of Hydrocarbons by CsK Na Alloys", IUPAC Symposium on Ions and Ion Pairs and Their Role in Chemical Reactions, Syracuse, N.Y., May 31, 1978.

(17) Murray A., III; Williams, D. L. "Organic Syntheses with Isotopes"; Interscience: New York, 1958; Part 1, p 900.

(18) The general procedure was as follows. NaK (0.5 g) was added to a mixture of 20 mL of glyme and 20 mL of triglyme in a 300-mL round-bottom flask (argon sweep) which had been cooled to −40 °C. The mixture was stirred until a constant blue color was achieved. The solution was warmed to 0 °C and 1 g of substrate was added. The mixture was stirred at 0 °C for 3 h. Methyl-^{14}C iodide[13] (1-2 mL) was added dropwise until the solution was clear yellow. The mixture was cooled to <20 °C and excess NaK was removed mechanically. Pentane (or benzene, depending on substrate) (20 mL) was added, followed by 100 mL of H_2O. After separation of organic layer, it was concentrated and subjected to GC (with carbon-14 monitor) analysis (Barber-Coleman Model 5000). The products were identified by preparative GC (Varian Aerograph Series 2860) separation followed by NMR analysis (both ^1H and ^{13}C)

(19) (a) Ott, E. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2139. (b) ^1H NMR spectra of *meso-* and *dl*-1,2-diphenylbutane: the methyl resonance of the meso isomer was a doublet centered at 1.03 ppm, whereas the methyl doublet of the *dl* isomer was centered at 1.29 ppm downfield from the meso isomer as expected; the methine hydrogen of both isomers was a poorly resolved multiplet centered at 2.90 ppm; both isomers had broadened aromatic resonance at 7.15 ppm.

(20) (a) Goldschmidt, G. *Monatsh. Chem. Verw. Teile Anderer Wiss.* **1881**, *2*, 433. See also "Beilstein's Handbuch der Organische Chemie"; Band 5, System Number 708, 3rd Suppl. Vol., p 2324. (b) The ^1H NMR spectrum of the benzylbiphenyl that we isolated consists of one peak at 4.08, an intense aromatic peak at 7.30, and complex aromatic peaks between 7.27 and 7.75 ppm. The ^{13}C NMR spectrum consisted of one aliphatic carbon at 42.02, eight protonated carbons between 124.92 and 128.48, and three peaks, one intense, for quarternary carbons between 141.48 and 140.95 ppm. We thank Dr. E. W. Hagaman for the ^{13}C NMR spectrum.

(21) Vernon, J. M.; Robinson, G. E. *J. Chem. Soc. C* **1970**, 2586.

(22) *p*-Benzylbiphenyl was prepared by the Friedel-Crafts alkylation of biphenyl with benzyl bromide and $AlCl_3$. The para isomer (mp 84 °C) exhibited ^1H and ^{13}C NMR spectra similar to, but not identical with, those of the substances isolated from reaction 3. From the spectra of the mixture of ortho and meta isomers of benzylbiphenyl left after isolation of the para isomer, we conclude that the substances isolated from reaction 3 are mixtures of all three isomers. Independent syntheses of the ortho and meta isomers are now underway. Friedel-Crafts acylation of biphenyl with *p*-toluyl chloride followed by reduction of the ketone yielded the *p*-(*p*-methylbenzyl)biphenyl (mp 86-87 °C) whose ^1H and ^{13}C NMR spectra were identical with those of the substances isolated from reaction 4. Once again, a mixture of all three isomers seems likely. Details will be published later.

(23) Kryger, R. D.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589. We are indebted to a referee for calling our attention to this fact.

(24) Visiting Scientist, May-Sept 1978. Correspondence can be addressed to this author at the Max-Planck Institut für Kohlenforschung, 4330 Mülheim (Ruhr), Kaiser-Wilhelm Platz 1, West Germany.

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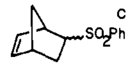
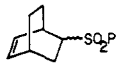
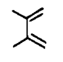
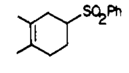
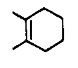
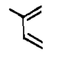
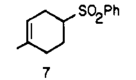
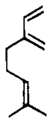
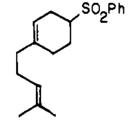
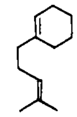
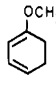
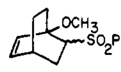
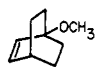
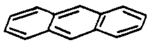
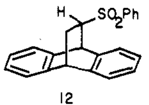
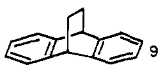
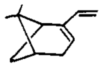
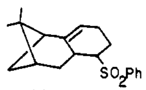
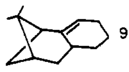
Received May 21, 1979

An Ethylene and Terminal Olefin Equivalent in [4 + 2] π Cycloadditions. General Synthetic Application of Phenyl Vinyl Sulfone to the Construction of Functionalized Six-Membered Rings

Sir:

The widespread use of the Diels-Alder reaction in synthetic organic methodology stems in large part from the frequent need to elaborate six-membered rings and the customarily high efficiency of such cycloadditions. A long-standing restriction to the universal application of this chemistry materializes when the diene and dienophile have no π-donor-acceptor complementarity. This phenomenon is witnessed perhaps most acutely in the case of ethylene,[1-4] although allyl compounds in general also exhibit slight dienophilic reactivity.[5,6] Despite the serious constraints caused by the natural reluctance of such olefinic partners to enter into concerted cycloaddition,[1c] no general, suitably mild, and regiospecific (for terminal olefinic synthons) alternative has yet been devised. In this communication, we demonstrate that phenyl vinyl sulfone[7] can serve very conveniently as an ethylene equivalent in [4 + 2] cycloadditions. Furthermore, since **1** is captured by unsymmetrical dienes with high regioselectivity, the α-sulfonyl carbanion centers in the adducts are available for the regiospecific attachment of appendages and/or functional groups. As a result, these intermediates are utilizable in manifold ways as terminal olefin equivalents. Exploitation of these results should serve to augment our ability to elaborate complex cyclohexane derivatives more expeditiously.

Table I. Ethylene Equivalency. Cycloadditions of Phenyl Vinyl Sulfone and Reductive Desulfonylation of the Adducts

diene	reactn conditions	adduct structure	cycloaddn yield, %[a]	desulfonyln product[b]	yield, %[a]
	25 °C, 110 hr.	 [c] **1**	100	 **2**	80
	125 °C, 17 hr.	 [d] **3**	89	 **4**	78
	135 °C, 32 hr.	 **5**	94	 **6**	76
	120 °C, 28 hr	 **7**	93	- - - - -	
	155 °C, 22 hr.	 [e] **8**	98	 **9**	92
	135 °C, 18 hr.	 [f] **10**	88	 **11**	91
	155 °C, 100 hr.	 **12**	96	 **13**	94
	150 °C, 28 hr.	 **14**	98	 **15**	97

[a] The yields are based upon quantities of pure material isolated after column chromatography except in the cases of **2**, **4**, and **6** which were purified by distillation. [b] All products exhibited satisfactory IR, NMR, mass, and microanalytical data unless known previously; in these circumstances, direct spectral comparisons with authentic samples were made. [c] 22% exo, 78% endo mixture (see ref 8i). [d] 19% exo, 81% endo mixture. Regiochemistry assigned on the basis of analogy to **7**. [f] 18% exo, 82% endo (syn to double bond) mixture.

The concept of utilizing simple α,β-unsaturated sulfones as dienophiles is not new. Isolated examples of their use by various investigators have been reported.[8] The objectives of the past studies range from comparisons of relative rate ratios and analyses of exo-endo stereoselectivities to the incorporation of a sulfone group for chemical purposes. Because symmetrical dienes were always employed, no information has been previously uncovered concerning the regiochemistry of these

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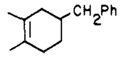
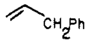
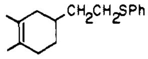
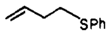
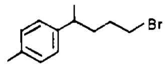
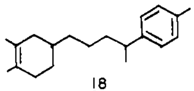
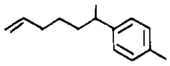
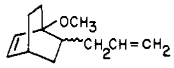
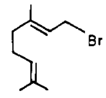
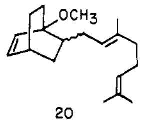
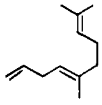
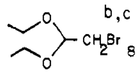
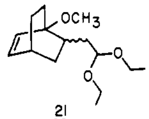
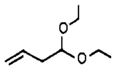
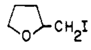
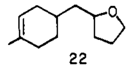
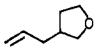
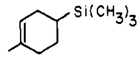
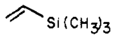
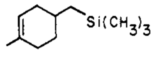
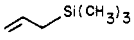
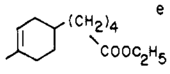
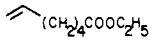
Table II. Terminal Olefin Equivalency. Sequential Alkylation-Desulfonylation of Selected Adducts

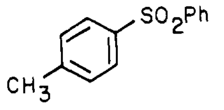
adduct	electrophile	alkyln yield, %[a]	desulfonyln product	desulfonyln yield, %[a]	synthon represented
5	$PhCH_2Br$	89	 **16**	96	
5	$PhSCH_2CH_2Br$	86	 **17**	83	
5		81	 **18**	93	
10	$CH_2{=}CHCH_2Br$	87	 **19**	95	
10	 [b]	95	 **20**	93	
10	 [b,c]	83	 **21**	80	
7	 [b]	73	 **22**	84	
7	$(CH_3)_3SiCl$	86	 **23**	79	
7	$(CH_3)_3SiCH_2OSO_2CF_3$	78	 **24**	92	
7	$I(CH_2)_4COOC_2H_5$ [b,c,d]	87	 **25**	81[e]	

[a] The yields are based upon quantities of pure material isolated after column chromatography. All products exhibited satisfactory IR and ^1H NMR spectra. In addition, **16–25** were characterized by mass spectral and combustion analysis. [b] In contrast to the usual alkylation solvent employed (anhydrous tetrahydrofuran), these reactions were conducted in 90% tetrahydrofuran-10% hexamethylphosphoramide solution. [c] An inverse addition procedure was used. [d] Purification by preparative layer chromatography. [e] Reduction conducted at room temperature in ethanol-tetrahydrofuran (4:1) instead of the customary methanol-tetrahydrofuran (4:1) solvent system to preclude ester interchange.

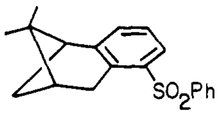
reactions. In a relevant finding, Konovalov demonstrated that ethyl vinyl sulfone is ~50% less reactive than methyl acrylate toward cyclopentadiene and 2,3-dimethylbutadiene.[8g]

Our general process for cycloadditions to phenyl vinyl sulfone consists of admixture of the diene and dienophile in a small amount of benzene (typically 1 mL/g of sulfone) and heating as required (see Table I), in a sealed tube if necessary. Commonly, the reactions proceed smoothly and essentially quantitatively to give crystalline products. The generally available Lewis acid catalysts give no evidence of accelerating these reactions; some darkening and product destruction occur instead.

Direct ^1H and ^{13}C NMR analysis of adducts **7** and **8**, in tandem with thin layer chromatography, indicated that single isomers had been produced. Further, DDQ dehydrogenation of **7** gave phenyl *p*-tolylsulfone (**26**);[9] the indicated addend regiochemistry was thereby established. Comparable treatment of **14** led to **27** whose 1,2,3-trisubstituted benzene nature was clearly apparent from its ^1H NMR spectrum.[10]



26



27

Reductive desulfonylation of the adducts was best accomplished through the use of excess 6% sodium amalgam in disodium hydrogen phosphate buffered methanol at −20 °C.[11] The yields proved excellent in every case. Although regiospecificity has been observed in the relevant examples examined to date, this criterion is not of consequence where ethylene equivalency is desired, since both dienophilic carbon centers are ultimately converted into unsubstituted methylene groups (Table I).

The most notable advantage of the high regiochemical control imparted by phenyl vinyl sulfone materializes when the original adducts are subjected to an alkylation-desulfonylation sequence (Table II). Through reaction of the derived α-sulfonyl carbanions with a variety of electrophiles, site specific functionalization becomes possible. In most instances, tetrahydrofuran is an adequate solvent to achieve quite acceptable yields. However, smooth alkylation with less reactive or more recalcitrant coreagents is assisted by HMPA as cosolvent (10%).

Subsequent removal of the phenyl sulfonyl residue provides for facile directed incorporation of widely varied side chains. A particular advantage of the method is the stability of numerous functional groups, e.g., $-SPh$, $-Si(CH_3)_3$, $-COOC_2H_5$, etc., to the action of sodium amalgam. Control of the pH of the reaction medium is considered significant here. In any event, a rich selection of terminal olefinic synthons are made available in this fashion. Some of the more notable examples of Table II include allylbenzene, 1,4-pentadiene, and ethyl 6-heptenoate, all of which would likely experience prototropic shift and/or polymerization upon attempted Diels-Alder reaction with a nonactivated conjugated diene. Furthermore, electronic factors in these substrates, and their congeners as well, are insufficiently dominant to guarantee useful regiochemical control. Another feature of the present methodology is the ease with which vinylsilane and allylsilane synthons can be regiospecifically incorporated.

In summary, phenyl vinyl sulfone is a conveniently prepared reagent which constitutes a highly efficient synthetic equivalent for ethylene and a wide range of terminal olefins in [4 + 2] π cycloadditions. Further studies involving utilitarian extensions of this and related chemistry are in progress.[12]

References and Notes

(1) (a) Wheeler, R. V.; Wood, W. L. *J. Chem. Soc.* **193**, 1819-1828. (b) Joshel, L. M.; Butz, L. W. *J. Am. Chem. Soc.* **1941**, *63*, 3350-3351. (c) Bartlett, P. D.; Schueller, K. E. *Ibid.* **1968**, *90*, 6071-6077.

(2) The more strained nature of the norbornene double bond causes molecules of this ilk to be more reactive: (a) Alder, K.; Stein, G.; Finzehagen, H. *Justus Liebigs Ann. Chem.* **1931**, *485*, 223-246. (b) Alder, K.; Stein, G.; Reese, J.; Grassmann, W. *Ibid.* **1932**, *496*, 204-251.

(3) Dienophiles of exceptionally high reactivity are known to facilitate cycloaddition to unactivated olefins. See, for example, Eaton, P. E.; Chakraborty, U. R. *J. Am. Chem. Soc.* **1978**, *100*, 3634-3635.

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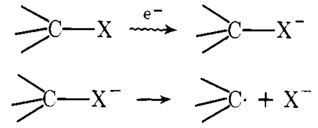
Bond Cleavage of the Solvated Methyl Chloride Anion: A Primary Electrochemical Event

Sir:

Although the specificity of electrochemical reactions lies in the facile reaction pathways provided by removal or addition of electron(s) to the reactants at the electrode,[1] little is known about the actual potential surfaces for these pathways. As an example, the cathodic reduction of alkyl halides has been the topic of ample mechanistic discussion.[2] There seems to be general agreement that the first step involves capture of an electron from the cathode together with, or followed by, cleavage of the halide radical anion:



(1)

One prerequisite to the understanding of the mechanism of eq 1 is the knowledge of the detailed form of the potential surface for dissociation of the anion.[3] We have therefore calculated, using the ab initio GAUSSIAN 70 program,[4] the energy surface for cleavage of CH_3Cl^-, with a crude "solvation shell" of two water molecules.

The choice of basis set is a compromise beteen several requirements: that it include the orbitals appropriate for describing both starting anion CH_3Cl^- and terminal anion Cl^-, while at the same time it be not too large (<50 orbitals) to handle by the available configuration interaction package for doublet states along the dissociation pathway. We therefore used a minimal basis STO-3G set *augmented* by (a) a group of very diffuse s,p Gaussians on carbon to describe the initial anion, with the extra electron trapped in the dipole field of the molecule;[5] (b) a group of semidiffuse "expanded" s,p Gaussians on chlorine, to describe adequately the valence shell of Cl^-, expanded by Coulombic self-repulsion. Diffuse orbitals on Cl added to the previous set give no improvement (<0.03 eV). Extra diffuse s orbitals on the hydrogen atoms do lower the energy (by 0.7 eV), but the configuration interaction becomes intractable because of the great number of very low-lying vacant configurations built on intermixing diffuse orbitals; also diffuse orbitals on hydrogens are not expected to contribute significantly to the dissociation process.

Table I. Energy of CH_3Cl^- and Electron Affinity (Relative to CH_3Cl Calculated with the Same Orbital Set) as a Function of ζ_c, the Gaussian Exponent of the Diffuse Carbon Orbital ($\zeta_{Cl}^{s,p} = 0.5$)

	ζ_c			
	0.1	0.05	0.01	0.005
$E(CH_3Cl^-)$, au	−493.7191	−493.8026	−493.8852	−493.8918
$EA(CH_3Cl)$, eV	−5.35	−2.97	−0.45	−0.23

We first varied the Gaussian exponent ζ_c of the diffuse orbital on C, $\sigma_{Cl}^{s,p}$ being fixed. The results for CH_3Cl^- are shown for $\zeta_{Cl}^{s,p} = 0.5$ in Table I.[6] Although the energy of the anion decreases quite rapidly at first and approaches more and more closely that of the neutral, there is no minimum in the energy. The odd electron tends to "fall off" the molecule and become free. It is possible that a very elaborate set of diffuse orbitals would finally yield a bound anion,[7] as required by the "dipole theorem" for $\mu > 1.625$ D.[5] Here we cannot answer the difficult question of whether CH_3Cl^- is very weakly bound;[8] we can, however, choose a carbon exponent $\zeta_c = 0.01$ which already provides an energy for the anion within 0.5 eV of the neutral calculated with the same basis set. This corresponds to a radius of 4.2 Å for the diffuse orbitals on carbon. Finally we choose for the expanded orbitals on chlorine the exponents $\zeta_s = 1.30$ and $\zeta_p = 0.09$ which optimize the energy of Cl^- at −454.8297 au. This gives a 2.82-eV electron affinity for Cl (calculated with the same basis set as Cl^-)[9] compared with the experimental value of 3.61 eV.[10]

Initially, the methyl group carries most of the negative charge (−0.59 at $R_{C\text{-}Cl} = 2.05$ Å), with less charge (−0.41) on chlorine. At the end, of course ($CH_3^{\cdot} + Cl^-$), all of the charge is on chlorine. Because of the movement of charge, there will certainly be an important solvent motion accompanying the dissociation, with the water molecules moving from carbon to chlorine. Several test calculations show, however, that little or no stabilization (1-2 kcal/mol) is obtained by placing discrete OH_2 molecules initially near carbon (whether along the CC axis or in a direction perpendicular to it): apparently the carbon charge is so very diffuse that it is smeared out over a large volume, and any electrostatic stabilization in solution must come from the macroscopic long-range effect of the solvent. We therefore placed the two OH_2 molecules on either side of the C-Cl bond, on an axis running through the chlorine atom and perpendicular to the bond (optimized distance $R_{Cl\text{-}O} = 3.5$ Å,[11] Figure 1), where they interact with a more compact, albeit smaller, net charge. As the C-Cl bond is stretched, the OH_2 molecules are made to accompany the Cl atom. The energy curves for CH_3Cl^- and for $CH_3Cl^- \cdot 2H_2O$ were then calculated including configuration interaction between all singly and doubly excited configurations built by excitation from σ_{CCl}, and from the odd-electron orbital, to the five lowest vacant orbitals (including the diffuse orbitals and σ^*_{CCl}). Figure 1 shows that the energy first rises in a way which parallels that for neutral molecules,[12] reaches a maximum, and then descends. For isolated CH_3Cl^- there is a 24.6-kcal/mol calculated barrier to dissociation at $R_{C\text{-}Cl} = 2.65$ Å. Its calculated enthalpy of dissociation is +10 kcal/mol, compared with the "experimental" value ($E(CH_3Cl) = 84$,[13] $EA(Cl) = -83$ kcal/mol) of +1 kcal/mol. For the solvated $CH_3Cl^- \cdot 2H_2O$ the barrier drops to 16 kcal/mol, with a shorter transition state ($R_{C\text{-}Cl}$ near 2.45 Å).

The change in behavior of the potential energy at $R = 2.65$ Å can be readily traced to the intersection between the diffuse orbital on carbon, which initially contains the odd electron, and

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