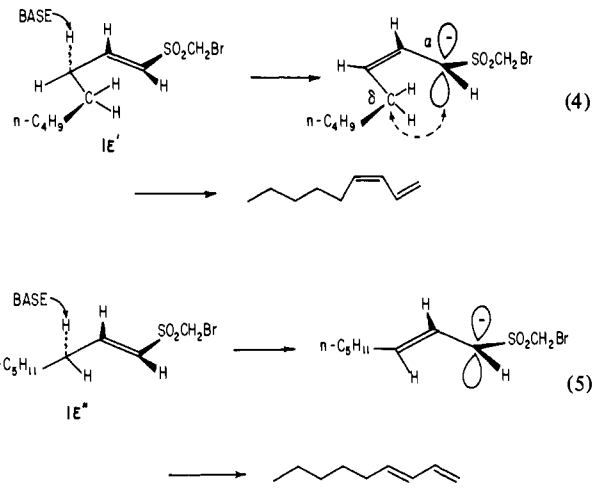
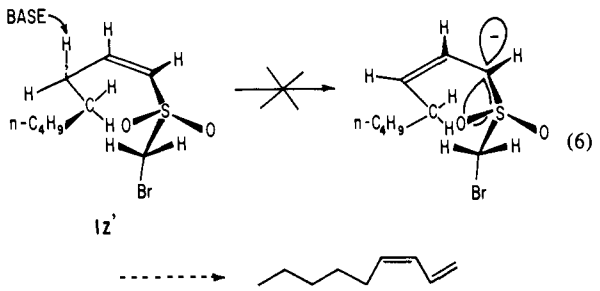
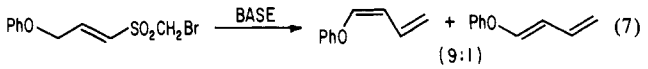
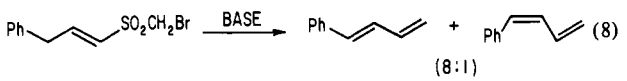


is assumed that the isomerization is kinetically controlled. In **1Z** the possibility of a stabilizing syn interaction between the α- and δ-position is precluded for steric reasons if **1Z'**, eq 6, is assumed

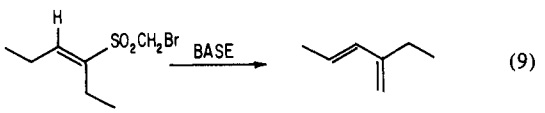


to be the transition state required for formation of *Z* diene. The syn effect is still seen with the replacement of the δ-CH_2 group in **1E** by oxygen[15] but not by a phenyl group (eq 7 and 8). On

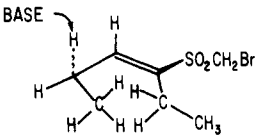




the other hand, replacement of the α-hydrogen in (*E*)-1-alkenyl bromomethyl sulfones by an alkyl group (see eq 9) results in



exclusive formation of the *E* diene upon treatment with base; syn interaction is sterically precluded here (see **7**).



7

Acknowledgment. We gratefully acknowledge support for this work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Prof. Shelton Bank and Henry Kuivila for helpful discussions and the Callery Chemical Co. for chemical samples.

(15) Compare halogen syn effects: Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1963**, *10*, 622.

Registry No. **1E** (R = n-C_5H_{11}), 86823-63-4; **1E** (R = C_6H_5O), 86823-64-5; **1E** (R = C_6H_5), 86823-65-6; **1Z** (R = n-C_5H_{11}), 86823-66-7; **2**, 54730-18-6; **3** (R = n-C_5H_{11}), 86823-67-8; **4**, 86823-68-9; **5**, 86823-69-0; **6**, 86823-70-3; (*Z*)-1,3-nonadiene, 77192-27-9; (*E*)-1,3-nonadiene, 56700-77-7; (*E*)-1-octenyl phenyl sulfone, 77144-81-1; (*Z*)-2-octenyl phenyl sulfone, 86823-71-4; (*E*)-3-((bromomethyl)sulfonyl)-3-hexene, 86823-72-5; (*Z*)-1-phenoxy-1,3-butadiene, 25752-60-0; (*E*)-1-phenoxy-1,3-butadiene, 52752-61-1; (*E*)-1-phenyl-1,3-butadiene, 16939-57-4; (*Z*)-1-phenyl-1,3-butadiene, 31915-94-3; (*E*)-2-ethyl-1,3-pentadiene, 69530-49-0; 1,3,5-trithiane, 291-21-4; 1-octene, 111-66-0; methylenecylohexane, 1192-37-6; 2-methyl-2-butene, 513-35-9; 2-octene, 111-67-1.

α-Haloalkanesulfonyl Bromides in Organic Synthesis. 2. A Useful New 1,3-Diene Synthesis[1]

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The preceding communication[1c] describes a new reaction whereby α,β-unsaturated bromomethyl sulfones are converted into 1,3-dienes with base. Since these sulfones can be made from olefins by addition of readily accessible[1c] bromomethanesulfonyl bromide ($BrCH_2SO_2Br$, **1**) followed by dehydrobromination, the overall process is a three-step transformation of olefins into 1,3-dienes bearing one more carbon atom. The same process can be achieved in two steps if the olefin–**1** adducts are treated with an excess of base (eq 1). We wish to report that these sequential

$$RCH_2CH{=}CH_2 \xrightarrow{1} RCH_2CHBrCH_2SO_2CH_2Br \xrightarrow{\text{base}} RCH_2CH{=}CHSO_2CH_2Br \xrightarrow{\text{base}} RCH{=}CHCH{=}CH_2 \quad (1)$$

reactions work admirably with a wide range of acyclic and cyclic olefins and diolefins, constituting an easy and economical synthesis of dienes, and that this procedure represents a fundamentally new synthetic method for attachment of methylene groups to interior carbon atoms in chains (eq 2) or to ring carbon atoms, providing access to compounds that would be otherwise difficult to prepare.[2]

$$RCH_2CH{=}CHCH_2R \xrightarrow[2.\ \text{base}]{1.\ 1} (E)\text{-}RCH_2C(=CH_2)CH{=}CHR \ (60\text{–}70\%) \quad (2)$$

Table I illustrates the application of our procedure to the synthesis of terminal, branched internal, and heterosubstituted acyclic 1,3-dienes and bis(1,3-dienes) as well as 1-vinyl- and 3-methylene-1-cycloalkenes and 1,2-bismethylenecycloalkanes. In a representative case, (*E*)-7-tetradecene (0.02 mol; Table I, entry 2) in CH_2Cl_2 (1:1 v/v) in a Pyrex tube is chilled to −15 °C[3] and treated with **1** (0.03 mol) in CH_2Cl_2 (1:1 v/v). After 2-h irradiation at −15 °C,[4] Et_3N (0.03 mol) in 90 mL of CH_2Cl_2 was

(1) (a) The material covered in this communication is the subject of a U.S. Patent Application filed by the Research Foundation of the State University of New York. (b) Presented in part at the International Symposium on Heteroatoms for Organic Synthesis, Montreal, August 16, 1983 and at the 186th ACS National Meeting, Washington, D.C., September 1, 1983. (c) Part 1: Block, E.; Aslam, M. *J. Am. Chem. Soc.*, preceding communication in this issue.

(2) Lengthy syntheses are required for 3-methylenecycloalkenes: Dauben, W. G.; Poulter, C. D.; Suter, C. *J. Am. Chem. Soc.* **1970**, *92*, 7408–7412. Short, M. R. *J. Org. Chem.* **1972**, *37*, 2201–2202.

(3) Components should be chilled to −15 °C before mixing since **1** undergoes vigorous, spontaneous, exothermic reactions with particularly reactive olefins. Due caution should be exercised in scaling up reactions of **1**.

(4) A 450-W Hanovia lamp was used. With more reactive olefins irradiation times can be reduced to as short as 15 min and 1 equiv of **1** can be used.

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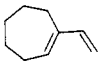
Table I. Diene Synthesis with Bromomethanesulfonyl Bromide

	olefin	product (isomer ratio[a])	yield, %[b]
1	n-$C_6H_{13}CH{=}CH_2$	n-$C_5H_{11}CH{=}CHCH{=}CH_2$ (2:1)[c]	61
2	(*E*)-n-$C_6H_{13}CH{=}CH$-n-C_6H_{13}	(*E*)-n-$C_5H_{11}CH{=}CHC(n\text{-}C_6H_{13}){=}CH_2$	71[d]
3	(*E*)-n-$C_5H_{11}CH{=}CHCH_3$	(*E*)-n-$C_4H_9CH{=}CHC(CH_3){=}CH_2$ + $CH_2{=}CHC(n\text{-}C_5H_{11}){=}CH_2$	52 15
4			74
5			49[e]
6			56
7	$PhCH_2CH{=}CH_2$	$PhCH{=}CHCH{=}CH_2$ (1:8)	85
8	$PhOCH_2CH{=}CH_2$	$PhOCH{=}CHCH{=}CH_2$ (9:1)	54
9	$HO(CH_2)_9CH{=}CH_2$	$HO(CH_2)_8CH{=}CHCH{=}CH_2$ (5:1)	86
10	$(CH_3)_3SiCH_2CH{=}CH_2$	$(CH_3)_3SiCH{=}CHCH{=}CH_2$ (1:10)	41
11			35[e,g]
12	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	$CH_2{=}CH(CH_2)_5CH{=}CHCH{=}CH_2$	49[f,g,h]
13	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	$CH_2{=}CHCH{=}CH(CH_2)_4CH{=}CHCH{=}CH_2$	40[i,j]

[a] *Z*/*E* ratio. [b] Overall yield of distilled product. [c] *Z*/*E* ratios 5:1 and 1:16 from (*E*)- and (*Z*)-1-octenyl bromomethyl sulfones, respectively.[1c] [d] Analysis by GC showed <1% *Z* isomer. [e] Et_3N step omitted. [f] Isomers not resolved by GC. [g] Two equivalents of diene used. [h] Ca. 5% of 1,3,9,11-dodecatetraene. [i] Two molar equivalents of **1** used. [j] 80% *Z*,*Z*.

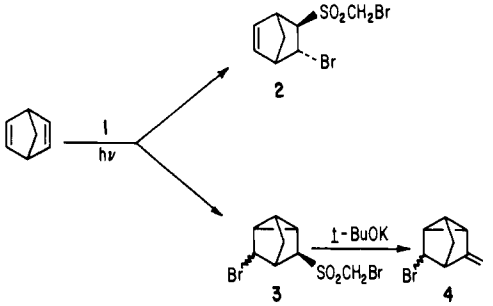
added,[5] the mixture was refluxed for 1 h, washed (aqueous HCl), dried, concentrated in vacuo, dissolved in 30 mL of 1:9 THF/*t*-BuOH, and added to a well-stirred solution of *t*-BuOK (0.06 mol) in 100 mL of 1:9 THF/*t*-BuOH at 0 °C. The solution was warmed to 20 °C, diluted with 200 mL of water, and extracted (hexane). Workup (partitioning in water–hexane) and distillation afforded (*E*)-2-*n*-hexyl-1,3-nonadiene (<1% *Z* isomer)[6] in 71% overall yield. The entire synthesis may be completed in a day.

Following this procedure 10-undecen-1-ol (entry 9) was converted into (*E*)- and (*Z*)-9,11-dodecadien-1-ol, which was acetylated giving 9,11-dodecadien-1-ol acetate (71% overall yield, 5:1 Z/E), the sex pheromone of the red bollworm moth. While other syntheses of this pheromone have been reported,[7] our approach is particularly attractive because of its simplicity, high yield, low cost of reagents, and use of commercially available starting material. Also noteworthy is the conversion of allyltrimethylsilane into 1-(trimethylsilyl)-1,3-butadiene (entry 10) making this useful diene readily available. Previous attempts to add sulfonyl *chlorides* to allyltrimethylsilane led to chlorotrimethylsilane and allyl sulfones (eq 3);[9] a similar reaction occurs when the addition of **1** to allyl trimethylstannane is attempted (eq 4).

$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{MeSO_2Cl,\ Cu_2Br_2} Me_3SiCl + CH_2{=}CHCH_2SO_2Me \quad (3)$$

$$Me_3SnCH_2CH{=}CH_2 \xrightarrow{1,\ h\nu} Me_3SnBr + CH_2{=}CHCH_2SO_2CH_2Br \quad (4)$$

Another novel result is our observation that 1,2-bis(methylene)cycloalkanes are formed from the 1-methyl-1-cycloalkene–**1** adducts (entry 6) by a process that must involve regiospecific deprotonation. We have also examined the reaction of **1** with various *diolefins* (entries 11–13). If *2 equiv* of **1** are used per mol of diolefin, reasonable yields of bis dienes are obtained.[10] If *1 equiv* of **1** is used, or in some cases excess diolefin, addition of a single equivalent of **1** can be readily achieved. In the case of 1,5-cyclooctadiene, no product resulting from intramolecular rearrangement could be detected. However, when **1** was treated with excess norbornadiene a 1:1 mixture of *endo*-6-bromo-*exo*-5-norbornen-2-yl bromomethyl sulfone, **2**,[8] and 5-bromo-3-nortricyclyl bromomethyl sulfone (exo/endo mixture), **3**,[8] could be isolated in 96% yield (eq 5), a result consistent with a homolytic



(5)

pathway for addition of **1**. Treatment of **3**, isolated by chromatography, with *t*-BuOK gave 5-bromo-3-methylenenortricyclane (6.2:1 exo/endo ratio), **4**,[8] in 32% distilled yield; the same product could also be obtained from the original mixture of **2** and **3**. On the basis of previous studies of radical addition of benzenesulfonyl halides to norbornadiene,[11] the above results suggest that **1** is a more efficient radical chain transfer agent than benzenesulfonyl bromide.

Our observations that **1** may be easily prepared from inexpensive starting materials (e.g., formaldehyde, hydrogen sulfide, and bromine), that **1** displays high reactivity toward most olefins with good regioselectivity and minimal side reactions, and that the olefin–**1** adducts may be transformed rapidly, stereoselectively, and under mild conditions with simple reagents into dienes in good

(5) This step conserves the more expensive *t*-BuOK and circumvents the yield-lowering vigorous reaction of the latter reagent with the olefin-**1** adduct.

(6) $Bp_{0.034\ mm}$ 60–62 °C; IR 1610, 970, 890 (all m) cm^{-1}; ^1H NMR δ 0.7–1.7 (20 H), 1.7–2.3 (m, 4 H, $CH_2C{=}$), 4.62 (s, 2 H, $={CH_2}$), 5.0–5.6 (d of t, J = 6, 15 Hz, 1 H, CH=), 5.82 (d, J = 15 Hz, 1 H, CH=); ^{13}C NMR δ_c 14.1, 22.66, 22.76, 28.48, 29.29, 29.45, 31.56, 31.88, 32.42, 32.6, 112.79, 130.16, 132.21, 146.67.

(7) (a) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1982**, *23*, 3277–3280. (b) Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1979**, *44*, 3723–3724. (c) Hayashi, T.; Yanagida, M.; Matsuda, Y.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2665–2668 and references therein.

(8) All new compounds have been fully characterized by spectral means.

(9) Pillot, J. P.; Dunogues, J.; Calas, R. *Synthesis* **1977**, 469.

(10) Poor yields of some of these compounds are realized by using Wittig methodology, e.g., by using bis ylides and acrolein: Hauser, C. F.; Brooks, T. W.; Miles, M. L.; Raymond, M. A.; Butler, G. B. *J. Org. Chem.* **1963**, *28*, 372–379.

(11) Cristol, S. J.; Davies, D. I. *J. Org. Chem.* **1964**, *29*, 1282–1284.

yields and high purity suggest that the reactions described herein will prove particularly useful in both small- and large-scale synthesis. Preliminary experiments indicate that $ClCH_2SO_2Br$[12] can be substituted for **1** in eq 1 providing added flexibility and reduced cost. Additional synthetic applications of **1** and related reagents will be described elsewhere.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the Phillips Petroleum Co. and Prof. W. Closson for generously providing us with samples of a variety of olefins used in this study.

(12) $ClCH_2SO_2Br$ can be readily prepared in 60–70% yield by treatment of $ClCH_2SO_2Na$ (obtained by Na_2SO_3 reduction of $ClCH_2SO_2Cl$) or $ClCH_2SSCH_2Cl$ with Br_2/H_2O.

Charge-Transfer Excitation of Electron Donor–Acceptor Complexes. Direct Observation of Ion Pairs by Time-Resolved Picosecond Spectroscopy

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Electron donor–acceptor (EDA) complexes have been observed experimentally[3] and have been proposed as intermediates in many types of chemical reactions.[4] Among the earliest and most important examples are the 1:1 EDA complexes of various dienes and dienophiles involved in the Diels–Alder reaction,[5,6] Indeed, theoretical studies have delineated the importance of charge-transfer (CT) interactions in thermal [4 + 2] as well as [2 + 2] cycloadditions.[7] Experimental support for such formulations is found in the observation of a direct relationship between the second-order rate constant (log k) for the Diels–Alder cycloaddition and the CT transition energy ($h\nu_{CT}$) for the EDA complexes of various anthracenes with tetracyanoethylene.[8-10]

The EDA complex consisting of either 9-cyanoanthracene (CNA) or indene (IN) with tetracyanoethylene (TCNE) is ideally suited for picosecond spectroscopic studies since the CT absorption bands (Figure 1) are well separated from the absorption bands of the uncomplexed donors and TCNE. Thus we are assured that irradiation with the available 532-nm, 25-ps laser pulse (~1–2 mJ)[11] specifically populates only the CT excited state of the EDA complex.[12,13]

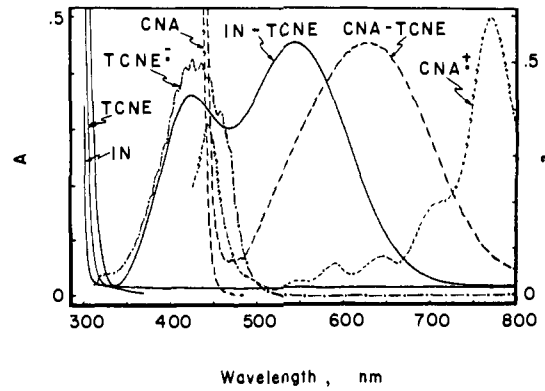

Figure 1. Electronic absorption spectra of CNA, IN, TCNE, CNA–TCNE EDA complex, IN–TCNE EDA complex, $TCNE^{-\cdot}$, and $CNA^{+\cdot}$ in CH_2Cl_2. The absorbances of IN, TCNE, and IN–TCNE were plotted relative to the left ordinate while CNA and CNA–TCNE were plotted relative to the right ordinate; concentrations of IN, CNA, and TCNE were uniformly 0.015 M. The radical ions, whose spectra are plotted in relative absorbance units, were generated electrochemically in CH_2Cl_2 containing 0.1 M TBAP at room temperature.

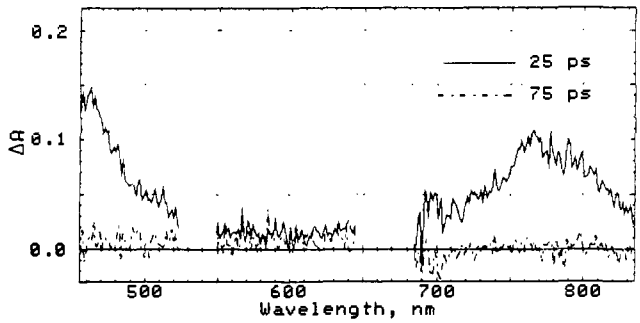

Figure 2. Difference absorption spectra measured for the CNA–TCNE (0.08 M each) EDA complex in CH_2Cl_2 at 25 and 75 ps after excitation with a 532-nm, 25-ps laser pulse.

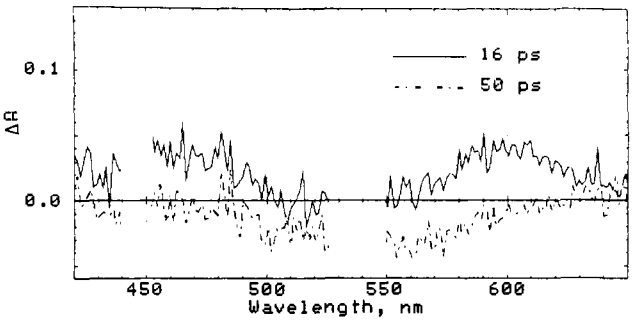

Figure 3. Difference absorption spectra measured for the IN–TCNE (0.05 M each) EDA complex in CH_2Cl_2 at 16 and 50 ps after excitation with a 532-nm, 25-ps laser pulse.

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(11) See: Kelley, D. F.; Rentzepis, P. M. *Chem. Phys. Lett.* **1982**, *85*, 85. Reynolds, A. H.; Rentzepis, P. M. *Biophys. J.* **1982**, *38*, 15.
(12) In most other systems examined previously, the CT bands were not sufficiently well separated from the absorption bands of either component to allow unambiguous excitation of only the CT band. Compare: (a) Kobayashi, T.; Matsumoto, S.; Nagakura, S. *Chem. Lett.* **1974**, 235. (b) Hinatu, K.; Yoshida, F.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, *59*, 80; Masuhara, H.; Shimada, M.; Tsujino, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3310. Masuhara, H.; Tsujino, N.; Mataga, N. *Ibid.* **1973**, *46*, 1088. (c) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153 and references therein.

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