compound **17**, which crystallized from *N,N*-dimethylformamide: mp 338–340 °C; 40 mg, 8%; NMR δ 7.48 (m, 4 H), 7.68 (m, 4 H), 7.88 (m, 3 H), 8.04 (s, 1 H), 8.48 (s, 1 H); $UV_{max}^{CHCl_3}$ 315 (log ϵ 5.26), 330 (4.91), 340 (4.59), 365 (4.12), 362 (4.13), 384 (4.15), 408 (4.11), 432 (4.31) nm; *m/e* (relative intensity) 458 (50), 460 (100), 462 (50), 379 (5), 381 (5), 302 (5), 301 (26), 300 (84), 298 (34), 232 (8.6), 230 (17.2), 229 (8.6), 148 (9), 148.5 (5), 149 (26), 149.5 (8.6), 150 (43), 150.5 (9).

Anal. Calcd for $C_{24}H_{12}Br_2$: C, 62.60; H, 2.65; Br, 34.75. Found: C, 62.42; H, 27.74; Br, 34.44.

Reaction of 2,3-Bis(dibromomethyl)naphthalene (21) with 1,3-Diphenylisobenzofuran and Potassium *tert*-Butoxide. A solution of the tetrabromide **21** (1.69 g) and 1,3-diphenylisobenzofuran (0.97 g) in tetrahydrofuran (45 mL) was added to 150 mL of a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (1 M, 150 mL). After 4 days of stirring at room temperature under nitrogen, the mixture was diluted with water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and was evaporated to dryness. The residue was purified by silica preparative layer chromatography, developing with cyclohexane–benzene (4:1). The product **19**, obtained in 32% yield (666 mg), crystallized from benzene–ethanol as white needles, mp 254.5–255.5 °C.

Anal. Calcd for $C_{32}H_{20}Br_2O$: C, 66.32; H, 3.47; Br, 27.56. Found: C, 66.37; H, 3.47; Br 27.60.

Reduction of Adduct (19). To a solution of adduct **19** (89 mg) in benzene (3 mL) and absolute alcohol (3 mL) was added 5% palladium/carbon (150 mg) and hydrazine hydrate (99%, 8 mL). After 3 h of refluxing, the reaction mixture was filtered. Benzene was added to the filtrate and the solution was washed with water. The benzene layer was separated, dried over magnesium sulfate, and evaporated. The residue crystallized from benzene and hexane to give the debrominated adduct **22** (46.4 mg, 80%), mp 198.5–200 °C; the melting point was undepressed on admixture with the endo adduct (**22**) of naphtho[*b*]cyclobutadiene (**3**) and 1,3-diphenylisobenzofuran.

Debromination of 1,1,2,2-Tetrabromonaphtho[*b*]cyclobutene (4) with Zinc in the Presence of 1,3-Diphenylisobenzofuran. To 1,1,2,2-tetrabromonaphtho[*b*]cyclobutene (**4**, 468 mg) and 1,3-diphenylisobenzofuran (**42**, 412 mg) in 40 mL of benzene was added activated zinc dust (2 g). The mixture was refluxed with stirring for 6 h and filtered. The filtrate was evaporated to dryness, giving an oily yellow residue which was purified by preparative layer chromatography on alumina (NI), developing with cyclohexane. Crystallization from benzene–hexane gave golden yellow needles of 5,12-diphenyldibenzo[*b,h*]biphenylene (**20**, 250 mg, 62%), mp 225–226 °C; the melting point was undepressed on admixture with material obtained by dehydration of the adducts of naphtho[*b*]cyclobutadiene and 1,3-diphenylisobenzofuran. NMR and infrared spectral data also showed both samples to be identical.

Acknowledgment. We thank the National Science Foundation for a grant in support of this research.

Registry No. **1**, 6827-31-2; **3**, 277-98-5; **4**, 71382-94-0; **5**, 41634-34-8; **6**, 2169-87-1; **7**, 7149-49-7; **10a**, 71382-95-1; **10b**, 71382-96-2; **11**, 71382-97-3; **12**, 71382-98-4; **13**, 71382-99-5; **17**, 71383-00-1; **19**, 71411-05-7; **20**, 38998-31-1; **21**, 71383-01-2; **22**, 38998-28-6; **42**, 5471-63-6; methyl bromide, 74-83-9.

Enones with Strained Double Bonds. 3. Cycloadducts from Bicyclo[3.3.1]non-1-en-3-one[1]

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Reaction of the bicyclic bromo ketone **2b** with triethylamine yields the bridgehead enone **1** which is rapidly trapped by any nucleophile present in the reaction solution. In the absence of competing nucleophiles, the enone **1** is trapped by a slower reaction with furan to form the Diels–Alder adducts **9** and **10**. If the reaction solution contains neither nucleophiles nor furan, the enone **1** undergoes a 2 + 2 cycloaddition reaction with itself to form the symmetrical dimers **14**, **15**, and **16**. These same dimers are produced in approximately the same proportions when the enone **1** is generated by a retro-Diels–Alder reaction of the adducts **9** and **10** in a pyrolysis tube.

Our initial efforts to prepare the bridgehead enone **1** (Scheme I) involved either dehydrochlorination[2] of the chloro ketone **2a** with a base or the thermal decomposition of a related structure **2** (X = S(O)Ph, Se(O)Ph, OAc). In each of these cases, we were unsuccessful either in isolating the enone **1** or in generating a sufficient concentration of the enone **1** so that it could be trapped in a cycloaddition reaction. In the high-temperature thermal decompositions, rearranged products derived from the enone were isolated. In all other cases, products resulting from the conjugate addition of some nucleophile to the enone were formed. It seemed likely that the use of relatively weak, sterically hindered bases (e.g., tertiary amines) in inert solvents might allow significant concentrations of the enone **1** to exist. Although the previously studied β-chloro ketone **2a** failed to react with various tertiary amine bases,[2] we have now found that the known[2a,3] β-bromo ketone **2b** is satisfactorily dehydrobrominated by various tertiary amines. This paper describes the reactions of the enone **1** generated in solution by this procedure.

The previously described[2-4] ketol **2c** served as the starting material for our studies. Although reaction of this ketol **2c** with PBr_3 had been reported[3] to form a very unstable bromo ketone **2b**, we have independently prepared[2a] and characterized the bromo ketone **2b** and found it to be stable in the absence of impurities (especially acids). Consequently, the bromo ketone **2b** was readily obtained as a stable crystalline solid by reaction of the ketol **2c** with PBr_3 with suitable precautions to remove acidic impurities. Reaction of the bromo ketone **2b** with the amidine **3** (DBU) in PhH, a nonnucleophilic solvent,

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(1) This research has been supported by Public Health Service Grant R01-GM-20197 from the National Institute of General Medical Science. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

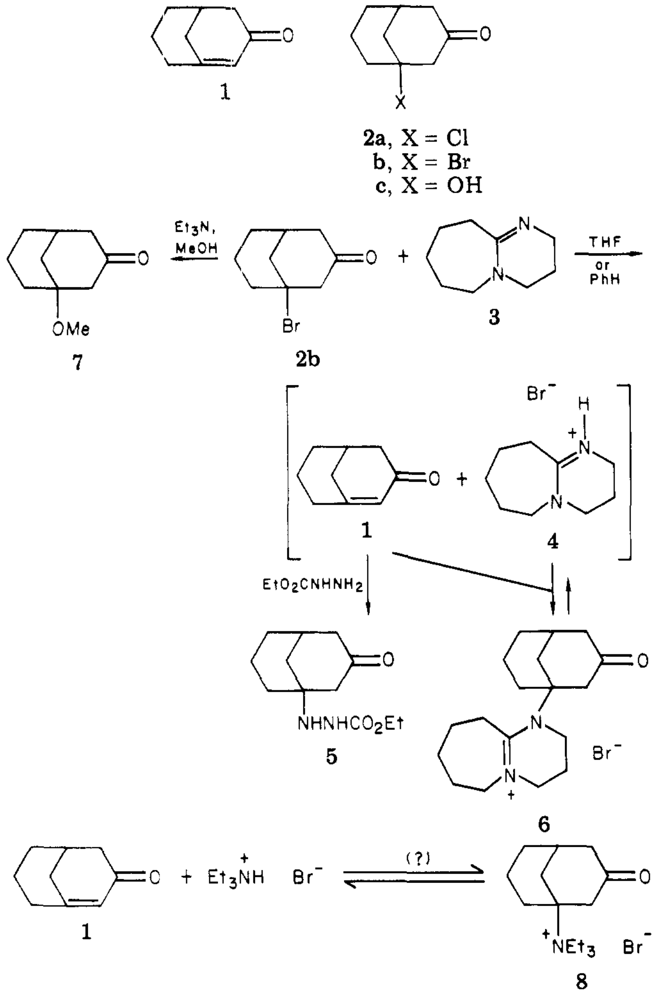
(2) (a) H. O. House, W. A. Kleschick, and E. J. Zaiko, *J. Org. Chem.*, 43, 3653 (1978); (b) H. O. House and T. V. Lee, *ibid.*, 44, 2819 (1979).

(3) T. Momose and O. Muraoka, *Chem. Pharm. Bull.*, 26, 288 (1978).

(4) W. D. K. Macrosson, J. Martin, W. Parker, and A. B. Penrose, *J. Chem. Soc. C*, 2323 (1968).

0022-3263/79/1944-3793$01.00/0

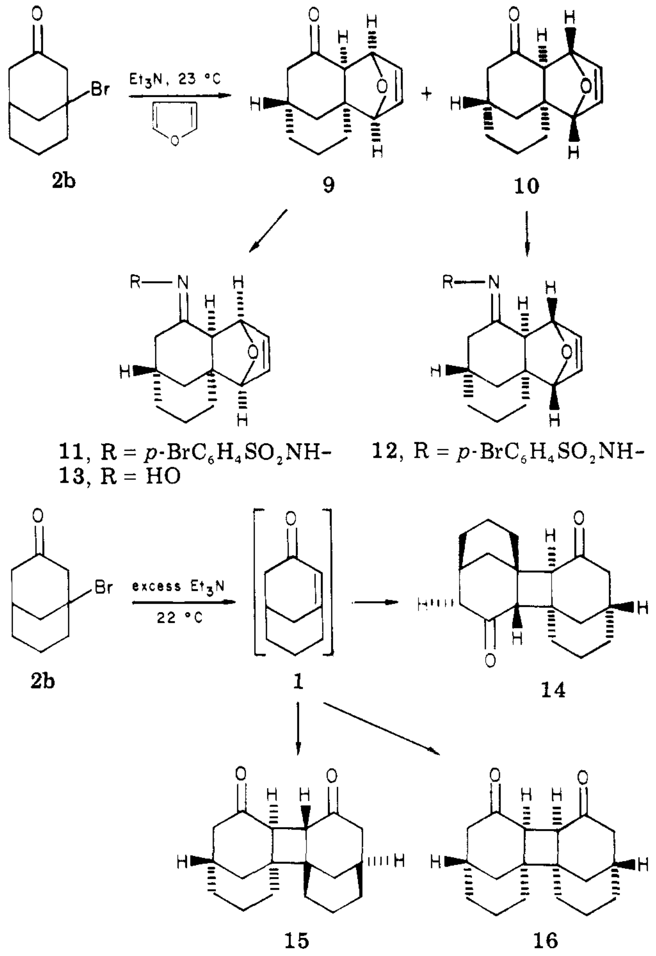
Scheme I



produced a mixture of salts believed to be **4** and **6** from which we were unsuccessful in isolating a pure sample of the adduct **6**. A similar mixture of salts was obtained on reaction of the bromo ketone **2b** with the related amidine 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in benzene solution. When the bromo ketone **2b** was treated with the amidine **3** in THF solution with EtO_2CNHNH_2 present as a nucleophile, the hydrazide **5** was isolated in 84% yield. Similarly, reaction of the bromo ketone with Et_3N in MeOH solution formed the methoxy ketone **7** in 85% yield. This same methoxy ketone **7** was formed by heating the crude crystalline salt mixture containing **6** with MeOH. The use of Et_3N as a base for dehydrobromination of the bromo ketone **2b** was experimentally simpler than use of one of the amidine bases DBN or DBU. Consequently, we have used Et_3N as the base in all of our subsequent studies.

Our present data do not allow us to decide whether the enone **1**, generated from Et_3N and the bromo ketone **2b**, is present in equilibrium with the Et_3N adduct **8**. However, the presence of the free enone **1** in these solutions could be demonstrated by carrying out the dehydrobromination of the bromo ketone **2b** with Et_3N in excess furan (Scheme II). This reaction yielded a mixture of two diastereoisomeric Diels–Alder adducts **9** (major) and **10** (minor). This result can be contrasted with earlier experiments[2,5] in which the chloro ketone **2a** was treated with metal alkoxide bases in excess furan (or other dienes) to form only the conjugate adducts of the enone **1**. These results indicate that although the enone **1** is a relatively reactive dienophile, it is far more reactive as an acceptor in Michael reactions.

Scheme II



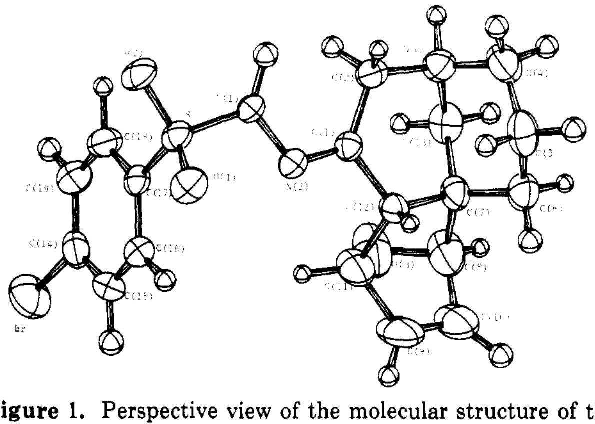


Figure 1. Perspective view of the molecular structure of the *p*-bromophenylsulfonylhydrazone **11**. (For clarity, the H atom thermal parameters have been reduced.)

Although a pure sample of the minor furan adduct **10** could be separated by liquid chromatography, we obtained a sample of the major adduct by isolation of the crystalline oxime **13** and subsequent hydrolysis to yield the pure adduct **9**. The structure and stereochemistry of each adduct **9** or **10** were established by converting each adduct to its *p*-bromophenylsulfonylhydrazone **11** or **12** for X-ray crystallographic analysis. The structure of the sulfonylhydrazone **11** is presented in Figure 1. Figure 2 presents the structure of sulfonylhydrazone **12**.

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(5) For examples of the formation of furan adducts from other strained olefins, see (a) H. Hart and E. Dunkelblum, *J. Am. Chem. Soc.*, **100**, 5141 (1978); (b) E. Stamm, L. Walder, and R. Keese, *Helv. Chim. Acta*, **61**, 1545 (1978).

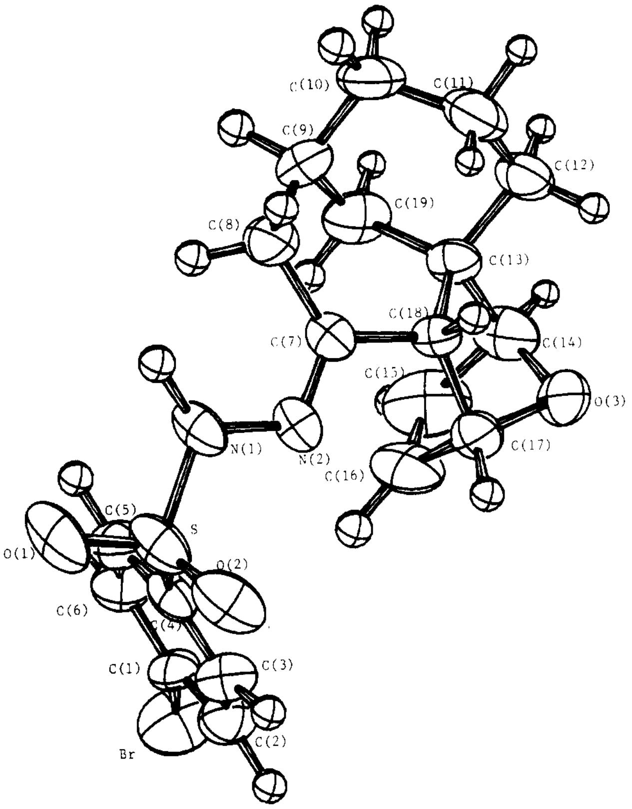


Figure 2. Perspective view of the molecular structure of the *p*-bromophenylsulfonylhydrazone **12**. (For clarity, the H atom thermal parameters have been reduced.)

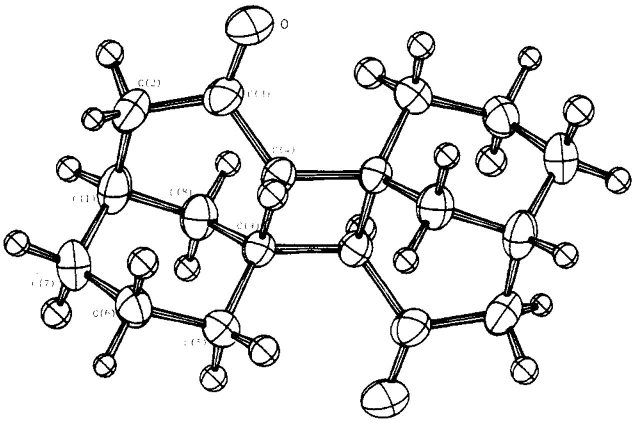


Figure 3. Perspective view of the molecular structure of the dimer **14**. (For clarity, the H atom thermal parameters have been reduced.)

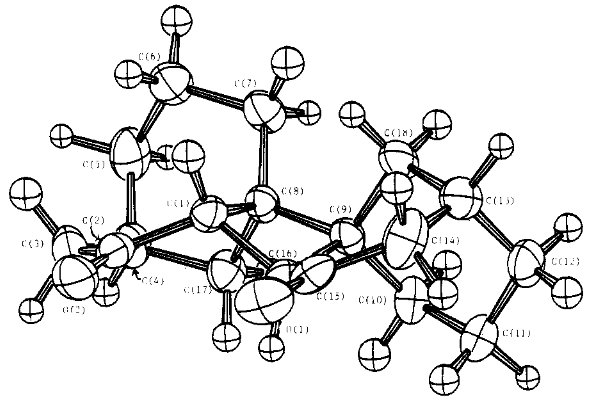


Figure 4. Perspective view of the molecular structure of dimer **15**. (For clarity, the H atom thermal parameters have been reduced.)

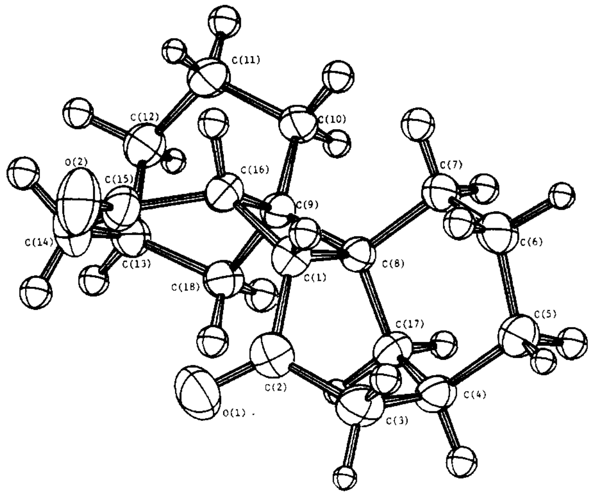
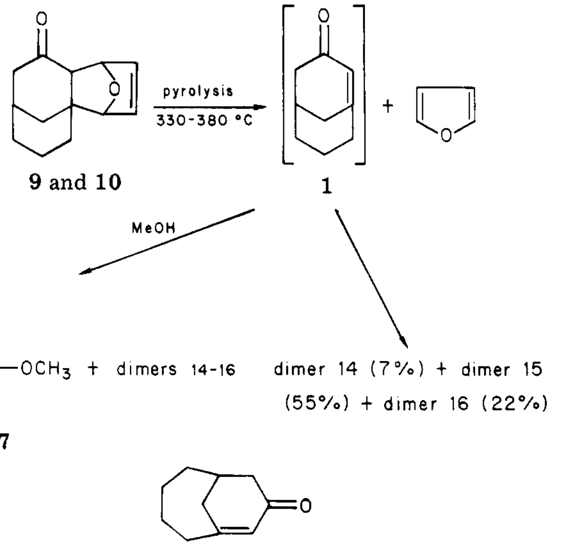


Figure 5. Perspective view of the molecular structure of dimer **16**. (For clarity, the H atom thermal parameters have been reduced.)

Scheme III



Since this experiment in furan demonstrated the formation of solutions containing the desired enone **1**, the dehydrobromination was repeated in the absence of furan, employing excess Et_3N as both the base and the reaction solvent. This experiment formed a mixture of at least three products that proved to be dimers **14** (5% yield), **15** (57% yield), and **16** (18% yield) of the desired enone **1**.[6] The structure and stereochemistry of each crystalline dimer were established by X-ray crystallographic analysis. Figure 3 illustrates the structure of dimer **14**. The structure of dimer **15** is presented in Figure 4, and the structure of dimer **16** is given in Figure 5. In keeping with the symmetry of these structures, the ^{13}C NMR spectrum of each dimer exhibits only 9 signals or less.

The foregoing experiments involve sets of competitive reactions that indicate the relative rates of various reactions with the enone **1** to lie in the following order: conjugate addition of nucleophiles > 2 + 4 cycloaddition

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(6) For examples of the dimerization of olefins with strained double bonds, see (a) K. B. Becker and J. L. Chappins, *Helv. Chim. Acta*, **62**, 34 (1979); (b) R. G. Salomon, K. Falting, W. E. Strieb, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 1145 (1974); (c) P. E. Eaton, G. D. Andrews, E. P. Krebs, and A. Kunai, *J. Org. Chem.*, **44**, 2824 (1979).

of the enone 1 to furan > 2 + 2 cycloaddition of the enone 1 to itself. When a similar dehydrobromination experiment was performed by stirring the bromo ketone **2b** with several equivalents of Et_3N in excess cyclohexene, the bromo ketone **2b** was very slowly dehydrohalogenated to form a comparable mixture of dimers **14–16**. We found no evidence to indicate the formation of a cycloadduct involving the enone **1** and cyclohexene.

We expected the pyrolyses of the furan adducts **9** and **10** (Scheme III) also to serve as a method for the generation of the enone 1.[7] This transformation was readily accomplished by passing a gas stream containing a mixture of the adducts **9** and **10** and N_2 through a glass tube packed with glass beads and heated with an oven at 330–380 °C. The major products were approximately the same mixture of dimers **14–16** as had been obtained from dehydrohalogenation of the bromo ketone **2b** with Et_3N. Thus, the formation of the dimers **14–16** does not require the presence of a base such as Et_3N. We attempted to intercept the monomeric enone **1** by passing the gas stream leaving the pyrolysis tube into a trap containing MeOH (with or without added Et_3N). Although a small amount (ca. 4%) of the appropriate methoxy ether adduct **7** was isolated in one experiment, it was apparent that most of the enone **1** had already dimerized before the gas stream reached the trap containing MeOH. We cannot presently exclude the possibility that the retro-Diels–Alder reaction, **9** or **10** → **1**, and the subsequent dimerization, **1** → **14–16**, both occurred on the heated glass surface within the pyrolysis tube. We are continuing to explore the pyrolysis reaction in an effort to find conditions that will allow us to collect the monomeric enone **1** on a suitable cold surface.

It will be noted that both the 2 + 4 cycloaddition of furan to the enone **1** to form adducts **9** and **10** and the 2 + 2 cycloaddition reactions of the enone **1** with itself to form dimers **14–16** appear to involve additions to each enone carbon–carbon double bond in a suprafacial manner. Although this stereochemical result is to be expected for concerted, thermal 2 + 4 cycloaddition, it is not the predicted stereochemical outcome of concerted, thermal 2 + 2 cycloadditions.[8] Rather, a thermally allowed concerted dimerization of the enone **1** is predicted to occur with suprafacial addition to one carbon–carbon double bond and antarafacial addition to the other double bond (i.e., ${}_{\pi}2_s + {}_{\pi}2_a$ cycloaddition). Clearly, none of the 2 + 2 cycloaddition products **14–16** we have isolated possess this stereochemistry. Until we have obtained one or more of the predicted unsymmetrical cycloadducts, it will be difficult to provide a rigorous test of the possibility that the dimers isolated are the result of epimerization of initial products prior to isolation. However, we have no evidence at present to suggest that such epimerization has occurred. If this presumption is correct, then we are forced to conclude either that the dimers **14–16** are not formed by concerted cycloaddition or that the considerations upon which the above predictions are based do not apply to the cycloadditions we have observed.

We also wish to call attention to the remarkable difference in the thermal stability of the enone **1** and its next higher homologue **17**. Although the enone **1** has undergone either dimerization or some other more rapid reaction under any condition where we have successfully generated it, the homologous enone **17** was found to be stable for prolonged periods of time even at 190 °C.[2b] We suspect that this difference in reactivity is attributable to differences in the extent to which substituents at the carbon–carbon double bond are deformed from the plane of the olefinic double bond and hope to provide evidence on this point with investigations in progress.

Experimental Section[9]

Preparation of the Ketol 2c. Following a slight modification of several previously described procedures,[2-4] we treated a solution of NaOMe, from 5.40 g (234 mmol) of Na and 250 mL of MeOH, successively with 31.8 g (236 mmol) of $CH_3COCH_2CO_2Et$ and with 21.4 g (223 mmol) of cyclohexenone. After the resulting solution had been refluxed for 35 h, it was concentrated, neutralized with 100 mL of aqueous 4 M HCl, and partitioned between CH_2Cl_2 and aqueous NaCl. The organic phase (containing the crude β-keto ester, IR and NMR analysis) was concentrated under reduced pressure (110 °C at 0.1 mm) to remove low-boiling components and then dissolved in a mixture of 17.4 g (233 mmol) of KOH, 200 mL of EtOH, and 200 mL of H_2O. After the resulting solution had been refluxed for 15 h, it was concentrated under reduced pressure and extracted with CH_2Cl_2. The organic extract was washed successively with aqueous NaCl and with H_2O and then dried and concentrated to leave 28.6 g of the crude ketol **2c** as a brown liquid. Repeated recrystallization from Et_2O (EtOH free) separated 24.1 g (70%) of the ketol **2c** as colorless plates, mp 232–234 °C dec (lit.[2] mp 233–240 °C dec[10]). This product was identified with previously described samples[2,4] by comparison of IR and NMR spectra.

Preparation of Bromo Ketone 2b. Employing a modification of a previously described procedure,[3] we treated a cold (4–5 °C) solution of 15.44 g (100 mmol) of the ketol **2c** in 110 mL of PhH with a solution of 10.37 g (38.3 mmol) of PBr_3 in 20 mL of PhH, and the resulting solution was stirred at 20 °C for 19 h during which time the mixture turned yellow-brown and a second liquid phase separated. The supernatant PhH phase was decanted, and the more dense liquid phase was hydrolyzed with 50 mL of H_2O and then extracted with PhH. After this extract had been washed with H_2O and with aqueous $NaHCO_3$, it was combined with the original PhH layer, and the combined layers were washed successively with H_2O, with aqueous $NaHCO_3$, and with H_2O and then concentrated under reduced pressure. The residual bromo ketone **2b** amounted to 20.75 g (96%) of colorless prisms, mp 82.8–83.8 °C. Recrystallization from PhH afforded the pure bromo ketone **2b**, mp 83.4–84.4 °C (lit.[2] mp 84.5–85.5 °C), that was identified with an earlier sample[2] by comparison of IR and NMR spectra.

Preparation of the Hydrazide 5. To a cold (–65 °C) solution of 215 mg (1.00 mmol) of the bromo ketone **2b** and 595 mg (5.72 mmol) of EtO_2CNHNH_2 in 5 mL of THF was added, dropwise and with stirring, 161 mg (1.05 mmol) of the amidine **3**. The mixture was stirred and allowed to warm to 20 °C over 1 h during which time a precipitate separated. After the mixture had been partitioned between CH_2Cl_2 and aqueous 0.7 M HCl, the organic phase was dried and concentrated. The residual liquid (246 mg) was distilled in a short-path still (160 °C at 0.2 mm) to separate 199 mg (84%) of the hydrazide **5** that crystallized as colorless prisms: mp 71.5–72.8 °C; IR (CCl_4), 1722 (C=O) and 1705 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 6.8–7.0 (1 H, m, NH), 4.14 (2 H, q, J = 7 Hz, ethoxyl CH_2), 3.7–4.0 (1 H, m, NH), 1.1–3.0 [16 H, m,

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[7] For example, the retro-Diels–Alder reaction of a suitable adduct at 450 °C has served as a suitable route to substituted allenes. M. Bertrand, J. L. Gras, and B. S. Galledon, *Tetrahedron Lett.*, 2873 (1978).

[8] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, pp 65–113.

[9] All melting points are corrected, and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The proton NMR spectra were determined at 60 MHz with a Varian Model T-60A NMR spectrometer, and the ^{13}C NMR spectra were determined at 25 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) Model RMU-7 or a Varian MAT Model 112S mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

[10] As noted previously[2] the lower melting point values reported elsewhere (189–191 °C[3] and 192–193 °C[4]) may represent a different crystalline form of the ketol **2c**.

aliphatic CH including an ethoxyl CH_3 triplet (J = 7 Hz) at 1.25]; ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 211.0 (s), 157.7 (s), 61.1 (t), 58.4 (s), 50.3 (t), 45.7 (t), 36.3 (t), 35.7 (t), 31.1 (t), 29.9 (d), 19.1 (t), 14.5 (q) ppm; mass spectrum, *m/e* (rel intensity) 240 (M^+, 18), 197 (19), 137 (19), 109 (31), 104 (40), 95 (100), 93 (58), 81 (21), 67 (64), 55 (40), 53 (24), 41 (62), 39 (26).

Anal. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66. Found: C, 59.81; H, 8.43; N, 11.63.

Reaction of the Keto Bromide 2b with Et_3N in MeOH. A solution of 633 mg (2.92 mmol) of the bromide **2b** and 0.72 g (7.1 mmol) of Et_3N in 8 mL of MeOH was stirred at 22 °C for 3 h at which time none of the starting keto bromide **2b** remained (TLC analysis). After the mixture had been partitioned between CH_2Cl_2 and aqueous 0.05 M HCl, the organic layer was dried, concentrated, and distilled in a short-path still (80 °C at 0.3 mm) to separate 415 mg (85%) of the methoxy ketone **7** as a colorless liquid, $n^{25}{}_D$ 1.4890 (lit.[2] $n^{25}{}_D$ 1.4887), that was identified with the previously described sample by comparison of IR and NMR spectra.

Preparation of the Furan Adducts 9 and 10. A solution of 6.14 g (28.3 mmol) of the bromo ketone **2b** in 20 mL of furan was treated with 7.98 g (79 mmol) of Et_3N. The solution, from which a colorless precipitate began to separate immediately, was stirred at 23 °C for 12 h and then partitioned between H_2O and CH_2Cl_2. After the organic phase had been dried and concentrated, the residual pale yellow liquid was distilled to separate 5.00 g (86%) of a mixture (NMR analysis) of furan adducts **9** (ca. 72% of mixture) and **10** (ca. 28% of mixture) as a colorless liquid, bp 117–120 °C (0.12 mm).

When a sample of this product was mixed with 1-phenylnaphthalene (an internal standard) in EtOAc solution, the following GLC peaks (silicone, No. 710, on Chromosorb W at 194 °C) were observed: adduct **10**, 22.6 min; adduct **9**, 27.1 min; 1-phenylnaphthalene, 37.7 min. Some decomposition of the furan adducts appeared to occur during GLC analysis. An 862-mg aliquot of the adducts was subjected to repeated low-pressure liquid chromatography on silica gel (E. Merck) with an EtOAc–hexane eluent (9:41 v/v) to separate 26.2 mg of a pure sample of the minor adduct **10** as a colorless solid: mp 68–69 °C; IR (CCl_4) 1707 cm^{-1} (C=O); UV max (95% EtOH) 285 nm (ϵ 29) with end absorption (ϵ 377 at 214 nm); mass spectrum, *m/e* (rel intensity) 204 (M^+, 72), 161 (98), 136 (92), 108 (99), 107 (24), 94 (56), 93 (38), 91 (50), 82 (100), 81 (38), 80 (23), 79 (54), 77 (40), 53 (22), 41 (25), 39 (41); ^1H NMR ($CDCl_3$) δ 6.2–6.6 (2 H, m, vinyl CH), 5.12 (1 H, d of d, J = 5.2 and 0.6 Hz, bridgehead CH–O), 4.44 (1 H, d, J = 0.4 Hz, bridgehead CH–O), 2.73 (1 H, d, J = 5.2, CHCO coupled to bridgehead CH–O at 5.12), 0.5–2.7 (11 H, m, aliphatic CH); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 213.4 (s), 134.5 (d, 2 C atoms), 85.5 (d), 79.1 (d), 56.3 (d), 46.1 (s), 44.1 (t), 36.9 (t), 35.3 (t), 31.9 (t), 31.2 (d), 19.8 (t) ppm.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.32; H, 7.94.

A solution of 253 mg (1.00 mmol) of p-$BrC_6H_4SO_2NHNH_2$, 172 mg (0.842 mmol) of the adduct **10**, and 0.05 mL of HOAc in 3.0 mL of EtOH was stirred at 23 °C for 24 h and then concentrated. The sulfonylhydrazone **12** was collected as 323 mg (87%) of colorless rods: mp 162–163 °C; IR ($CHCl_3$) 3310 (NH), 1172 cm^{-1} (SO_2); UV max (95% EtOH) 234 nm (ϵ 12 400), 278 (shoulder, 1500); ^1H NMR ($CDCl_3$) δ 7.6–8.1 (4 H, m, aryl CH), 6.0–6.4 (2 H, m, vinyl CH), 5.08 (1 H, d of d, J = 5.0 and 0.5 Hz, bridgehead CH–O), 4.37 (1 H, br s, bridgehead CH–O), 0.6–3.0 (13 H, m, NH and aliphatic CH); mass spectrum, *m/e* (rel intensity) 438 (M^+, 2), 436 (M^+, 2), 370 (10), 368 (9), 217 (53), 149 (100), 109 (20), 105 (20), 91 (38), 81 (32), 77 (41), 41 (25), 39 (20).

Anal. Calcd for $C_{19}H_{21}BrN_2O_3S$: C, 52.18; H, 4.84; Br, 18.27; N, 6.41; S, 7.33. Found: C, 52.18; H, 4.84; Br, 18.24; N, 6.42; S, 7.30.

Since our efforts to isolate a pure sample of the major adduct **9** by either liquid chromatography or gas chromatography were not successful, fractions enriched in the adduct **9** were converted to crystalline derivatives. A solution of 572 mg (2.28 mmol) of p-$BrC_6H_4SO_2NHNH_2$, 392 mg (1.92 mmol) of the crude adduct **9**, and 0.05 mL of HOAc in 9.8 mL of EtOH was stirred at 25 °C for 3 h. The sulfonylhydrazone derivative **11** separated as 789 mg (94%) of colorless rods: mp 160.5–161.5 °C; IR ($CHCl_3$) 3405 (NH), 1172 cm^{-1} (SO_2); UV max (95% EtOH) 234 nm (ϵ 14 000), 278 (shoulder, 1600); ^1H NMR ($CDCl_3$) δ 7.6–8.1 (4 H, m, aryl CH), 6.3–6.6 (2 H, m, vinyl CH), 5.3 (1 H, d, J = 0.6 Hz, bridgehead CH–O), 4.38 (1 H, d, J = 1 Hz, bridgehead CH–O), 1.3–3.0 (13 H, m, NH and aliphatic CH); mass spectrum, *m/e* (rel intensity) 438 (M^+, 3), 436 (M^+, 3), 370 (5), 368 (6), 218 (27), 217 (100), 200 (25), 157 (29), 155 (30), 149 (100), 147 (56), 145 (65), 117 (31), 108 (32), 93 (36), 91 (62), 81 (85), 79 (45), 77 (78), 76 (37), 75 (40), 41 (30), 39 (62).

Anal. Calcd for $C_{19}H_{21}BrN_2O_3S$: C, 52.18; H, 4.84; Br, 18.27; N, 6.41; S, 7.33. Found: C, 52,21; H, 4.85; Br, 18.25; N, 6.43; S, 7.30.

A solution of 131 mg (0.639 mmol) of the mixture of adducts **9** and **10**, 46.1 mg (0.663 mmol) of $HONH_3Cl$, and 297 mg (2.18 mmol) of $NaOAc \cdot 3H_2O$ in 1 mL of H_2O and 1.8 mL of EtOH was refluxed for 15 min and then cooled and diluted with 2 mL of H_2O. The oxime **13** crystallized as 107 mg (77%) of colorless plates: mp 186–187 °C; IR ($CHCl_3$), 3590, 3350 (OH), 1640 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 6.2–6.6 (2 H, m, vinyl CH), 5.41 (1 H, br s, bridgehead CH–O), 4.68 (1 H, s, OH), 4.41 (1 H, br s, bridgehead CH–O), 3.47 (1 H, d of d, J = 16 and 9 Hz equatorial CH of CH_2CO), 0.9–2.7 (11 H, m, aliphatic CH); mass spectrum, *m/e* (rel intensity) 151 (21), 123 (27), 93 (22), 91 (20), 79 (26), 68 (67), 41 (20), 39 (100); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 158.9 (s), 135.2 (d), 133.0 (d), 85.4 (d), 80.6 (d), 47.5 (d), 42.5 (s), 36.4 (t), 34.7 (t), 32.0 (t), 27.2 (d and t, two C atoms), 20.2 ppm (t)

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 71.14; H, 7.86; N, 6.39.

To a solution of 1.30 g (5.94 mmol) of the oxime **13** in 60 mL of EtOH and 25 mL of aqueous 1 M HCl was added, in five portions during 2 h with constant stirring, 1.06 g (15.3 mmol) of $NaNO_2$.[11] After each portion of $NaNO_2$ had been added, an additional 5-mL portion of aqueous 1 M HCl was also added. The resulting solution was stirred at 25 °C for 3 h and then treated with 2.0 g of urea and finally neutralized by the addition of aqueous 3 M NaOH. After the solution had been concentrated under reduced pressure to a volume of 75 mL, it was extracted with CH_2Cl_2. The organic extract was dried and concentrated, and the residual pale yellow liquid was chromatographed on silica gel with an EtOAc–hexane (3:7 v/v) eluent. The fractions containing the adduct **9** were distilled in a short-path still (120 °C and 0.07 mm) to separate 521 mg (43%) of the pure adduct **9** as a pale yellow liquid, $n^{25}{}_D$ 1.5323; a mixture of the adduct **9** and 1-phenylnaphthalene exhibited the following GLC peaks (silicone DC 710 on Chromosorb W): adduct **9**, retention time 19.0 min; 1-phenylnaphthalene, 25.1 min. The spectral properties of the adduct **9** follow: IR (CCl_4) 1712 cm^{-1} (C=O); UV max (95% EtOH) 285 nm (ϵ 18); ^1H NMR ($CDCl_3$) δ 6.2–6.6 (2 H, m, vinyl CH), 5.33 (1 H, br s, CH–O), 4.42 (1 H, br s, CH–O), 2.1–3.0 (4 H, m, CH and CH_2CO), 0.9–2.0 (8 H, m, CH_2); mass spectrum, *m/e* (rel intensity) 204 (M^+, 34), 161 (48), 136 (41), 108 (79), 94 (25), 82 (100), 79 (25), 41 (23), 39 (33); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonace decouplings) 210.0 (s), 134.1 (d), 132.3 (d), 84.2 (d), 78.1 (d), 54.1 (d), 44.4 (s), 42.7 (t), 36.1 (t), 33.5 (t), 31.4 (t), 28.5 (d), 20.0 ppm (t).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.37; H, 7.98.

Preparation of Dimers 14, 15, and 16. To 16 mL of Et_3N (freshly distilled from $LiAlH_4$) was added 6.08 g (28.0 mmol) of the bromo ketone **2b**. The resulting mixture, from which a colorless precipitate began to separate immediately, was stirred vigorously at 22 °C for 9 h and then partitioned between H_2O and CH_2Cl_2. After the organic solution had been dried and concentrated, the residual solid (4.02 g) was recrystallized from THF to separate 2.18 g (57%) of the dimer **15** as colorless plates: mp 231–232 °C; IR ($CHCl_3$), 1708 cm^{-1} (C=O); UV max (95% EtOH) 295 nm (ϵ 66); ^1H NMR ($CDCl_3$) δ 2.2–3.2 (8 H, m, CH and CH_2CO), 0.9–2.2 (16 H, m, CH_2); mass spectrum *m/e* (rel intensity) 272 (M^+, 38), 229 (34), 216 (22), 131 (20), 119 (21), 117 (23), 108 (21), 107 (21), 106 (21), 105 (42), 93 (35), 91 (83), 82 (20), 81 (29), 79 (61), 77 (54), 67 (40), 65 (29), 55 (57), 54 (25), 53 (40), 43 (22), 41 (100), 39 (55); ^{13}C NMR ($CDCl_3$, multiplicity in

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(11) This procedure for the hydrolysis of oximes has been described by M. L. Wolfrom, L. W. Georges, and S. Soltzberg, *J. Am. Chem. Soc.*, 56, 1794 (1934).

off-resonance decoupling) 213.3 (s), 49.8 (d), 44.6 (s), 43.7 (t), 32.4 (t), 31.9 (t), 30.4 (d), 30.4 (t), and 16.5 (t) ppm.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol wt 272.1776. Found: C, 79.38; H, 8.91; mol wt 272.1808.

An 826-mg aliquot of the mother liquors from separation of the dimer **15** was chromatographed on silica gel with an EtOAc–hexane eluent (3:7 v/v). The fractions containing dimer **14** were recrystallized from Et_2O–hexane to separate 141 mg (5% yield) of the pure dimer **14** as colorless rods, mp 222–224 °C.

The spectral properties of the dimer **14** follow: IR (CCl_4) 1702 cm^{-1} (C=O); UV max (95% EtOH) 298 nm (ϵ 62); ^{1}H NMR ($CDCl_3$) δ 2.1–2.8 (8 H, m, CH and CH_2CO), 1.0–2.1 (16 H, m, CH_2); mass spectrum m/e (rel intensity) 272 (M$^+$, 11), 242 (24), 139 (28), 137 (100), 136 (27), 125 (53), 111 (39), 109 (32), 108 (52), 97 (70), 95 (98), 93 (65), 92 (32), 91 (34), 83 (37), 82 (54), 81 (69), 79 (75), 77 (34), 69 (28), 68 (30), 67 (64), 55 (90), 53 (37), 43 (100), 42 (28), 41 (90), 39 (72); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 212.3 (s), 59.0 (d), 43.9 (t), 42.4 (s), 40.9 (t), 35.0 (t), 31.6 (d), 29.9 (t), 18.2 ppm (t).

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.35; H, 8.90.

Other chromatography fractions containing (TLC) the dimer **16** were combined and recrystallized from an Et_2O–hexane mixture to separate 516 mg (18%) of the crude dimer **16**, mp 135–140 °C. Repeated recrystallization from a CH_2Cl_2–hexane mixture afforded the pure dimer **16** as colorless prisms: mp 149.5–151 °C; IR (CCl_4) 1720 and 1703 cm^{-1} (C=O); UV max (95% EtOH) 283.5 nm (ϵ 68); ^{1}H NMR ($CDCl_3$) δ 3.11 (2 H, s, CHCO), 2.1–2.9 (6 H, m, CH and CH_2CO), 0.9–2.1 (16 H, m, aliphatic CH); mass spectrum, m/e (rel intensity) 272 (M$^+$, 53), 244 (52), 229 (98), 201 (84), 107 (47), 105 (52), 93 (50), 91 (100), 81 (47), 79 (81), 77 (60), 67 (50), 55 (52), 53 (46), 41 (92), 39 (48); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 212.1 (s), 49.9 (d), 46.4 (s), 44.1 (t), 36.1 (4 superimposed signals, 1 d and 3 t), 19.1 (t) ppm.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.87.

When mixtures of the three dimers **14–16** were subjected to TLC analysis on a plate coated with silica gel and eluted with EtOAc–hexane (1:4 v/v), the R_f values were as follows: **14**, 0.75; **15**, 0.20; **16**, 0.42.

Pyrolysis of the Furan Adducts 9 and 10. A 46.1-mg (0.23-mmol) sample of the adducts (76% of **9** and 24% of **10**, NMR analysis) was heated to 115 °C while a stream of N_2 (90 mL/min) was passed through the material. The gas stream containing a low concentration of the adducts **9** and **10** was passed through a tube packed with a 1.5 × 15 cm region of 4-mm glass beads and heated with an oven maintained at 380 °C. The exit gases from the pyrolysis tube were passed through two traps in series. Each trap contained 25 mL of MeOH and was cooled with a bath at −78 °C. The combined pyrolysate recovered from the end of the pyrolysis tube and from the cold traps was fractionally crystallized from THF to separate 12.7 mg of the dimer **15**, mp 227–229 °C. The mother liquors from this recrystallization were subjected to liquid chromatography on a column packed with silica gel and eluted with an EtOAc–hexane mixture (1:4 v/v). The products separated were 2.2 mg (7%) of the dimer **14**, mp 220–222 °C, 7.0 mg (23%) of the crude dimer **16**, mp 141–143 °C, and 4.1 mg (total yield 16.8 mg or 55%) of the dimer **15**, mp 229–231 °C. Each of these dimeric products **14–16** was identified with a previously described sample by a mixture melting point determination and by comparison of IR spectra.

A similar experiment was performed in which a 138-mg (0.68-mmol) sample of the adducts **9** (73%) and **10** (27%) was heated to 125 °C and swept into the pyrolysis tube (oven temperature 330 °C) with a stream of N_2 (150 mL/min). The first trap below the pyrolysis tube contained a mixture of 60 mL of MeOH and 1 mL of Et_3N at 25 °C and the second trap contained 40 mL of MeOH cooled to −78 °C. The pyrolysate (67.2 mg) recovered from the lower end of the pyrolysis tube had an NMR spectrum consistent with the presence of the three dimers **14–16**. The material collected in the traps (21.4 mg) had an NMR spectrum consistent with the present three dimers and a small amount of the methyl ether **7**. After this material had been triturated with EtOH, the EtOH-soluble material contained the ether **7**. A collected (GLC, silicone, No. 710, on Chromosorb W) sample of the ether **7** (estimated yield 4%) was identified with an authentic sample by comparison of GLC retention times and IR and mass spectra.

Crystal Structure of the *p*-Bromophenylsulfonylhydrazone 11. A. Data Collection. A crystal of the derivative **11** with approximate dimensions 0.1 × 0.1 × 0.7 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.7 mm, was approximately parallel to the fiber axis. Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) using Mo Kα radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 7.73 to 19.39° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were a = 6.570 (3) Å,[12] b = 10.051 (5) Å, c = 14.657 (8) Å, α = 98.69 (4)°, β = 94.56 (4)°, γ = 93.02 (4)°, and V = 951.6 (9) Å^3. The calculated density of 1.54 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.52 g cm^{-3} measured by the flotation method using a mixture of pentane and CCl_4. ω scans of low 2θ angle reflections gave peak widths at half-height of less than 0.24°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed, consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[13] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.02 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (200, 030, 006) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship

$$I = \mathrm{CT} - (\mathrm{TR})(\mathrm{bgd1} + \mathrm{bgd2})$$

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{CT} + (\mathrm{TR})^2(\mathrm{bgd1} + \mathrm{bgd2})]^{1/2}$$

from a total of 3313 reflections collected in a complete hemisphere of data out to 2θ = 50°; 2379 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed by using standard programs;[14] all computations were carried out on the CDC Cyber 74 System. For structure factor calculations the scattering factors were taken from Cromer and Mann's tabulation.[15] The agreement factors are defined in the usual way as

$$R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$$

$$R_w = \frac{[\sum(|F_o| - |F_c|)(w^{0.5})]}{[\sum(|F_o|)(w^{0.5})]}$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 1.87/[\sigma(F)^2 + 0.0002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 255 for 2379 observations. Parameters

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(12) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

(13) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1952.

(14) Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

(15) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, pp 72–98.

varied included a scale factor, coordinates of all atoms except hydrogen, anisotropic thermal parameters for all atoms except H atoms, and isotropic thermal parameters for H atoms. Hydrogen atoms were refined in the riding mode. The full-matrix least-squares refinement converged at $R = 0.0523$ and $R_w = 0.0441$. The final atomic coordinates and thermal parameters are available as supplementary material Table VI, and the list of bond distances and angles is available as supplementary material Table I. The list of calculated and observed structure factors is available from the authors.

Crystal Structure of the *p*-Bromophenylsulfonylhydrazone 12. A. Data Collection. A crystal of the derivative **12** with approximate dimensions 0.7 × 0.3 × 0.2 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.7 mm, was approximately parallel to the fiber axis. Unit cell parameters were determined as described above. Fifteen reflections whose 2θ values ranged from 8.58 to 23.10° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 6.517$ (2) Å, $b = 19.052$ (4) Å, $c = 15.179$ (5) Å, $\beta = 91.02$ (2)°, and $V = 1884.5$ (9) Å^3. The calculated density of 1.53 g cm^{-3} for 4 formula units per unit cell agrees with the experimental density of 1.53 g cm^{-3} measured by the flotation method using a mixture of pentane and CCl_4. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the monoclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. The absence of $h0l(l = 2n + 1)$ and $0k0(k = 2n + 1)$ reflections is consistent with only space group $P2_1/c$ (No. 14).[13]

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 2.93 to 29.30°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (200, 080, 008) monitored every 97 reflections. Intensities were calculated as described above. From a total of 3334 reflections collected in a complete quadrant of data out to $2\theta = 50°$, 2258 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as described above. In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 1.81/[\sigma(F)^2 + 0.002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct-methods program of SHELX-76. The total number of parameters varied was 255 for 2258 observations. The full-matrix least-squares refinement converged at $R = 0.0805$ and $R_w = 0.0802$. The final atomic coordinates and thermal parameters are available as supplementary material Table VII, and the list of bond distances and angles is available as supplementary material Table II. The list of calculated and observed structure factors is available from the authors.

Crystal Structure of the Dimer 14. A. Data Collection. A crystal of the dimer **14** with approximate dimensions 0.6 × 0.4 × 0.3 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.6 mm, was approximately parallel to the fiber axis. Unit cell parameters were determined as described above. Fifteen reflections whose 2θ values ranged from 5.03 to 21.84° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 6.811$ (2) Å, $b = 9.999$ (5) Å, $c = 6.471$ (3) Å, $\alpha = 101.83$ (4)°, $\beta = 91.69$ (4)°, $\gamma = 122.95$ (3)°, and $V = 356.5$ (3) Å^3. The calculated density of 1.27 g cm^{-3} for 1 formula unit per unit cell agrees with the experimental density of 1.26 g cm^{-3} measured by the flotation method using a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed, consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[13] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.02 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (003, 010, 300) monitored every 97 reflections. Intensities were calculated as described above. From a total of 1265 reflections collected in a complete hemisphere of data out to $2\theta = 50°$, 1031 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as described above. In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 9.39/[\sigma(F)^2 + 0.0002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 106 for 1031 observations. The full-matrix least-squares refinement converged at $R = 0.0500$ and $R_w = 0.0492$. The final atomic coordinates and thermal parameters are available as supplementary material Table VIII, and the list of bond distances and angles is available as supplementary material Table III. The list of calculated and observed structure factors is available from the authors.

Crystal Structure of the Dimer 15. A. Data Collection. A crystal of the dimer **15** with approximate dimensions 0.8 × 0.45 × 0.05 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.8 mm, was approximately parallel to the fiber axis. Unit cell parameters were determined as described above. Fifteen reflections whose 2θ values ranged from 4.12 to 16.03° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 11.403$ (8) Å, $b = 6.463$ (3) Å, $c = 11.267$ (5) Å, $\alpha = 91.73$ (3)°, $\beta = 121.73$ (4)°, $\gamma = 92.91$ (4)°, and $V = 703.7$ (7) Å^3. The calculated density of 1.28 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.26 g cm^{-3} measured by the flotation method using a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed, consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[13] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.02 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (400, 020, 003) monitored every 97 reflections. Intensities were calculated as described above. From a total of 2472 reflections collected in a complete hemisphere of data out to $2\theta = 50°$, 1807 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as described above. In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 1.26/[\sigma(F)^2 + 0.0035F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 205 for 1807 observations. The full-matrix least-squares refinement converged at $R = 0.0636$ and $R_w = 0.0739$. The final atomic coordinates and thermal parameters are available as supplementary material Table IX, and the list of bond distances and angles is available as supplementary material Table IV. The list of calculated and observed structure factors is available from the authors.

Crystal Structure of the Dimer 16. A. Data Collection. A crystal of the dimer **16** with approximate dimensions 0.6 × 0.6 × 0.5 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.6 mm, was approximately parallel to the fiber axis. Unit cell parameters were determined as described above. Fifteen reflections whose 2θ values ranged from 5.21 to 18.38° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 11.544$ (4) Å, $b = 10.218$ (5) Å, $c = 6.425$ (3) Å, $\alpha = 104.26$ (3)°, $\beta = 104.15$ (3)°, $\gamma = 92.62$ (3)°, and $V = 707.7$ (5) Å^3. The calculated density of 1.27 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.26 g cm^{-3} measured by the flotation method using a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed, consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[13] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.93 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (500, 040, 002) monitored every 97 reflections. Intensities were calculated as described above. From a total of 2498 reflections collected in a complete hemisphere of data out to $2\theta = 50°$, 2255 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as described above. In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 3.902\ [\sigma(F)^2 + 0.002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 205 for 2255 observations. The full-matrix least-squares refinement converged at $R = 0.0540$ and $R_w = 0.0738$. The final atomic coordinates and thermal parameters are available as supplementary material Table X, and the list of bond distances and angles is available as supplementary material Table V. The list of calculated and observed structure factors is available from the authors.

Registry No. 1, 71370-30-4; **2b**, 66077-98-3; **2c**, 20498-02-6; **3**, 6674-22-2; **5**, 71370-25-7; **7**, 66921-79-7; **9**, 71423-34-2; **10**, 71423-35-3; **11**, 71370-26-8; **12**, 71423-36-4; **13**, 71370-27-9; **14**, 71370-28-0; **15**, 71370-29-1; **16**, 71423-37-5; $CH_3COCH_2CO_2Et$, 141-97-9; cyclohexenone, 930-68-7; PBr_3, 7789-60-8; EtO_2CNHNH_2, 4114-31-2; furan, 110-00-9; p-$BrC_6H_4SO_2NHNH_2$, 2297-64-5; $HONH_3Cl$, 5470-11-1.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables VI–X) and tables of bond distances and bond angles (Tables I–V) (14 pages). Ordering information is given on any current masthead page.

Reactions of 2-Methyleneallyl Dianion with Aldehydes, Ketones, Epoxides, and Allyl Halides

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Reactions of 2-methyleneallyl dianion with aldehydes, ketones, ethylene oxide, and allyl chloride gave diaddition products in 49–76% yield, always accompanied by some monoadduct (5–37% yield). Elimination was the only reaction observed with epichlorohydrin. Phthalaldehyde gave a cyclic diaddition product in 9% yield, but none was obtained from benzil or quinone. Attempts to obtain a mixed diadduct in good yield by reacting the dianion with two different electrophiles failed. An improved procedure is given for the preparation of the dianion.

Metalating systems such as n-butyllithium/tetramethylethylenediamine (TMEDA) and n-butyllithium/potassium *tert*-butoxide have yielded a variety of delocalized polyanions[1-3] not readily accessible through other routes such as halogen–metal exchange. Because of the availability of these polylithiated species, we are interested in exploring their synthetic utility. Delocalized carbanions have recently been used in the preparation of terpenoids.[4]

We chose to examine the reactions of 2-methyleneallyl dianion (**1**) because of the simplicity of its product mixtures and because of current interest in the "aromaticity" of cross-conjugated polyanions possessing a Hückel number of electrons.[5] Reactions of **1** with mono-[2] and dihaloalkanes[6] have been described. We now report the results

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