The disulfoxides **2–9** listed in Table I were prepared similarly. Except for the bis(benzylsulfinyl) compounds (**4**), the disulfoxides are substantially water soluble and several were sufficiently hygroscopic to present difficulties in handling and analysis.

Compounds 1 and 2 (Method of Bell and Bennett).[12] The procedure with hydrogen peroxide in glacial acetic acid gave essentially the results previously reported: **1**α, mp 164–165°; **1**β, mp 129–130.5° (lit.[12a] α, 163–164°; β, 128–130°); **2**, mp 146–147° (lit.[12b] 150°). The ir spectrum of **1**β is essentially the same as that of **1**α.

Compound 1α (Method of Leonard and Johnson).[13] The procedure with $NaIO_4$ was essentially as described, except that the water solution of the product was deionized by passing successively through Dowex 1-X4 and Dowex 50W-X8 resins, followed by evaporation and three crystallizations from ethyl acetate, mp 165–167° (lit.[12a] 163–164°).

Registry No.—**1,** 10349-04-9; **2,** 10483-95-1; *dl*-**3,** 56391-04-9; *meso*-**3,** 56348-32-4; *dl*-**4,** 56348-33-5; *meso*-**4,** 56348-34-6; **5,** 56348-35-7; **6,** 56348-36-8; **7,** 56348-37-9; **8,** 56348-38-0; **9,** 50512-41-9; Me_2SO, 67-68-5; 1,2-bis(methylthio)ethane, 6628-18-8; 1,2-bis(ethylthio)ethane, 5395-75-5; 1,2-bis(propylthio)ethane, 22037-97-4; 1,2-bis(benzylthio)ethane, 24794-19-2; 1,3-bis(methylthio)propane, 24949-35-7; 1,4-bis(methylthio)butane, 15394-33-9; 1,4-bis(propylthio)butane, 56348-39-1; 1,5-bis(methylthio)pentane, 54410-63-8; 1,6-bis(methylthio)hexane, 56348-40-4.

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(15) (a) C. C. Price and S. Oae, "Sulfur Bonding", Ronald Press, New York, N.Y., 1962, p 73 ff, assign sulfone group frequencies in the regions 1100–1200 and 1300–1400 cm^{-1}. (b) We prepared the disulfone 1,2-bis(methylsulfonyl)ethane by the method of A. E. Wood and E. G. Travis, *J. Am. Chem. Soc.*, **50,** 1226 (1928), mp 192–193° [P. Allen, Jr., *J. Org. Chem.*, **7,** 23 (1942) reports mp 190°]: ir (KBr) 492, 528, 1118, 1150 (shoulder at 1140), and 1331 cm^{-1}. (c) We prepared 1,2-bis(ethylsulfonyl)ethane as in ref 15b, mp 136° (P. Allen, Jr., reports mp 136–137°): ir (KBr) 533, 568, 1142, and 1275 cm^{-1} (broad band).
(16) Product of Aldrich Chemical Co.: ir (neat, NaCl disks).
(17) Three bis(methylthio) compounds (n = 3, 4, and 5) were prepared from methyl mercaptan and the appropriate dichlorides by the procedure of S. T. Morgan and W. Ledburg, *J. Chem. Soc.*, **121,** 2882 (1922): bp° 83–86.5 (13 mm), 87–89 (6 mm), and 84 (2 mm) [M. Protiva et al., *Chem. Listy*, **47,** 580 (1953); *Chem. Abstr.*, **49,** 155 (1955), report 92 (15 mm), 121–123 (28 mm), and 112–114 (8 mm), respectively]. 1,2-Bis(benzylthio)ethane was prepared from *S*-benzylthiouronium chloride and ethylene dibromide by the method of R. H. Baker, R. M. Dodson, and B. Riegel, *J. Am. Chem. Soc.*, **68,** 2636 (1946), mp 38–39° [S. Mathias, *Bol. Fac. Filos. Cienc. Let., Univ. Sao Paulo, Quimica*, **14,** 75 (1942); *Chem. Abstr.*, **40,** 2792 (1946), reports mp 39.4–40.4°].
(18) 12 *M* HCl was added to the mixture or premixed with Me_2SO to concentration of 0.2–0.5 *M* HCl. Premixed solutions, stored on the shelf for months, retained their titer and reactivity.
(19) *Caution.* Benzene should be trapped to avoid noxious vapors.

A Convenient New Procedure for Synthetic Reactions of Gaseous Alkenes via Automatic Gasimetry

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Syntheses involving gaseous alkenes often prove problematic, especially where stoichiometric control of reagents is desired. Where justified by continual need, a variety of systems have been developed, e.g., the use of constant-pressure controllers coupled with wet test flow meters. In most cases, however, the occasional user resorts to one of three methods. Either the gas is passed through the reaction mixture in considerable excess (*resulting in* loss and disposal requirements for considerable quantities of flammable gas) or *contained in* gas burets (*cumbersome for* all but very small scale), or else the reaction is run in a pressurized autoclave (*with complications* for subambient temperature operation). Of these three, only the gas buret is readily amenable to stoichiometric control. In connection with other work, we have had occasion to carry out such reactions and find a marked convenience in quantitative automatic gasimetry.

Quantitative automatic gasimetry[1] has proven valuable both in synthesis and in reaction studies. With this technique—first employed in hydrogenation—the gaseous reagent is generated as needed to supply the reaction at a constant pressure, the gas being generated by automatically controlled mixing of two solutions. In addition to hydrogen,[1,2] HCl,[3] CO,[4] O_2,[5] and CO_2[6] have been utilized. In many cases considerably higher yields are obtained through ready optimization of reaction times.[3,5]

Gaseous alkenes are readily prepared by addition of the corresponding 1,2-dibromoalkane to a hot suspension of zinc powder in ethylene glycol. Of the numerous methods envisioned which have been tested, this alone met the requirements: rapid *and* quantitative alkene generation; lack of gel or precipitate formation; and available, inexpensive reagents. Reactions were carried out in an apparatus (Figure 1) modified from the hydrogenator previously described[1] by addition of heating for the generator and insertion of a U-tube packed with porous $CaCl_2$ as a trap between the generator and reactor. The concentration of neat

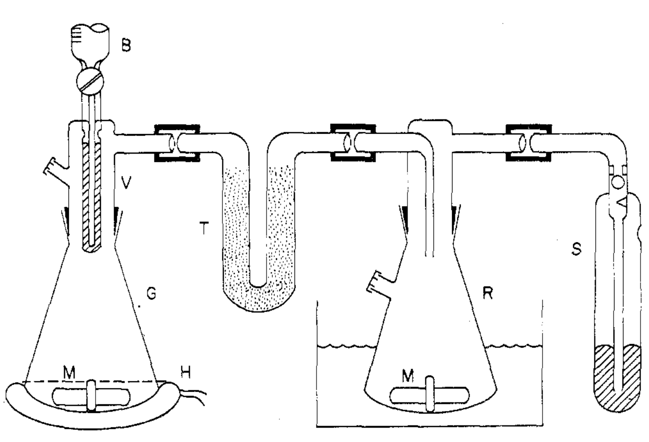
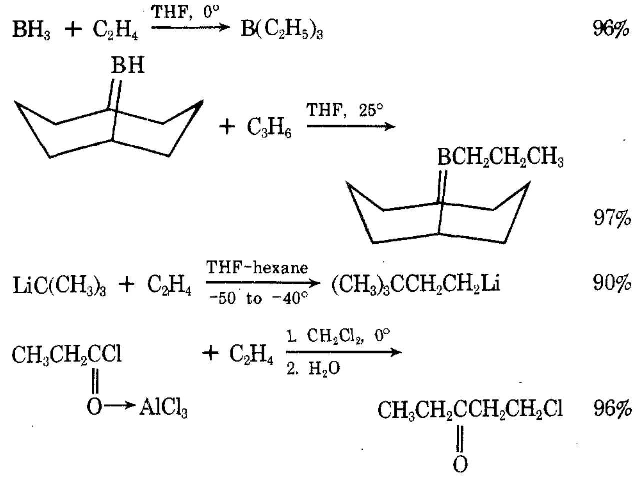


Figure 1. Automatic gasimeter adapted from Brown^{2} hydrogenator (Delmar Scientific Glass Division of Coleman Instruments Co., Maywood, Ill.): ////, mercury; B, buret containing dibromide; V, mercury valve for regulating addition of dibromide to maintain constant gas pressure; G, generator flask; H, heating mantle; M, poly-TFE covered magnetic stirring bar; T, trap packed with $CaCl_2$; R, reactor flask; S, mercury safety bubbler with anti-backup check valve.

Scheme I[a]



[a] 0.95–1.05 equiv of alkene uptake in all cases.

1,2-dibromoethane and 1,2-dibromopropane, 11.6 and 9.6 *M*, respectively, proved excessive for use with common laboratory-scale reactions (10–200 mmol); 2–5 *M* solutions of the dibromoalkane in diethylene glycol or ethylcarbitol were employed.

The technique has proven useful for hydroboration,[7] anionic addition of organolithium,[8] and aliphatic acylation,[9] as shown in Scheme I. The last reaction has particular potential, as β-chloroethyl ketones are precursors of two versatile synthetic intermediates—isomerically pure vinyl ketones and Mannich bases of methyl ketones.[10]

Experimental Section

Ethylene (General Procedure). A 5 *M* solution of 1,2-dibromoethane (dried over $CaCl_2$, 94.0 g, 43.1 ml, per 100 ml solution) in diethylene glycol or similar solvent was placed in the buret. The 250-ml generator flask was charged with 35–40 g of technical zinc *powder* and 100 ml of ethylene glycol. The mixture in the generator was aggitated with a magnetic stirrer and heated to 90–100°. The apparatus was purged with dry nitrogen and the reaction mixture was introduced into the reactor. Then 0.5 ml of 1,2-dibromoethane was added to the generator. When gas evolution was observed at the bubbler, 8–9 ml of *neat* 1,2-dibromoethane was added to maintain vigorous gas evolution, purging the reactor with ethylene (~2.5 l. is produced). Upon cessation of gas evolution, stirring was begun in the reactor; the stirring rate was adjusted so that ethylene uptake did not exceed 7.5 mmol/min.

A parallel procedure was used to generate propylene from 1,2-dibromopropane. With 5.0 *M* dibromide solution, 20.5–21 ml produced 100 mmol of alkene.

***B*-Ethyl-9-borabicyclo[3.3.1]nonane.** A 125-ml reaction flask (magnetic stirring bar, injection port sealed with a rubber septum) was attached to the gas generator and purged with dry nitrogen. Into the flask was placed 56 ml (25.0 mmol) of 0.44 *M* 9-borabicyclo[3.3.1]nonane (9-BBN) in THF.[11a] The flask was placed in a 20° water bath and purged with ethylene; reaction was initiated by slowly bringing the stirrer up to the desired speed. After an initial surge saturating the solution with ethylene (0.09 mmol of C_2H_4/ml of solution) absorption continued until 25.0 mmol of ethylene had been consumed in 1.0 hr. Prolonged further stirring had no effect. Hydrolysis of a sample of the reaction mixture with THF–methanol showed no active hydride remaining.[11b] Oxidation of the reaction mixture at 0° with NaOH–H_2O_2[12] produced 24.3 mmol of ethanol by GLC (decane standard, UCON Polar liquid phase), a yield of 97% based on B–H or on ethylene.

***B*-*n*-Propyl-9-borabicyclo[3.3.1]nonane.** In the manner described for the *B*-ethyl compound, 9-BBN was reacted with propylene. The solution dissolves 0.55 mmol of propylene/ml. The reaction was complete in 1.0 hr, absorbing 26.1 mmol of propylene. The yield was 97% based on B–H, 93% based on propylene.

1-Chloro-3-pentanone. The 1:1 complex of propionyl chloride with aluminum chloride was ethenated in dichloromethane (2.0 *M* concentration) at 0° as described by McMahon et al.[10c] After 60 min (104 mmol of C_2H_4 used) the reaction mixture was hydrolyzed with 6.5 molar equiv of water and the $AlCl_3 \cdot 6H_2O$ sand was separated. GLC of the filtrate (decane standard, polyester column) showed 96% yield of 1-chloro-3-pentanone.

Neohexyllithium. *tert*-Butyllithium was ethenated at −40 to −50° in pentane–THF as described by Bartlett et al.[8] in 90% yield, based on reaction of the product with methyl borate and then oxidation to neohexyl alcohol.[13]

Registry No.—1,2-Dibromoethane, 106-93-4; ethylene, 74-85-1; propylene, 115-07-1; *B*-ethyl-9-borabicyclo[3.3.1]nonane, 52102-17-7; 9-borabicyclo[3.3.1]nonane, 280-64-8; *B*-*n*-propyl-9-borabicyclo[3.3.1]nonane, 1127-78-2; 1-chloro-3-pentanone, 32830-97-0; propionyl chloride 1:1 complex with aluminum chloride, 36379-65-4; neohexyllithium, 6909-52-0; *tert*-butyllithium, 594-19-4.

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Basicity of the Carbonyl Group. V. Applicability of the Taft–Pavelich Equation to Cyclic Systems with Reference to the Complexation Enthalpy of Cyclic Ketones Using Boron Trifluoride

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Experimental calorimetric data verify the Taft–Pavelich equation for inductive and steric effects in substituted five- and six-membered rings.

The use of linear free energy relationships of the form log $k/k_0 = \rho^*\sigma^* + \delta E_s$ (I) (the Taft–Pavelich equation) has spread to numerous fields of experimental science[1] since the initial work of Taft[2] on the separation of the polar and steric effects of substituents.

We have recently shown[3] that eq II

$$\Delta H^0_R = (3.74 \pm 0.22)\sigma^* - (0.77 \pm 0.17)E_s - 18.21 \text{ kcal mol}^{-1} \quad \text{(II)}$$

can be applied in a satisfactory manner to the reaction enthalpy of CH_3COR ketones with boron trifluoride over a