(+)-α-pinene of high rotation.

Registry No. $IpcBH_2$, 64234-27-1; $2IpcBH_2$·TMED, 67826-92-0; $IpcBR_2$ (R = 2-methylbut-1-yl), 83615-68-3; IpcBHR R = 2-methylbut-1-yl), 83632-57-9; IpcBHR (R = *sec*-butyl), 83615-69-4; IpcBHR (R = 2-methylbut-3-yl), 83615-70-7; IpcBHR (R = 2-methylpent-3-yl), 83615-71-8; IpcBHR (R = 2-methylcyclopentyl), 83615-72-9; IpcBHR (R = 2-ethylcyclopentyl), 83615-73-0; IpcBHR (R = 3-phenylpent-2-yl), 83615-74-1; IpcBHR (R = 2-phenylcyclopentyl), 83679-39-4; IpcBHR (R = 2-phenylcyclohexyl), 83615-75-2; boranemethyl sulfide, 13292-87-0; (+)-α-pinene, 7785-70-8; 2-methyl-1-butene, 563-46-2; *trans*-2-butene, 624-64-6; 2-methyl-2-butene, 513-35-9; 2-methyl-2-pentene, 625-27-4; 1-methylcyclopentene, 693-89-0; 1-ethylcyclopentene, 2146-38-5; (*E*)-3-phenyl-2-pentene, 4165-86-0; 1-phenylcyclopentene, 825-54-7; 1-phenylcyclohexene, 771-98-2; (*S*)-(−)-2-methyl-1-butanol, 1565-80-6; (*S*)-(+)-2-butanol, 4221-99-2; (*S*)-(+)-3-methyl-2-butanol, 1517-66-4; *cis*-2-butene, 590-18-1; (*S*)-(+)-3-hexanol, 6210-51-1; *trans*-3-hexene, 13269-52-8; (*R*)-(+)-2,2,5,5-tetramethyl-3-hexanol, 79449-64-2; *trans*-2,2,5,5-tetramethyl-3-hexene, 692-48-8; (*R*)-(−)-1,2-diphenyl-1-ethanol, 41822-67-7; *trans*-stilbene, 103-30-0; (*S*)-(+)-2-pentanol, 26184-62-3; 3-pentanol, 584-02-1; *trans*-2-pentene, 646-04-8; (*S*)-(+)-4-methyl-2-pentanol, 14898-80-7; (*S*)-(−)-2-methyl-3-pentanol, 70492-65-8; *trans*-4-methyl-2-pentene, 674-76-0; 4,4-dimethyl-2-pentanol, 6144-93-0; (*R*)-(+)-2,2-dimethyl-3-pentanol, 38636-36-1; *trans*-4,4-dimethyl-2-pentene, 690-08-4; (*R*)-(+)-1-phenyl-1-propanol, 1565-74-8; *trans*-β-methylstyrene, 873-66-5; (1*S*,2*S*)-(+)-*trans*-2-methylcyclopentanol, 39947-48-3; (1*S*,2*S*)-(+)-*trans*-2-ethylcyclopentanol, 83708-72-9; (1*S*,2*S*)-(+)-*trans*-2-methylcyclohexanol, 15963-37-8; 1-methylcyclohexene, 591-49-1; (*R*)-(+)-1-phenyl-2-methyl-1-propanol, 14898-86-3; (2*S*,3*R*)-(+)-*threo*-3-phenyl-2-butanol, 53319-09-8; (2*S*,3*S*)-(−)-*erythro*-3-phenyl-2-butanol, 74365-65-4; (2*S*,3*R*)-(−)-*threo*-3-phenyl-2-pentanol, 74365-66-5; (2*S*,3*S*)-(+)-*erythro*-3-phenyl-2-pentanol, 74365-67-6; (1*S*,2*R*)-(+)-*trans*-2-phenylcyclopentanol, 38805-89-9; (1*S*,2*R*)-(+)-*trans*-2-phenylcyclohexanol, 34281-92-0; β,β-dimethylstyrene, 768-49-0; (*E*)-2-phenyl-2-butene, 768-00-3; (*Z*)-2-phenyl-2-butene, 767-99-7; (*Z*)-3-phenyl-2-pentene, 4165-78-0; isopinocampheol, 27779-29-9.

1,4-Dimethoxy-1,3-butadiene as a Donor Diene in Diels–Alder Cycloadditions

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The title compound (DMBU) is a useful diene in [4 + 2] cycloadditions. Since DMBU is readily obtained in two steps from 1,4-dihydroxy-2-butyne, it should be regarded as an inexpensive and abundant starting material. Diels–Alder products were obtained from DMBU and the dienophiles, dimethyl acetylenedicarboxylate, ethyl propiolate, benzyne, fumaronitrile, tetracyanoethene, maleic anhydride, 1,2-dibenzoylethene, diethyl azodicarboxylate, and four 1,4-quinones. The aromatization of some of these products was studied. As determined by gas chromatography and ^1H NMR, DMBU is normally obtained as three isomers *Z,Z*/*Z,E*/*E,E* = (60 ± 3):(34 ± 3):(6 ± 2). While the *Z,Z* form is less reactive, the *Z,E* and *E,E* isomers react with tetracyanoethene at rates similar to that of 1-methoxy-1,3-butadiene.

The work reported here began with the notion that 1,4-dimethoxy-1,3-butadiene (DMBU) could be a useful "donor" diene in Diels–Alder reactions. In fact, the *E,E* isomer had already been used in two isolated cases.[1] One of the features of DMBU was its potential reactivity: of 26 dienes tested, the reactivity with tetracyanoethene (TCNE) was calculated to be highest for DMBU, according to frontier molecular orbital (FMO) theory.[1a] On the basis of rate constants at 20 °C, DMBU ranked fifth at 7.9 on a scale of 9.5 for cyclopentadiene to 0.6 for *cis*-1-methylbutadiene.[1a]

Although the reported synthesis of (*E,E*)-DMBU has the important virtue of being stereospecific, it does require six steps.[1b] There is also a synthesis of DMBU based on the pyrolysis of the not very common tetramethoxybutane.[2a] On the other hand, the two-step path from the readily available 1,4-dihydroxy-2-butyne (eq 1) is quite simple.[2b] Therefore, we proceeded to investigate the diene capabilities of DMBU.

$$HOCH_2C{\equiv}CCH_2OH \xrightarrow{Me_2SO_4} MeOCH_2C{\equiv}CCH_2OMe \xrightarrow{base} \underset{\text{DMBU}}{MeOCH{=}CHCH{=}CHOMe} \quad (1)$$

Table I. Products from 1,4-Dimethoxy-2,3-dicarbomethoxy-1,4-cyclohexadiene (3a)

conditions, eq 3[a]	product	yield, %
NaOH–EtOH/H_2O	4c	75
5% Pd/C, xylene	4b	86
Br_2, $CHCl_3$	4b	78
MnO_2, PhH	4b	86
Me_2SO, 120 °C	4b	67
NBS, CCl_4	4a	100

[a] At reflux temperature unless otherwise noted.

Structurally the closest diene for which DMBU might be a replacement is 1,4-diacetoxy-1,3-butadiene, although either alkoxy or acetoxy groups might be favored for special applications. Currently this diacetate is prepared in 41–49% yield in three steps from cyclooctatetraene.[3a] Because of the versatility of Diels–Alder synthesis, there has been a veritable industry in the last few years devoted to variations in the pattern of dienes with oxy and thio substituents, e.g., alkoxy, siloxy, acetoxy, and furans.[3,4]

(1) (a) Rücher, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663. (b) Meister, H. *Chem. Ber.* **1963**, *96*, 1688.

(2) (a) Shavrygina, O. A.; Makin, S. H. *Khim. Farm. Zh.* **1969**, *13*, 17; *Chem. Abstr.* **1969**, *71*, 124112. (b) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971; pp 173, 144.

(3) (a) Carlson, R. M.; Hill, R. K. *Org. Synth.* **1970**, *50*, 24. (b) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, 104, 358. (c) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 40. (d) Cameron, D. W.; Fuetrill, G. I.; Perlmutter, P. *Tetrahedron Lett.* **1981**, 3273. (e) Cameron, D. W.; Feutrill, G. I.; McKay, P. G. *Tetrahedron Lett.* **1981**, 701. (f) Roberge, G.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 4161. (g) Schmidt, R. R.; Wagner, A. *Synthesis* **1981**, 273. (h) Murai, A.; Takahashi, K.; Taketsuru, H.; Masamune, T. *J. Chem. Soc., Chem. Commun.* **1981**, 221.

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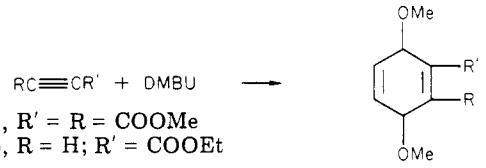
Cycloadditions. We quickly established that DMBU is a suitable diene in the Diels–Alder synthesis. As is the case with many other dienes, its range of application is not unlimited. Nevertheless, the scope of a reaction such as this one can often be extended by judicious variation in the dienophile or changes in reaction conditions, e.g., solvent, temperature, pressure, or in the use of catalysts, radical scavengers, etc. Late in this work, it was found, for example, that one of the DMBU isomers showed relatively low reactivity; increased amounts of [4 + 2] products would presumably be obtained in some cases by adjusting the starting concentration of DMBU to compensate for the "slow" *Z,Z* form. At this stage we believe that our examples should be taken only as rough indications of the utility of DMBU.

Three alkynes combined with DMBU (eq 2). Since loss

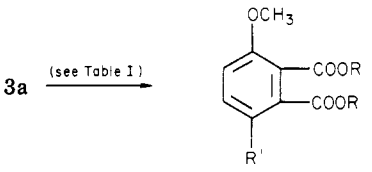


(2)

2a, R' = R = COOMe
b, R = H; R' = COOEt

3a, R = R' = COOMe
b, R = H; R' = COOEt

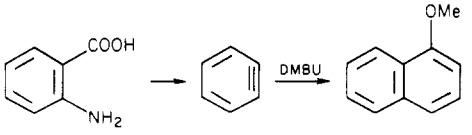
of methanol from **3a** and its analogues was facile, it was of interest to find alternative ways to treat it so that both methoxy groups were retained. Different reagents were tested on the diester **3a** (eq 3) with the results shown in Table I. Clearly aromatization through elimination of methanol can be bypassed, but not without considerable care.



(3)

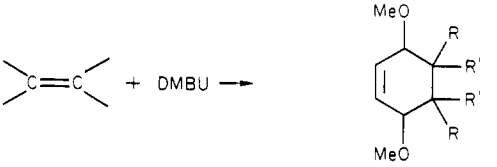
4a, R = Me; R' = OCH_3
b, R = Me; R' = H
c, R = R' = H

If one can judge by the strenous conditions used in its preparation and by the lower yield of **3b** (14%) relative to **3a** (53%), the dienophile **2b** is less reactive than **2a** in process 2. Of course, the yield reactivity parallel is quite unreliable as shown in parallel cases.[5] Our example is the benzyne reaction with DMBU (eq 4); despite the high reactivity of benzyne, the yield of product was low (~ 10%).



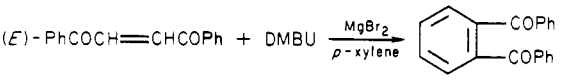
(4)

We give several examples of alkenes as dienophiles. All of them had activating (electron-withdrawing) groups at the alkene carbon (eq 5). In the case of (*E*)-dibenzoylethene, it proved useful to use a Lewis acid as catalyst (eq 6). Incidentally, a stronger Lewis acid such as aluminum chloride appeared to attack DMBU.



(5)

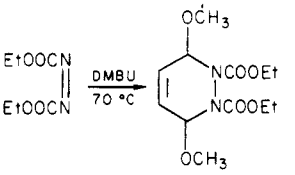
cis- and *trans*-**5a**, R = R' = CN
b, R = H; R' = CN
c, R = H; R'-R' = CO-O-CO



(6)

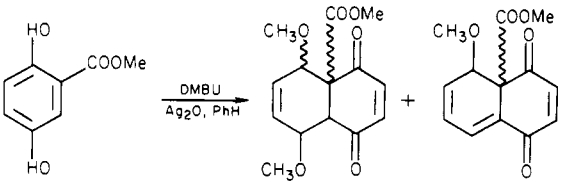
5d

The reaction of diethyl azodicarboxylate proceeded to give the expected product (eq 7). Attempts to dehydrogenate it, e.g., with lead tetracetate, were not successful.



(7)

A number of adducts were obtained from *p*-quinones. Methyl 2,5-dihydroxybenzoate was converted to *p*-quinone in situ[6] and trapped with DMBU (eq 8). This reaction

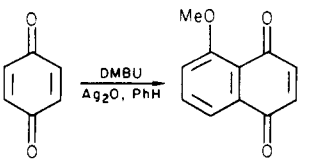


(8)

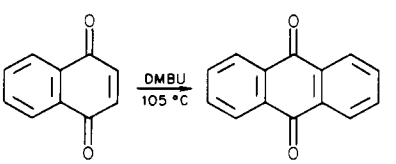
6a and **6b** **7**

and the "internal" substituent in the product (**6**) is entirely analogous to one reported for the same ester with several dienes, e.g., 1-(trimethylsiloxy)-3-methyl-1,3-pentadiene.[6] As for the trienone (**7**), this is one of three possible structures that can arise from **6** by the loss of CH_3OH. On the basis of the ^1H NMR data on **7** and compounds such as **5b**, **5c**, and **6**, all of which have one or both hydrogens of the type MeOCH< and O=CCH< with the usual range of $\delta > 4$ and $\delta < 4$, respectively, we assigned the structure of **7** as shown.

With 1,4-benzoquinone and 1,4-naphthoquinone DMBU yielded adducts that lost one and two molecules of methanol, respectively (eq 9 and 10). Although 2 equiv of oxidant were used in eq 9, only 1 mol of hydrogen was normally removed, probably from the first adduct, after which methanol was lost.



(9)



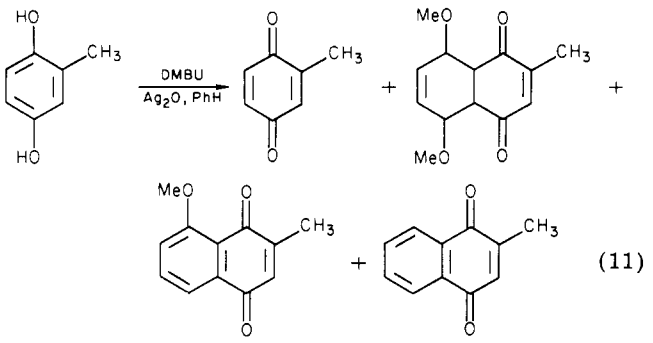
(10)

(4) (a) Hirai, K.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, 3413. (b) Trost, B. M.; Godleski, S. A.; Ippen, J. *J. Org. Chem.* **1978**, *43*, 4559. (c) Keana, J. F. W.; Eckler, P. E. *Ibid.* **1976**, *41*, 2625. (d) Banks, R. E.; Miller, J. A.; Nunn, M. J.; Stanley, P.; Weakley, T. J. R.; Ullah, Z. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1096.

(5) Tanimoto, S.; Matsumura, Y.; Sugimoto, T.; Okano, M. *Tetrahedron Lett.* **1977**, 2899.

(6) (a) Kraus, G. A.; Taschner, M. J. *J. Org. Chem.* **1980**, *45*, 1174. (b) Kojima, Y.; Kato, N. *Tetrahedron* **1981**, *37*, 2527.

Finally, the cycloaddition of eq 11 should be contrasted with that of eq 8: the electron-donating methyl group directs addition to the remote, while the electron-withdrawing carbomethoxy group directs mainly to the proximate, double bond in benzoquinone. This regioselectivity



(11)

has ample precedent and has been illustrated, discussed, and explained.[7,8]

Properties of DMBU. We established that the reactivity of (*E,Z*)- and (*E,E*)-DMBU toward TCNE is comparable, i.e., ca. 0.6 of that of 1-methoxy-1,3-butadiene (MBU) while that of the *Z,Z* isomer is much slower (see Experimental Section for details). Our qualitative result is consistent with reported rate constants (10^6 M^{-1} s^{-1}) at 20 °C for *trans*-MBU (7.935), *cis*-MBU (6.279), and (*E,E*)-DMBU (7.925).[1a] On this reactivity scale it appears that $k < 1 \times 10^6$ M^{-1} s^{-1} for (*Z,Z*)-DMBU, which places it at the bottom of the group of dienes that was surveyed.[1a,9] It seems that the near coplanar conformation required for reaction of *Z,Z* may be difficult to attain for steric reasons. Apart from their theoretical interest, the qualitative and quantitative scales of reactivity for partners in the Diels–Alder process[1a,9] have some obvious practical (synthetic) applicability.

Chemically, DMBU is sensitive to some acids and oxidants that may be considered as ingredients of a Diels–Alder reaction mix. In attempting to catalyze some cycloadditions, we found that Lewis acids such as boron trifluoride in ether, aluminum chloride, and zinc chloride rapidly destroyed DMBU; on the other hand, magnesium bromide could be used successfully (eq 6). Reactions with, or in the presence of, proton acids (HA) such as acrylic or cinnamic gave what appeared to be adducts of HA.

Unless it is distilled and stored under nitrogen, DMBU quickly discolors, turning light yellow then brown.[1b] In fact, it is probable that exposure of DMBU to air facilitates its decomposition on silica gel during TLC. As for other oxidants, it survives mercury(II) and silver(I) oxides for the most part but is destroyed by selenium dioxide and is acyloxylated by lead tetracetate,[10] as in eq 12. More-

$$\text{DMBU} + \text{Pb(OAc)}_4 \rightarrow \text{CH}_3\text{COO(CH}_3\text{O)CHCH=CHCH(OCH}_3\text{)OOCCH}_3 \quad (12)$$

over, 1,4-quinones, e.g., benzoquinone and tetrachlorobenzoquinone, appear to dehydrogenate DMBU and form hydroquinones (and corresponding quinhydrones) that are then inert to cycloaddition. By oxidizing 1,4-hydroquinones to quinones (eq 8, 11), added silver(I) oxide appears to "protect" DMBU, at least for the duration of some of our Diels–Alder syntheses (eq 9).

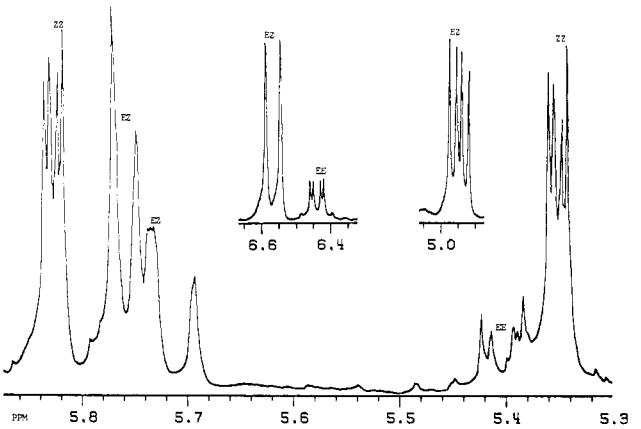


Figure 1. ^{1}H NMR spectrum at 300 MHz of the alkene region of the isomers of 1,4-dimethoxy-1,3-butadiene in $CDCl_3$. Peak assignments are tentative.

As obtained by us, DMBU consisted of three isomers whose distribution is *Z,Z*/*Z,E*/*E,E* ≃ (59 ± 5):(35 ± 5):(6 ± 3), according to GC analysis of several samples at different times. The isomer fractions indicated above may deviate somewhat from the equilibrium composition for several reasons. Because the history of each sample varied in purification and storage, it is probable that there could be some variation in the final composition that we examined, even though it probably began as an equilibrium mixture. By storing DMBU under nitrogen in a refrigerator it was possible to avoid most but not all of the usual spurious impurity peaks[1a] in the NMR spectra and the GC chromatograms which complicate the analysis. Fortunately one of our redistilled samples, for which a 300-MHz spectrum was obtained, appeared to be clean. On the basis of integrals of the well-separated ^{1}H NMR methoxy peaks, we obtained the ratio *Z,Z*/*Z,E*/*E,E* ≃ 62:33:5.

A portion of the ^{1}H NMR spectrum of DMBU is given in Figure 1. The apparent complexity of the alkene region must be ascribed largely to the overlap of the spectra of the three isomers. Because assignments of both δ and J have been made in several dienes with siloxy, acetoxy, and alkoxy substituents,[1a,4,8] it is probable that the 1,4- are downfield from the 2,3-protons and that the largest J values must be associated with the trans protons. Guided by literature data on (*E,E*)-DMBU,[1a] we can identify its peaks. Our *Z,E* and *Z,Z* assignments in Figure 1 must be regarded as tentative at this time, because of peak overlap and somewhat uncertain integrals.

By adding the shift reagent Eu(fod)$_3$ to DMBU we were able to separate the methoxy peaks in the ^{1}H NMR spectrum and integrate them. From the peak integrals, we obtain the ratio *Z,Z*/*Z,E*/*E,E* as 62:30:8. There was an interesting and unaccounted splitting of the *Z,Z* peak observed in the presence of shift reagent. The obvious explanation, namely, that one of the peaks derives from *Z,E*, leads to problems with assignments of δ and their integrals in the absence of Eu(fod)$_3$. Nevertheless, support for our structural assignment is provided here by a study of the shift reagent Eu(dpm)$_3$ on several methoxystyrenes:[11] if the effect on δ (CH_3O) of the remote double bond in DMBU is parallel to that of phenyl in these styrenes, then one would expect the largest downfield shifts in the *E* structures, which is what was observed.

(7) (a) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3012. (b) Rozeboom, M. D.; Tegmo-Larsson, I-M.; Houk, K. N. *J. Org. Chem.* **1982**, *46*, 2338. (c) Eisenstein, O.; Lefour, J. M.; Anh, N. T. *Tetrahedron* **1977**, *33*, 523.

(8) Hiranuma, H.; Miller, S. I., unpublished results on 1,4-*tert*-butoxy-1,3-butadiene.

(9) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(10) Moriarty, R. M. In "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley: New York, 1972; p 183.

(11) Huet, J.; Fabre, O.; Zimmermann, D. *Tetrahedron* **1981**, *37*, 3739.

The stability order $Z,Z > Z,E > E,E$ may be of some interest. 2-Alkyl-1-methoxyethenes generally show stability of $Z > E$, where alkyl is t-C_4H_9, C_3H_7, and C_2H_5.[12] The DMBU isomers conform; in fact, they parallel those of 1,4-dichloro- and 1,4-difluoro-1,3-butadiene, which have analogous electronegative and lone electron pair substituents.[13]

Experimental Section

General Procedures. All boiling points and melting points are uncorrected. Melting points were determined on a Fisher-Johns apparatus. Infrared spectra were determined with Pye Unicam 3-300 or Perkin-Elmer Model 337 spectrometers in KBr or as films on NaCl plates. NMR spectra were obtained in a Varian T60 spectrometer with tetramethylsilane as an internal standard. Certain NMR spectra were taken on a Bruker 300-MHz instrument in $CDCl_3$. Mass spectra were taken at ca. 70 eV in our Varian MAT CH 7 and in an AEI 30 instrument of the University of Illinois, Chicago. Neutral alumina or silica (60–200 mesh) were used in column chromatography. EM silica gel (60 Å, PF 254) was used for preparative thin-layer chromatography. Silica on plastic sheet (Eastman) or on glass slides was used for TLC. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL, and by Geulph Chemical Laboratories, Guelph, Ontario.

1,4-Dimethoxy-1,3-butadiene (DMBU). Brandsma's procedure was used (eq 1).[2b] Starting with 1,4-dihydroxy-2-butyne (43.05 g, 0.5 mol), we obtained 1,4-dimethoxy-2-butyne (46.5 g, 81.5%), which had the following: bp 54 °C (12 mm) [lit.[2b] bp 54° (12 mm)]; NMR ($CDCl_3$) δ 4.23 (s, 4 H), 3.46 (s, 6 H). A solution of 1,4-dimethoxy-2-butyne (22.8 g, 0.2 mol) and potassium *tert*-butoxide (1.5 g, 0.013 mol) in dimethyl sulfoxide (40 mL) was heated at 55–60 °C for 1.5 h. (A freshly opened commercial sample of *tert*-butoxide was satisfactory; material freshly prepared by us from potassium and *tert*-butyl alcohol in Me_2SO was equally effective, but there was the hazard of potassium fires. Some samples of "aged" potassium *tert*-butoxide could be used successfully, if more than 0.013 equiv was used.) It is recommended that the course of the isomerization be checked by ^1H NMR. After cooling, the mixture was poured into water and extracted with ether. The extracts were washed with brine, dried over sodium sulfate, and evacuated at ca. 30 °C to remove ether. The remaining oil was distilled under nitrogen to give DMBU (15.8 g, 69%): bp 45 °C (7 mm) [lit.[13] bp 71–72 °C (30 mm)]; IR (NaCl) 1660, 1610, 1250, 1210 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ for Z,Z 3.63 (s, 3 H), 5.35 (dd, 2 H, J = 3.6, 1.3 Hz), 5.83 (dd, 2 H, J = 3.6, 1.3); for E,Z 3.58 (s, 3 H), 4.95 (q, 1 H, J = 10.8, 6.26 Hz), 5.72 (m, 1 H, $J \cong$ 12.7 Hz), 5.76 (m, 1 H, $J \cong$ 6.7 Hz), 6.57 (d, 1 H, J = 12.9 Hz); for E,E 3.55 (s, 3 H), 5.40 (dd, 2 H, J = 9.3, 2.5 Hz), 6.44 (dd, 2 H, 9.3, 2.5 Hz) [lit.[1a] δ 5.4 (m), 6.45 (dd)].

In addition to an estimate of isomer composition carried out on the above solution by integration of the methoxy peaks another experiment was used at 60 MHz. In carbon tetrachloride the Z,Z, E,Z, and E,E, δ values of DMBU were 3.71, 3.65, and 3.6, respectively. In deuteriochloroform (0.72 mL), DMBU (41 mg, 0.36 mmol) and $Eu(fod)_3$ (149 mg, 0.15 mmol) showed δ values reversed, 3.61 + 3.63, 4.03, and 4.17 for the same isomers. Integration of peak areas in this solution yielded $Z,Z/Z,E/E,E \cong 62:30:8$.

DMBU should be stored in a stoppered bottle under nitrogen in a refrigerator. DMBU was exposed to several sets of reaction oxidizing or acidic conditions to test its stability. On TLC plates coated with silica gel or silanized silica gel (Whatman KC_{18} reversed phase) DMBU showed extensive decomposition. More specifically, a solution of DMBU (342 mg, 3 mmol), carbon tetrachloride (3 mL), and benzene (0.3 mL), as internal standard, was divided into three portions for reaction with mercuric(II) oxide (216 mg, 1 mmol), silver(I) oxide (231 mg, 1 mmol), and selenium dioxide (111 mg, 1 mmol), respectively. The suspensions were stirred for 6 h at ca. 25 °C and then examined by ^1H NMR. With the mercury and silver oxides there was a small amount of decomposition marked by the appearance of a broad NMR peak in the methoxy region at δ ~3.2. In the case of selenium dioxide, DMBU was completely decomposed and δ ~3.2 became the dominant ^1H NMR peak.

Other DMBU Properties. A rough comparison of reactivity of DMBU and 1-methoxy-1,3-butadiene (MBU) toward tetracyanoethene was carried out. Cycloadducts of each were prepared and their GC retention times were determined on a 20% SE-30 column in a Varian Aerograph Model 700 Gas Chromatograph. A solution containing DMBU (114 mg, 1 mmol), MBU (84 mg, 1 mmol), TCNE (12.8 mg, 0.1 mmol), and benzene (5.0 mL) was heated at reflux for 3 h. After the solvent was evaporated, the residual oil was analyzed by GC. The ratio of MBU to DMBU product was 4/1. Since the DMBU product derives chiefly from the E,Z and E,E isomers, which comprise ca. 40% of the starting material, the relative reactivity, MBU to DMBU, is 1.6 under the conditions given.

To determine the isomeric composition of DMBU we used a Varian Aerograph flame-ionization gas chromatograph (2400 series). Resolution of the three compounds was virtually complete on a thin-wall SE 30 glass column (25 m, SCOT) kept at ca. 20 °C: retention times were 5.11, 5.54, and 7.19 min for Z,Z, Z,E, and E,E, respectively.

1,2-Dicarbomethoxy-3,6-dimethoxy-1,4-cyclohexa-1,4-diene (3a). DMBU (1.14 g, 10 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) were heated at 130 °C for 14 h in a nitrogen atmosphere. The distilled product (1.35 g, 53%) had the following: bp 143 °C (1 mm); IR (film) 1720, 1260 cm^{-1}; NMR ($CDCl_3$) δ 3.23 (s, 6 H), 3.80 (s, 6 H), 4.86 (s, 2 H), 6.20 (s, 2 H); MS, m/e 257 $(M + 1)^+$, 256 (M^+).

Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25, H, 6.25. Found: C, 56.36; H, 5.98.

Transformations of 1,2-Dicarbomethoxy-3,6-dimethoxy-1,4-cyclohexa-1,4-diene. A solution of the diene (256 mg, 1 mmol) and sodium hydroxide (400 mg) in water–ethanol (1:1, 4 mL) was heated at reflux temperature for 2 h. After cooling, the solution was acidified with 10% hydrochloric acid and extracted with ether. Workup yielded 3-methoxyphthalic acid (147 mg, 75%), which had the following: mp 173–175 °C (lit.[14] mp 173–174 °C); IR (KBr) 1720, 1700, 1685 cm^{-1}; NMR ($CDCl_3$–$(CD_3)_2SO$) δ 3.91 (s, 3 H), 7.1–7.6 (m, 3 H), 10.86 (br s, 2 H). Other methods that led to the same product are given in Table I.

When a solution of the diene (0.6 g, 2.3 mmol) and 5% palladium on carbon (0.35 g) was heated at reflux in xylene (10 mL) 1 h and then evaporated, dimethyl 3-methoxyphthalate (**4c**) remained. On recrystallization from ether and petroleum ether, the white needles (0.45 g, 87%) had the following: mp 70–71 °C (lit.[15] mp 73–74 °C); IR (KBr) 1725, 1282 cm^{-1}; NMR ($CDCl_3$) δ 3.83 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 3 H), 7.1–7.7 (m, 3 H).

After a solution of the diene (256 mg, 1 mmol) and *N*-bromosuccinimide (390 mg, 2.2 mmol) in carbon tetrachloride (10 mL) was heated at reflux temperature and cooled, succinimide (mp 126 °C) was deposited. The filtrate was worked up to give dimethyl 3,6-dimethoxyphthalate (**4a**; 250 mg, 100%) from ether: mp 95–96 °C (lit.[16] mp 102–103 °C); IR (KBr) 1720, 1275, 1228 cm^{-1}; NMR ($CDCl_3$) δ 3.81 (s, 6 H), 3.86 (s, 6 H), 7.05 (s, 2 H).

***m*-Methoxybenzoic Acid.** DMBU (0.57 g, 5 mmol) and ethyl propiolate (0.49 g, 5 mmol) were heated at 120–130 °C for 20 h in a sealed tube. The distilled product (0.15 g, 14.1%), which had bp 118 °C (0.3 mm), was heated with sodium hydroxide (0.3 g) and aqueous ethanol (1:1, 6 mL) for 2 h. After the solution was evaporated, the residue was neutralized with 10% hydrochloric acid and extracted with ether. The extract was washed with water, dried over sodium sulfate, and evaporated to yield *m*-anisic acid (120 mg): mp 98–101 °C (lit.[17] 104–105 °C); mixture melting point, IR, and a NMR spectra identical with those of an authentic sample.

1-Methoxynaphthalene. A mixture of DMBU (0.64 g, 5.6

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mmol) and isoamyl nitrite (0.87 g, 7.4 mmol) in 1,2-dimethoxyethane (10 mL) was heated at reflux temperature. Anthranilic acid (1.3 g, 9.4 mmol) in 1,2-dimethoxyethane (10 mL) was added to this solution over a period of 30 min. After 5–10 min the solvent was evaporated and the residue taken up in ether and washed with 10% potassium carbonate and water. The ether solution was dried over sodium sulfate and evaporated in vacuo, and the residual oil was heated at reflux temperature with 10% sodium hydroxide (5 mL) for 5 h. Workup yielded 1-methoxynaphthalene, a clear liquid (56 mg, 9% yield), which was identical with an authentic sample by comparison of its IR, NMR spectra, and GC retention time.

3,6-Dimethoxy-1,1,2,2-tetracyanocyclohex-4-ene (5a). A solution of DMBU (342 mg, 3 mmol) and tetracyanoethylene (128 mg, 1 mmol) in benzene (10 mL) was heated at reflux and monitored periodically by GC analysis. After 2 h both (*E,Z*)- and (*E,E*)-DMBU were all consumed while some (*Z,Z*)-DMBU remained unreacted. The solution was evaporated and the residue was separated by preparative TLC into three zones. The zone with the highest R_f contained DMBU and/or decomposition products. The major isomer (crude yield was 154 mg, 63.6%) was obtained from the middle zone. The solid was recrystallized from ether–*n*-hexane to give white prisms (84 mg, 34.7%), which had the following: mp 118–120 °C; IR ($CHCl_3$) 2222 cm^{-1}; NMR ($CDCl_3$) δ 3.76 (s, 6 H), 4.60 (s, 2 H), 5.96 (s, 2 H); MS, *m/e* 243 $(M + 1)^+$, 242 (M^+). Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.13; N, 23.14. Found: C, 59.54; H, 4.21; N, 23.20. A minor isomer (30 mg, 12%) from the lowest zone was recrystallized from ether–*n*-hexane to give white needles (5 mg): mp 146–148 °C; NMR ($CDCl_3$) δ 3.80 (s, 6 H), 4.43 (s, 2 H), 6.10 (s, 2 H) (lit.[1a] mp 155–156 °C; NMR δ 3.75, 4.45, 6.15); MS, *m/e* 242 (M^+), 227.

1,2-Dicyano-3,6-dimethoxycyclohex-4-ene (5b). DMBU (228 mg, 2 mmol) and fumaronitrile (156 mg, 2 mmol) were heated at reflux for 14 h in xylene (10 mL) under nitrogen. The solvent was evaporated and the residue was purified by chromatography on silica gel. The solid eluted with ether was recrystallized from ether and petroleum ether as white prisms (180 mg, 47% yield): mp 146–147 °C; IR (KBr) 2195 cm^{-1}; NMR ($CDCl_3$) δ 2.93 (d, 1 H, J = 3 Hz), 3.03 (d, 1 H, J = 3 Hz), 3.50 (s, 6 H), 4.06 (d, 1 H, J = 3 Hz), 4.13 (d, 1 H, J = 3 Hz), 5.83 (s, 2 H); MS, *m/e* 192 (M^+). Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.50; H, 6.25. Found: C, 62.29; H, 6.24.

3,6-Dimethoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (5c). After DMBU (456 mg, 4 mmol), maleic anhydride (196 mg, 2 mmol), and acetonitrile (5 mL) were heated at 70–75 °C for 1 h, the solution was evaporated and the residue purified by chromatography on alumina. Recrystallization of the product from the ether eluate yielded white needles (170 mg, 40%): mp 118–120 °C dec (lit.[1b] mp 121–123 °C); IR (KBr) 1860, 1840, 1770 cm^{-1}; NMR ($CDCl_3$) 3.53 (s, 6 H), 3.6–4.0 (m, 2 H), 4.0–4.16 (m, 2 H), 6.15 (s, 2 H); MS, *m/e* 212 (M^+). Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.66. Found: C, 56.48; H, 5.61.

1,2-Dibenzoylbenzene (5d). A mixture of DMBU (456 mg, 4 mmol), *trans*-1,4-diphenyl-2-butene-1,4-dione (472 mg, 2 mmol), and freshly prepared, anhydrous magnesium bromide (30 mg) in xylene (10 mL) was heated at reflux for 16 h in a nitrogen atmosphere. After evaporation of the solvent, the residue was purified by silica gel chromatography. From the ether–petroleum eluate, DMBU (100 mg, 21%) was recovered. The black oil that was obtained from the chloroform eluate was heated at reflux with sodium methoxide (from Na, 230 mg) in methanol for 1 h. After cooling, the solution was neutralized with 10% hydrochloric acid and extracted with ether and the extract was dried over magnesium sulfate. The yellow solid that was recrystallized from acetone–petroleum ether gave light-yellow platelets (200 mg, 29% yield): mp 143–144 °C (lit.[18] 146–147 °C); IR (KBr) 1660 cm^{-1}; NMR ($CDCl_3$) δ 7.33–7.90 (m); MS, *m/e* 286 (M^+).

1,2-Dicarboethoxy-3,6-dimethoxy-1,2,3,6-tetrahydropyridazine. DMBU (1.14 g, 10 mmol) and diethyl azodicarboxylate (1.74 g, 10 mmol) were heated at 70 °C for 1 h in an atmosphere of nitrogen and then distilled. The fraction of bp 116 °C (0.5 mm) solidified. On recrystallization from petroleum ether, it yielded white needles (1.05 g, 36%), which had the following: mp 51–52 °C; IR (film) 1770, 1730, 1718, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (t, 6 H, J = 7 Hz), 3.46 (s, 6 H), 4.16 (q, 4 H, J = 7 Hz), 5.50 (br s, 2 H), 5.93 (d, 2 H, J = 2 Hz); MS, *m/e* 288 (M^+). Anal. Calcd for $C_{12}H_{20}N_2O_6$: C, 50.00; H, 6.94. Found: C, 49.74; H, 6.94.

5-Methoxy-1,4-naphthoquinone (Methyljuglone). A mixture of DMBU (228 mg, 2 mmol), benzoquinone (216 mg, 2 mmol), and silver(I) oxide (231 mg, 1 mmol) in benzene (5 mL) was stirred 14 h at ca. 25 °C and then filtered. The solid was washed with benzene and the (combined) filtrate was evaporated, leaving a dark material. Chromatography on alumina yielded a solid in the benzene eluate. On recrystallization from methanol, the yellow needles (160 mg, 43%) had the following: mp 182–183 °C (lit.[19] mp 187 °C); IR (KBr) 1658 cm^{-1}; NMR ($CDCl_3$) δ 4 (s, 3 H), 6.80 (s, 2 H), 7.2–7.3 (m, 1 H), 7.6–7.7 (m, 2 H); MS, *m/e* 188 (M^+).

Anthraquinone. Heating DMBU (342 mg, 3 mmol) and 1,4-naphthoquinone (158 mg, 1.0 mmol) at 105 °C for 15 h under nitrogen yielded a black solid. Chromatography of this material on silica gel yielded a yellow solid (130 mg, 63%) that on crystallization from ethanol had a melting point and mixture melting point of 283 °C and an IR spectrum identical with that of an authentic sample.

Reaction of DMBU with 2-Methylhydroquinone in the Presence of Silver(I) Oxide. Silver(I) oxide (693 mg, 3 mmol) was added to a stirred solution of DMBU (228 mg, 2 mmol), 2-methylhydroquinone (248 mg, 2 mmol), and benzene (10 mL). This stirred suspension was heated at reflux for 26 h, cooled, diluted with ether, and filtered. Evaporation of the filtrate yielded a residue of solid and oil, which on washing with ether left solid 2-methyl-5,8-dimethoxy-5,8-dihydro-1,4-naphthoquinone as white prisms (100 mg, 21%) from ether and *n*-hexane: mp 87–88 °C; IR (KBr) 1660, 1675 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (d, 3 H, J = 1.2 Hz), 3.13 (s, 3 H), 3.23 (d, 2 H, J = 1.4 Hz), 3.33 (s, 3 H), 3.87 (m, 1 H), 4.50 (m, 1 H), 6.10 (d, 2 H, J = 2 Hz), 6.57 (s, 1 H, J = 1.2 Hz). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.10; H, 6.78. Found: C, 66.08; H, 6.80.

The ether wash from the above procedure was evaporated and the residue purified by preparative TLC with petroleum ether/ether (1:1) as eluant (R_f values given below). 2-Methyl-1,4-benzoquinone (70 mg, 28%) was identical with an authentic sample prepared by oxidation of 2-methylhydroquinone: R_f 0.61; IR (KBr) 1660 cm^{-1}; NMR ($CDCl_3$) 2.10 (d, 3 H, J = 1.4 Hz), 6.60 (d, 1 H, J = 1.4 Hz), 6.70 (s, 2 H). 2-Methyl-1,4-naphthoquinone (45 mg, 13%) had the following: R_f 0.44; IR (KBr) 1660 cm^{-1}; NMR ($CDCl_3$) 2.18 (d, 3 H, J = 1.4 Hz), 6.75 (d, 1 H, J = 1.4 Hz), 7.5–8.20 (m, 4 H); MS, *m/e* 172 (M^+), 157 $(M - 15)^+$, 144 $(M - 28)^+$. The IR and NMR spectra were the same as those listed in standard compilations.[20] 2-Methyl-8-methoxynaphthoquinone (70 mg, 18%) had the following: mp 133–135 °C (lit.[21] mp 125 °C); R_f 0.23; IR (KBr) 1660 cm^{-1}; NMR ($CDCl_3$) 2.13 (br s, 3 H), 4.0 (s, 3 H), 6.70 (br s, 1 H), 7.17–7.33 (m, 1 H), 7.57–7.83 (m, 2 H); MS, *m/e* 202 (M^+), 187 $(M - 15)^+$, 174 $(M - 28)^+$. The presence of 2-methyl-8-methoxynaphthoquinone in the crude product is not excluded; from its reported mp 94 °C[21] we assume that it was absent from our purified products.

1-Carbomethoxy-7,10-dimethoxy-2,5-dioxobicyclo[4.4.0]deca-3,8-diene (6a,b) and 1-Carbomethoxy-10-methoxy-2,5-dioxobicyclo[4.4.0]deca-3,6,8-triene (7). (a) To a stirred solution of DMBU (114 mg, 1 mmol) and 2-carbomethoxy-1,4-hydroquinone (168 mg, 1 mmol) in benzene (10 mL) was added at once silver(I) oxide (462 mg, 2 mmol). The suspension was stirred overnight, diluted with ether, and filtered. The filtrate was partly evaporated to give prisms of isomer **6a** (95 mg, 34%) from ether and petroleum ether: mp 103–104 °C; IR (KBr) 1744, 1698, 1678 cm^{-1}; NMR ($CDCl_3$) δ 3.13 (s, 3 H), 3.30 (s, 3 H), 3.56 (s, 3 H), 3.93 (d, 1 H, J = 2 Hz), 4.30 (d, 1 H, J = 4 Hz), 4.46 (dd, 1 H, J = 2 Hz, 4 Hz), 6.0 (d, 1 H, J = 4 Hz), 6.13 (d, 1 H, J = 4 Hz), 6.66 (s, 2 H); MS, *m/e* 280 (M^+). Anal. Calcd for $C_{14}H_{16}O_6$: C,

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60.00; H, 5.71. Found: C, 60.06; H, 5.81.

The mother liquor from isomer **6a** was evaporated, and the residue was purified by preparative TLC (ether/petroleum ether, 1:1). Isomer **6b** was obtained as an oil (30 mg, 10.7%); IR (film) 1740, 1720, 1690; NMR ($CDCl_3$) δ 3.25 (s, 3 H), 3.28 (s, 3 H), 3.76 (s, 3 H), 3.50–3.90 (m, 2 H), 4.15 (s, 1 H), 5.97 (s, 2 H), 6.63 (s, 2 H); MS, *m/e* 280 (M^+). (b) To a stirred solution of DMBU (342 mg, 3 mmol) and 2-carbomethoxy-1,4-hydroquinone (168 mg, 1 mmol) in benzene (10 mL) was added at once silver(I) oxide (694 mg, 3 mmol). The suspension was stirred overnight, diluted with ether, and filtered. The filtrate was evaporated, and the residue was purified by preparative TLC (ether/petroleum ether, 1:1). From the lower band isomer **6b** (50 mg, 18%) was obtained. From the upper zone a mixture of isomer **6a** and 1-carbomethoxy-10-methoxy-2,5-dioxobicyclo[4.4.0]deca-3,6,8-triene was obtained. The triene was purified by column chromatography on alumina and eluted with ether/petroleum ether (1:4). The yellow plates (50 mg, 20%), from ether–*n*-hexane, had the following: mp 100–101 °C; IR (KBr) 1740, 1680, 1665 cm^{-1}; NMR ($CDCl_3$) δ 3.38 (s, 3 H), 3.63 (s, 3 H), 4.75 (d, 1 H, J = 5 Hz), 6.17–6.76 (m, 2 H), 6,83–7.31 (m, 3 H); MS, *m/e* 248 (M^+). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 5.71. Found: C, 62.79; H, 5.08.

1,4-Diacetoxy-1,4-dimethoxy-2-butene. In attempting to carry out a cycloaddition between DMBU and 3,6-pyridazinedione, we obtained 1,4-oxidation of DMBU. DMBU (1.14 g, 10 mmol) and maleic hydrazide (1.12 g, 10 mmol) in acetonitrile (40 mL) were stirred at ca. 25 °C. Lead tetraacetate (4.43 g) was gradually (20 min) added and the solution was stirred for 2 h. The suspension was filtered and the filtrate was evaporated in vacuo. The residue was distilled to give an oil (1.18 g, 51%): bp 106 °C (0.8 mm); IR (film) 1735, 1225 cm^{-1}; NMR ($CDCl_3$) δ 2.13 (s, 6 H), 3.46 (s, 6 H), 5.90 (s, 2 H), 6.08 (s, 2 H); MS, *m/e* no parent 232, 189 $(M - 43)^+$, 173 $(M - 59)^+$, 142 $(M - 90)^+$. Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.89. Found: C, 52.01; H, 6.82.

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Registry No. **2a**, 762-42-5; **2b**, 623-47-2; **3a**, 83650-24-2; **4a**, 65489-47-6; **4b**, 32136-52-0; **4c**, 14963-97-4; **5a**, 83650-25-3; **5b**, 83650-26-4; **5c**, 83650-27-5; **5d**, 1159-86-0; **6**, 83650-28-6; **7**, 83650-29-7; (*Z,Z*)-DMBU, 83650-30-0; (*E,Z*)-DMBU, 83650-31-1; (*E,E*)-DMBU, 74503-35-8; 1,4-dihydroxy-2-butyne, 110-65-6; 1,4-dimethoxy-2-butyne, 16356-02-8; *m*-methoxybenzoic acid, 586-38-9; 1-methoxynaphthalene, 2216-69-5; anthranilic acid, 118-92-3; tetracyanoethylene, 670-54-2; fumaronitrile, 764-42-1; maleic anhydride, 108-31-6; *trans*-1,4-diphenyl-2-butene-1,4-dione, 959-28-4; 1,2-dicarboethoxy-3,6-dimethoxy-1,2,3,6-tetrahydropyridazine, 83650-32-2; diethyl azodicarboxylate, 1972-28-7; methyljuglone, 4923-61-9; benzoquinone, 106-51-4; anthraquinone, 84-65-1; 1,4-naphthoquinone, 130-15-4; 2-methylhydroquinone, 95-71-6; 2-methyl-5,8-dimethoxy-5,8-dihydro-1,4-naphthoquinone, 83650-33-3; 2-methyl-1,4-benzoquinone, 553-97-9; 2-methyl-1,4-naphthoquinone, 58-27-5; 2-methyl-8-methoxynaphthoquinone, 22273-29-6; 2-carbomethoxyhydroquinone, 2150-46-1; 1,4-diacetoxy-1,4-dimethoxy-2-butene, 83650-34-4; 1,2,3,6-tetrahydro-3,6-pyridazine, 123-33-1.

α-Keto Dianion Precursors via Conjugate Additions to Cyclic α-Bromo Enones

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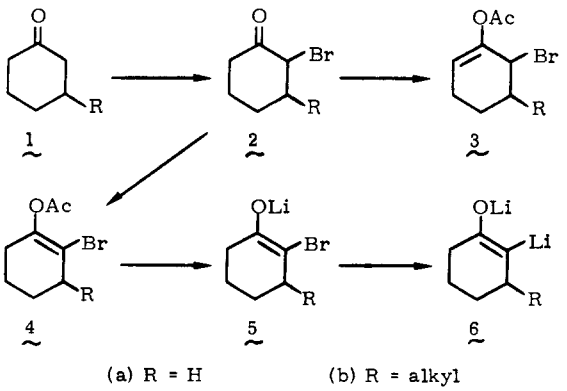
Successful conjugate additions to 2-bromocyclohexenone and 2-bromocyclopentenone have been achieved with a variety of lithium homocuprates, mixed cyanocuprates, and lithium tri-*sec*-butylborohydride as well. In all cases the resulting α-bromo enolate anions could be trapped on oxygen with acetic anhydride; 3-substituted 2-bromo enol acetates were thus obtained regiospecifically and in good yields (Table II, 65–95%). Attempts to extend this methodology to several acyclic bromo enones were largely unsuccessful, as was an attempt to utilize one of the cuprate-derived bromo enolate anions (**12**) directly for formation of an α-keto dianion (**13**). As expected, the α-keto dianion could be prepared in this system by using the corresponding bromo enol acetate (**14** → **13**). α-Bromo enones for all these studies were readily prepared by bromination/dehydrobromination of the corresponding enones in a one-pot procedure and in yields of 71–88% (Table I).

We have previously described[2] the preparation of α-keto dianions (e.g., **6a**, Scheme I) from the corresponding α-bromo enolate anions (**5a**) via metal halogen exchange using *tert*-butyllithium. For bromo ketones lacking enolizable hydrogens at the α′ position, bromo enolates are readily prepared by enolization using lithium hexamethyldisilazide.[2,3] For bromo ketones such as **2a**, however, enolization under these conditions occurs not only toward the bromine but also away, affording a mixture of enol acetates **4a** and **3a**, respectively, on quenching with acetic anhydride. The desired isomer for dianion preparation (**4a**) can be separated and obtained pure in 62% yield even in large-scale runs. While this is acceptable for cheap starting bromides such as **2a**, undesired formation

Scheme I



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