Kuester for preparation of quantities of 1 and 3.

Registry No. 1, 80398-84-1; 3, 80398-85-2; 4 (R_1, R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-86-3; 4 (R_1, R_2 = H; R_3 = Me_3Si), 80398-87-4; 4 (R_1 = CH_3; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-88-5; 4 (R_1 = CH_3; R_2 = H; R_3 = Me_3Si), 80398-89-6; 4 (R_1, R_2 = CH_3; R_3 = *t*-$BuMe_2Si$), 80398-90-9; 4 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-91-0; 4 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = Me_3Si), 80398-92-1; 4 (R_1 = $CH_3(CH_2)_3$; R_2 = H; R_3 = Me_3Si), 80398-93-2; 4 (R_1 = Ph; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-94-3; 4 (R_1 = Ph; R_2 = H; R_3 = Me_3Si), 80398-95-4; 4 (R_1 = H; R_2 = $(CH_2)_2CO_2Et$; R_3 = *t*-$BuMe_2Si$), 80398-96-5; (*E,E*)-5 (R_1, R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-97-6; (*E,Z*)-5 (R_1, R_2 = H; R_3 = *t*-$BuMe_2Si$), 80398-98-7; (*E,E*)-5 (R_1, R_2 = H; R_3 = Me_3Si), 80398-99-8; (*E,Z*)-5 (R_1, R_2 = H; R_3 = Me_3Si), 80399-00-4; (*E,E*)-5 (R_1 = CH_3; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80409-31-0; (*E,Z*)-5 (R_1 = CH_3; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80409-32-1; (*E,E*)-5 (R_1 = CH_3; R_2 = H; R_3 = Me_3Si), 80399-01-5; (*E,Z*)-5 (R_1 = CH_3; R_2 = H; R_3 = Me_3Si), 80399-02-6; (*E,E*)-5 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80399-03-7; (*E,Z*)-5 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80399-04-8; (*E,E*)-5 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = Me_3Si), 80409-33-2; (*E,Z*)-5 (R_1 = $CH_3(CH_2)_2$; R_2 = H; R_3 = Me_3Si), 80399-05-9; (*E,E*)-5 (R_1 = $CH_3(CH_2)_3$; R_2 = H; R_3 = Me_3Si), 80399-06-0; (*E,Z*)-5 (R_1 = $CH_3(CH_2)_3$; R_2 = H; R_3 = Me_3Si), 80399-07-1; (*E,E*)-5 (R_1 = Ph; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80399-08-2; (*E,Z*)-5 (R_1 = Ph; R_2 = H; R_3 = *t*-$BuMe_2Si$), 80399-09-3; (*E,E*)-5 (R_1 = Ph; R_2 = H; R_3 = Me_3Si), 80399-10-6; (*E,Z*)-5 (R_1 = Ph; R_2 = H; R_3 = Me_3Si), 80399-11-7; (*E,E*)-5 (R_1, R_2 = CH_3; R_3 = *t*-$BuMe_2Si$), 80399-12-8; (*E,Z*)-5 (R_1, R_2 = CH_3; R_3 = *t*-$BuMe_2Si$), 80399-13-9; (*E,E*)-5 (R_1 = H; R_2 = $(CH_2)_2CO_2Et$; R_3 = *t*-$BuMe_2Si$), 80399-14-0; (*E,Z*)-5 (R_1 = H; R_2 = $(CH_2)_2CO_2Et$; R_3 = *t*-$BuMe_2Si$), 80399-15-1; 7, 80399-16-2; (*E*)-2-[3-[2-(trimethylsilyl)oxymethyl]-1-thiophenylcyclopropyl]-2-propenyl]-2-methyl-1,3-dioxolane, 80399-17-3; (*X*,-*E*)-2-[7-[(trimethylsilyl)oxy]-4-thiophenyl-3,6-heptadienyl]-2-methyl-1,3-dioxolane, 80399-18-4; (*E*)-1,1,8,8-tetramethoxy-4-thiophenyl-4-nonene, 80399-19-5.

Supplementary Material Available: Spectral and analytical characterization for selected compounds (3 pages). Ordering information is given on any current masthead.

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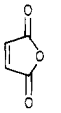
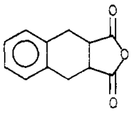
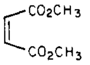
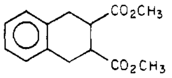
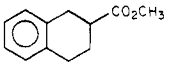
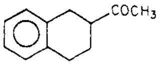
Organic Sonochemistry. Ultrasound-Promoted Reaction of Zinc with α,α′-Dibromo-*o*-xylene. Evidence for Facile Generation of *o*-Xylylene

Summary: α,α′-Dibromo-*o*-xylene and zinc powder react smoothly in the presence of dienophiles and sonic waves to give high yields of cycloaddition products. The reaction is believed to proceed via the reactive intermediate, *o*-xylylene.

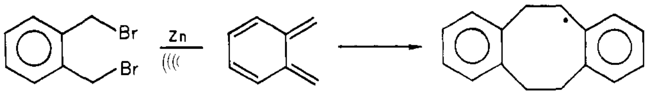
Sir: The effects of ultrasounds on the rates of chemical reactions have been of general interest.[1] In most cases, modest rate enhancements[2] have been the major benefit from using sonic waves although the number of examples of synthetically useful applications is increasing. Recent communications describing an improved modification of the Barbier reaction,[3] a facile reduction of α,α′-dibromo ketones,[4] coupling of organic[5] and organometallic[6] halides, and a new procedure for making thioamides[7] indicate considerable potential for ultrasound in synthesis. We have extended our investigations to organic dihalides and in this communication we report preliminary results of our studies of ultrasonically induced reactions of zinc powder with α,α′-dibromo-*o*-xylene (1).

Table I. Ultrasound-Induced Reaction of Zinc and α,α′-Dibromo-*o*-xylene in the Presence of Dienophiles

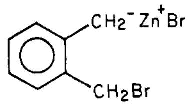
dienophile	time, h	product	isolated yield, %
	15		89
	12		70
$CH_2{=}CHCO_2CH_3$	12		67
$CH_2{=}CHCOCH_3$	12		87

We have found that ultrasound accelerates the reaction between zinc and 1 in dioxane, forming high yields of cycloaddition products when dienophiles are present in the reaction mixture. These results are summarized in Table I. No reaction occurs in the absence of ultrasound.

When a dioxane solution of 1 is treated with zinc and ultrasound in the absence of a reactive species, all of 1 is consumed, giving mostly polymer and small quantities (<5% by NMR) of bibenzo[*a*,*e*]-6,7,11,12-tetrahydrocyclooctadiene (3). These observations are consistent with the formation of *o*-xylylene (2) as an important intermediate in these reactions. Attempts to trap an ionic intermediate like 4 with trimethylchlorosilane were unsuccessful. However, some 3 was detected by NMR.



1 2 3



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In a typical experiment, 10 mmol of 1, 11 mmol of dienophile, and 23 mmol of activated zinc[8] were added to 10 mL of peroxide-free dioxane freshly distilled from KOH. The reaction mixture, contained in a 25-mL, round-bottom, single-neck flask under an atmosphere of nitrogen, was partly submerged in a common ultrasound laboratory cleaner (117 V, 150 W, 50/60 Hz). Bath temperatures were maintained at 20–25 °C by using a cooling coil.

Product isolation was straightforward: filtration of the crude product mixture to remove zinc bromide and excess

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