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$_2$Si), 80398-86-3; 4 (R_1, R_2 = H; R_3 = Me$_3$Si), 80398-87-4; 4 (R_1 = CH$_3$; R_2 = H; R_3 = t-BuMe$_2$Si), 80398-88-5; 4 (R_1 = CH$_3$; R_2 = H; R_3 = Me$_3$Si), 80398-89-6; 4 (R_1, R_2 = CH$_3$; R_3 = t-BuMe$_2$Si), 80398-90-9; 4 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = t-BuMe$_2$Si), 80398-91-0; 4 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = Me$_3$Si), 80398-92-1; 4 (R_1 = CH$_3$(CH$_2$)$_3$; R_2 = H; R_3 = Me$_3$Si), 80398-93-2; 4 (R_1 = Ph; R_2 = H; R_3 = t-BuMe$_2$Si), 80398-94-3; 4 (R_1 = Ph; R_2 = H; R_3 = Me$_3$Si), 80398-95-4; 4 (R_1 = H; R_2 = (CH$_2$)$_2$CO$_2$Et; R_3 = t-BuMe$_2$Si), 80398-96-5; (*E,E*)-5 (R_1, R_2 = H; R_3 = t-BuMe$_2$Si), 80398-97-6; (*E,Z*)-5 (R_1, R_2 = H; R_3 = t-BuMe$_2$Si), 80398-98-7; (*E,E*)-5 (R_1, R_2 = H; R_3 = Me$_3$Si), 80398-99-8; (*E,Z*)-5 (R_1, R_2 = H; R_3 = Me$_3$Si), 80399-00-4; (*E,E*)-5 (R_1 = CH$_3$; R_2 = H; R_3 = t-BuMe$_2$Si), 80409-31-0; (*E,Z*)-5 (R_1 = CH$_3$; R_2 = H; R_3 = t-BuMe$_2$Si), 80409-32-1; (*E,E*)-5 (R_1 = CH$_3$; R_2 = H; R_3 = Me$_3$Si), 80399-01-5; (*E,Z*)-5 (R_1 = CH$_3$; R_2 = H; R_3 = Me$_3$Si), 80399-02-6; (*E,E*)-5 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = t-BuMe$_2$Si), 80399-03-7; (*E,Z*)-5 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = t-BuMe$_2$Si), 80399-04-8; (*E,E*)-5 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = Me$_3$Si), 80409-33-2; (*E,Z*)-5 (R_1 = CH$_3$(CH$_2$)$_2$; R_2 = H; R_3 = Me$_3$Si), 80399-05-9; (*E,E*)-5 (R_1 = CH$_3$(CH$_2$)$_3$; R_2 = H; R_3 = Me$_3$Si), 80399-06-0; (*E,Z*)-5 (R_1 = CH$_3$(CH$_2$)$_3$; R_2 = H; R_3 = Me$_3$Si), 80399-07-1; (*E,E*)-5 (R_1 = Ph; R_2 = H; R_3 = t-BuMe$_2$Si), 80399-08-2; (*E,Z*)-5 (R_1 = Ph; R_2 = H; R_3 = t-BuMe$_2$Si), 80399-09-3; (*E,E*)-5 (R_1 = Ph; R_2 = H; R_3 = Me$_3$Si), 80399-10-6; (*E,Z*)-5 (R_1 = Ph; R_2 = H; R_3 = Me$_3$Si), 80399-11-7; (*E,E*)-5 (R_1, R_2 = CH$_3$; R_3 = t-BuMe$_2$Si), 80399-12-8; (*E,Z*)-5 (R_1, R_2 = CH$_3$; R_3 = t-BuMe$_2$Si), 80399-13-9; (*E,E*)-5 (R_1 = H; R_2 = (CH$_2$)$_2$CO$_2$Et; R_3 = t-BuMe$_2$Si), 80399-14-0; (*E,Z*)-5 (R_1 = H; R_2 = (CH$_2$)$_2$CO$_2$Et; R_3 = t-BuMe$_2$Si), 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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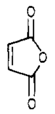
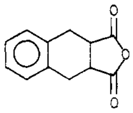
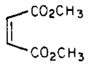
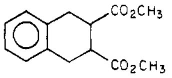
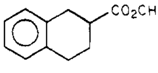
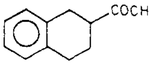
Organic Sonochemistry. Ultrasound-Promoted Reaction of Zinc with α,α′-Dibromo-*o*-xylene. Evidence for Facile Generation of *o*-Xylylene

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.

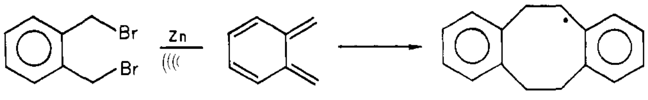
Sir: The effects of ultrasounds on the rates of chemical reactions have been of general interest.[1] In most cases, modest rate enhancements[2] have been the major benefit from using sonic waves although the number of examples of synthetically useful applications is increasing. Recent communications 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$_2$CH$_3$	12		67
CH_2=CHCOCH$_3$	12		87

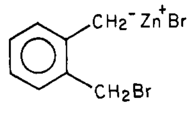
We have found that ultrasound accelerates the reaction between zinc and 1 in dioxane, forming high yields of cycloaddition products when dienophiles are present in the reaction mixture. These results are summarized in Table I. No reaction occurs in the absence of ultrasound.

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



1 2 3

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.



4

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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zinc, addition of the filtrate to 20 mL of saturated aqueous ammonium chloride, extraction with methylene chloride and chromatography of the dried solution ($CaCl_2$) on a short neutral alumina column, using methylene chloride as eluant. Chromatography was not necessary for the maleic anhydride adduct. Evaporation of CH_2Cl_2 after extraction gave an analytically pure sample. The other adducts were >95% pure (by NMR and GC) following chromatography. Our yields are based on quantities obtained after this step. Analytically pure samples were obtained by preparative gas chromatography. Structural assignments are based on NMR, IR, and mass spectral data and elemental analyses. The cis configuration of the product from the reaction of dimethyl maleate was assigned because it was the only product from that reaction and it was different from the single product obtained when dimethyl fumarate was used as the dienophile.

The production of **2** is strongly implied by these observations and, if so, ultrasound provides a convenient low-temperature route to this intermediate. That **1** is commercially available and inexpensive makes this procedure very attractive. Typically **2** is generated in synthetically useful quantities at high temperatures from intermediates requiring one or two synthetic steps.[9] Work is now in progress to broaden the scope of the reactions of **2** as well as to apply this technique to vicinal and geminal dihalides.

Acknowledgment. Fruitful discussions with Clayton H. Heathcock are gratefully acknowledged. We also thank the Air Force Office of Scientific Research for financial support through Grant No. AFOSR-80-0239.

Registry No. 1, 91-13-4; 2, 32796-95-5; 3, 1460-59-9; 2,5-furandione, 108-31-6; dimethyl (*Z*)-2-butenedioate, 624-48-6; methyl 2-propenoate, 96-33-3; 3-buten-2-one, 78-94-4; 3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione, 29811-05-0; dimethyl *cis*-1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylate, 80399-27-5; methyl 1,2,3,4-tetrahydro-2-naphthalenecarboxylate, 39246-30-5; 2-acetyl-1,2,3,4-tetrahydronaphthalene, 35060-50-5; zinc, 7440-66-6.

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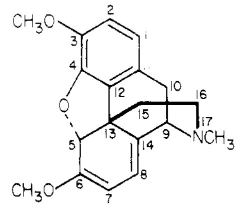
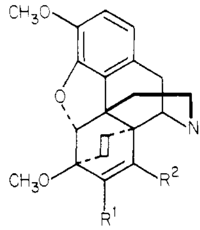
Thebaine and Acetylenic Dienophiles

Summary: Reaction of thebaine (**1**) with methyl propiolate (MP) in methanol gave the ketal **8** accompanied by the adduct **5**. Treatment of **8** with 1.5 equiv of a strong acid converted it to **5**. Larger amounts of acid gave the ketone **7**, whose structure was established by single-crystal X-ray structure determination. Prolonged hydrolysis of **8** with base gave the amine **9**, which when treated with MP gave the ketal **10** isomeric with **8**. The adduct **11** was obtained when **1** was treated with dimethyl acetylenedicarboxylate in methanol.

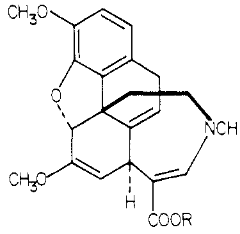
Sir: Rapoport and Sheldrick[1] reported that heating thebaine (**1**) and dimethyl acetylenedicarboxylate (DMAD) in benzene at 50 °C for 1 h gave the expected adduct **2** in 90% yield, but that under comparable conditions ethyl propiolate (EP) afforded **3** in only 6% yield. . In connection with our efforts to obtain opioids of biological interest from thebaine,[2] we had occasion to reexamine the reaction of **1** with acetylenic dienophiles. While our work was in progress, Hayakawa et al.[3] published a preliminary communication describing results of a similar study. They found, inter alia, that **1** and ethyl propiolate (EP) reacted at room temperature in acetonitrile to give the adduct **4** and that methyl propiolate (MP) furnished the corresponding methyl ester **5** in excellent yields. Mild acid hydrolysis of **4** and **5** gave the ketones **6** and **7**, respectively. The structural assignments were made primarily on the basis of spectroscopic data. We prepared **7** by a somewhat different route and established the structure by means of a single-crystal X-ray structure determination.[4] The structure and molecular geometry of **7** are shown in Figure 1.



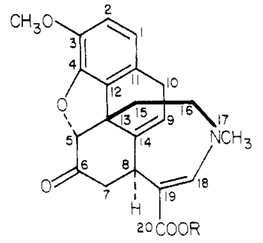
1



2, $R^1 = R^2 = COOCH_3$
3, $R^1 = COOC_2H_5$;
$R^2 = H$



4, $R = C_2H_5$
5, $R = CH_3$



6, $R = C_2H_5$
7, $R = CH_3$

Some of our observations differ substantially from those of Hayakawa et al.[3] For example, these investigators

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[1] H. Rapoport and P. Sheldrick, *J. Am. Chem. Soc.*, **85**, 1636 (1963).

[2] J. M. Bidlack, L. G. Abood, P. Osei-Gyimah, and S. Archer, *Proc. Natl. Acad. Sci.* U.S.A., **78**, 636 (1981).

[3] K. Hayakawa, S. Motohiro, I. Fujii, and K. Kanematsu, *J. Am. Chem. Soc.*, **103**, 4605 (1981). These investigators report that **5** melts at 160–162 °C and **7** at 231–233 °C.

[4] Crystal of **7** are orthorhombic with space group $P2_12_12_1$, $Z = 4$. The unit cell parameters are as follows: $a = 10.440$ (6) Å, $b = 11.915$ (4) Å, $c = 13.352$ (7) Å, $V = 1910$ (1) $Å^3$. The calculated density is 1.334 g/cm^3. Data were collected on a Syntex P2 diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) in the $\theta/2\theta$ mode to a maximum 2θ of 115°. Of the 1509 symmetry independent reflections measured, 1423 (94.3%) were considered observed at $I \geq 3\sigma(I)$. Data reduction, least-squares refinement procedures, and various electron density syntheses were calculated with the XRAY system (J. M. Stewart, G. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, (1972). "The Xray system", June 1972 version Tech. Rep. TR-192, Computer Science Center, University of Maryland, College Park, MD) Initial phasing was performed by MULTAN 78 (P. Main, S. E. Huss, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, "MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data", Universities of York, England, and Louvain, Belgium, 1978). The trial set with the highest combined figure of merit indicated 24 correct atomic positions of the 28 nonhydrogen atoms. After refining the positional coordinates and isotropic temperature factors of this trial structure with full-matrix least-squares analyses, the remaining four atoms were found with a difference electron density synthesis. The final refinement, using anisotropic temperature factors for all nonhydrogen atoms, gave a residual index of 0.075. Crystallographic tables with atomic positional coordinates, temperature factors, bond distances, and angles and a list of observed and calculated structure factors can be obtained from J.H.