of the nmr absorptions for the benzylic hydrogen and the nonbenzylic ring protons were in the ratio 1:8.[14,15] Allylbenzene from the deuterated chloride was 94% dideuterated and 6% monodeuterated; 24% of the material contained deuterium at C_1 and 76% at C_3, thereby indicating that the SN2′ process takes place to a greater extent than the SN2 for this system.

(2) From product yields in five experiments using both deuterated and undeuterated allyl chloride, it is clear that a substantial kinetic isotope effect exists, with the undeuterated material yielding phenylcyclopropane at the greater rate. This is strong evidence that a carbon–hydrogen bond is broken in the rate-determining transition state.

(3) Preliminary experiments have indicated that phenyllithium does, indeed, add to synthetic cyclopropene,[17] yielding phenylcyclopropane as the major product.

The experiments described above establish the α-elimination mechanism for cyclopropane formation. Work is continuing to determine the generality of this reaction with other substrates and other bases; we are also pursuing an investigation of the factors that influence the relative amounts of SN2 and SN2′ processes for allylic halides.

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is neutralized by proton abstraction from the major product, allylbenzene. Although 24% of the allylbenzene contains deuterium at the allylic position, a kinetic isotope effect favoring abstraction of a proton from the remaining 76% would lead to the formation of only a small amount of dideuterated phenylcyclopropane. Experiments are now in progress to determine if allylbenzene is, indeed, the proton source for the cyclopropyllithium.

(14) By the carbanion mechanism, the ratio should be 1:2; by the carbene mechanism, 1:7.

(15) The discrepancy between the observed value and that expected by the carbene mechanism may well be due to experimental errors arising from the small amount of material, from the problems inherent in integrating a weak nmr spectrum, and from the presence of both mono- and dideuterated materials in the sample. Since the observed ratio is in the direction expected[16] from a secondary deuterium isotope effect on the addition of phenyllithium to cyclopropene-1-d_1, we hope that further refinement of our data will establish whether this ratio is significantly different from 1:7.

(16) S. Seltzer, *J. Am. Chem. Soc.*, 83, 1861 (1961).

(17) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, 31, 638 (1966).

(18) National Defense Education Act Fellow.

Ronald M. Magid, J. Gary Welch[18]
Department of Chemistry, William Marsh Rice University
Houston, Texas 77001

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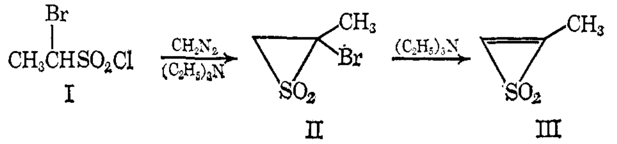
A New Synthesis of Vinylene Sulfones. Application to the Monomethyl Derivative

Sir:

We recently reported[1] the synthesis of 2,3-diphenylvinylene sulfone[2] and demonstrated the striking stability of this compound relative to its dihydro derivative. However the question as to whether this stability is in some part a reflection of dπ–pπ interaction is complicated by the presence of the phenyl substituents attached to the carbon–carbon double bond. We now wish to report a new method for the synthesis of vinylene sulfones and its successful application to an aliphatic example, the monomethyl derivative III. Treating 1,1-dibromoethane with sodium sulfite gave the sodium salt of α-bromoethanesulfonic acid which, with phosphorus pentachloride, was converted in 64% yield to α-bromoethanesulfonyl chloride[3] [I, bp 40° (0.5 mm); infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.24, 8.42, 8.59, 8.69 μ (SO_2); nmr ($CDCl_3$): δ 2.21 (3 H, doublet), 5.42 (1 H, quartet)]. Treating the sulfonyl chloride I with diazomethane in ether at 7–8° in the presence of triethylamine according to the method of Opitz and Fischer[4] gave in 64% yield 2-bromo-2-methylethylene sulfone[3] [II, mp 57–58° dec; infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.50, 8.67, 8.96 μ (SO_2); nmr ($CDCl_3$): δ 2.27 (3 H, singlet), 3.41 (2 H, singlet)]. The structure of II was confirmed by fragmentation to sulfur dioxide and 2-bromopropene upon gentle warming. Dehydrobromination of II by means of triethylamine at 3° over a period of 72 hr gave in 50% yield methylvinylene sulfone[3] [III, mp 59–60°; infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.22 (C=C) and 7.82, 8.42 μ (SO_2)]. In the accessible ultraviolet region the vinylene sulfone shows only end absorption with the extinction coefficient rising from 434 at 220 mμ to 932 at 210 mμ. The general shape of the curve is similar to that reported for other aliphatic α,β-unsaturated sulfones.[5]



Compound III appears to be stable indefinitely at room temperature but on heating to about 90° undergoes decomposition to give methylacetylene and sulfur dioxide.[6] Particularly interesting is the nmr spectrum ($CDCl_3$) of III which shows a doublet at δ 2.50 (3 H, methyl, $J = 1.1$ cps) and a quartet at δ 9.04 (1 H, vinyl, $J = 1.1$ cps). These positions are comparable to those observed by Breslow and Altman[7] for methylcyclopropenone (δ 2.40 and 8.70).[8]

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(1) L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, 87, 5804 (1965).

(2) Thiirene 1,1-dioxide according to *Chemical Abstracts* nomenclature.

(3) All new compounds gave correct elemental analyses and molecular weights (vapor osmometry) and consistent spectral data.

(4) G. Opitz and K. Fischer, *Z. Naturforsch.*, **18b**, 775 (1963); *Angew. Chem.*, 77, 41 (1965).

(5) E. S. Waight, *J. Chem. Soc.*, 2440 (1952).

(6) It has not yet been possible to synthesize the corresponding 2,3-dihydro derivative for direct comparison of its stability with that of III. However, a number of simple alkyl derivatives of ethylene sulfone have been described by Opitz and Fischer,[4] and these appear to be relatively unstable at room temperature. The precursor II undergoes decomposition on standing at room temperature in chloroform solution over a period of 1–2 days. In the crystalline state II rapidly loses weight on standing in the open at room temperature. A sample sealed in a small glass vial completely liquefied over a period of 8–10 hr. The liquid was shown to be 2-bromopropene.

(7) R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966).

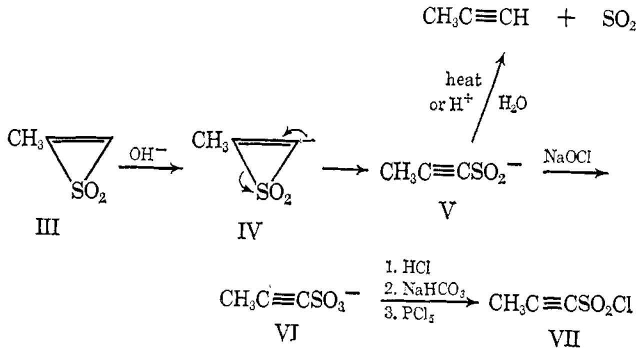
(8) Attempts to determine a "ring-current" shift[9,10] for the 2-methyl group did not give any meaningful results because of the lack of suitable model compounds.

(9) Compare (a) J. A. Elvidge, *Chem. Commun.*, 160 (1965); (b) R. J. Abraham and W. A. Thomas, *J. Chem. Soc., Sect. B*, 127 (1966). For a pungent criticism of the whole matter relating to "ring-current" shifts see J. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

(10) Apart from any similarity in electronic structure it would be expected that the methyl and vinyl absorptions of methylvinylene sulfone would be downfield from those of methylcyclopropenone. This is apparent from a comparison of simple ketones with the analogous sulfones. A comprehensive study of the latter has been published [P. Biscarini, F. Taddei, and C. Zauli, *Boll. Sci. Chim. Ind. Bologna*, **21**, 169 (1963)].

Consistent with its probable intermediacy in the Ramberg–Bäcklund reaction of α,α′-dibromodibenzyl sulfone, 2,3-diphenylvinylene sulfone gives 1,2-diphenylethylenesulfonic acid in 90% yield on treatment with aqueous sodium hydroxide. On the other hand no sulfonic acid was isolated on treatment of III under Ramberg–Bäcklund conditions. When the reaction was carried out at low temperatures (0°) an unstable intermediate was formed which underwent subsequent conversion to methylacetylene.[11] Immediately after addition of 2 *N* sodium hydroxide to an aqueous solution of III, the nmr spectrum shows disappearance of the vinyl absorption and shift of the methyl resonance from δ 2.5 to 2.0. Infrared examination of this solution shows sharp acetylenic absorption at 4.57 μ. Changes in the spectra showed that the species present decomposed rapidly on standing at room temperature. Warming to 50° or acidification caused the evolution of methylacetylene.[12] If the solution is first treated with sodium hypochlorite,[13] a new species is formed which no longer yields methylacetylene on warming or acidification. The oxidized solution contains a stable acetylenic sulfonic acid as shown by infrared absorption at 4.51 (C≡C) and 8.25, 9.40 μ (SO_2). Neutralizing the acidified hypochlorite-oxidized solution by means of sodium bicarbonate, evaporating, and treating the solid residue with phosphorus pentachloride in carbon tetrachloride gave in an over-all yield of 35% 1-propynesulfonyl chloride[3] [VII, bp 60–62° (6 mm); infrared: $\lambda_{max}^{CCl_4}$ 4.50 (C≡C) and 7.20, 8.47 μ (SO_2); nmr (CCl_4): δ 2.26 (singlet)]. The reactions described are outlined in Chart I. Hydroxide ion is presumably diverted from attack at the sulfone group by the pronounced acidity of the vinyl proton of methylvinylene sulfone.[14,15] Opening follows to give the stable sulfinate V which on oxidation yields the stable sulfonate VI, from which the isolable sulfonyl chloride VII is derived. It is apparent from these results that the recent suggestion[17] that the relative stabilities of substituted vinylene sulfones can be determined by comparison of the ratio of acetylenic to sulfonic acid products formed upon Ramberg–Bäcklund treatment of dihalo sulfones is untenable since the acetylenic products need not arise by thermal elimination of sulfur dioxide from the vinylene sulfone. Whether the stability order of the vinylene sulfones parallels that of the cyclopropenones therefore remains to be determined. Such an investigation of the stability and reactivity under comparable conditions of a varied group of isolable vinylene sulfones is currently in progress. The unusual reactivity of the vinylene sulfones, to be reported in due course, makes these compounds of considerable practical synthetic value.

Chart I



Acknowledgment. This work was generously supported by grants from the U. S. Army Research Office, Durham, and (in its earlier stages) by the Petroleum Research Fund, administered by the American Chemical Society.

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(11) A careful search for sulfonic acids and other by-products is in progress.

(12) Methylacetylene is not detectably soluble in aqueous sodium hydroxide solution (nmr) and must be derived from some relatively stable soluble precursor. That the anion IV is not stable is shown by the fact that maximum acetylenic absorption is developed immediately after addition of alkali, and just-as-rapid neutralization of this solution with hydrochloric acid regenerates none of the precursor III (nmr analysis).

(13) Sodium hypochlorite has been shown to oxidize sulfinates to sulfonates rapidly in aqueous solution. See L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, 18, 243 (1946).

(14) It is interesting in this connection that the α-vinyl proton of 2,3-dihydrothiophene 1,1-dioxide undergoes deuterium exchange in the presence of aqueous alkali. See C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).

(15) Confirmed by the large ^{13}C–H coupling constant (J = 230–232 cps) measured for this proton (concentrated water solution). The corresponding values for methylcyclopropenone[7] and methylacetylene[16] are 213 and 248 cps, respectively.

(16) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(17) L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).

Louis A. Carpino, Ronald H. Rynbrandt
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts

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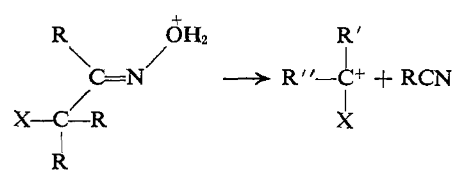
Evidence for and Synthetic Utility of the Beckmann Fission Intermediate of 2-Methoxycyclohexanone Oxime

Sir:

The feasibility of fragmentation in certain oximes under Beckmann rearrangement conditions has recently been recognized and has attracted considerable attention.[1] In general, the Beckmann fission is well demonstrated by oximes of structural types which furnish carbonium ions $^{+}CR'R''X$ possesing considerable stability, especially with substituents, X, of alkoxy, alkylamino, and alkylthio groups, and the synthetic application of the reaction has been cited in recent communications.[2–4]



We describe here not only strong evidence for but also a synthetically interesting utility of such carbonium ion intermediates. ω-Cyanoalkyl aldehydes are easily prepared in excellent yields by the treatment of α-alkoxy, α-alkylamino-, and α-ethylthiocycloalkanone oximes with thionyl chloride or phosphorus pentachloride followed by hydrolysis.[2] Among them, 5-cyanopentanal

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(1) (a) R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962), and references contained therein; (b) C. A. Grob, H. P. Fischer, W. Raudenbusch, and J. Zergenzi, *Helv. Chim. Acta*, **47**, 1003 (1964), and references contained therein; (c) R. K. Hill, R. T. Conley, and O. T. Chortyk, *J. Am. Chem. Soc.*, **87**, 5646 (1965).

(2) M. Ohno, N. Naruse, S. Torimitsu, and I. Terasawa, *ibid.*, **88**, 3168 (1966).

(3) R. L. Autrey and P. W. Scullard, *ibid.*, **87**, 3284 (1965).

(4) Y. L. Chow, *ibid.*, **87**, 4642 (1965).