Table I. Carbonyl Stretching Frequencies (cm^{-1}) of $Mn(CO)_5(SO_2R)$ Complexes[a]

Complex	Solvent	CO stretches			
		$A_1^{(2)}$	B_1	E	$A_1^{(1)}$
$Mn(CO)_5(SO_2CH_3)$	CCl_4	2139 (m-w)	2090 (w)	2059 (s), 2044 (s)	2027 (m)
	$CHCl_3$	2142 (m-w)	2095 (w)	2055 (s)	2037 (m, sh)
$Mn(CO)_5(SO_2CH_2C_6H_5)$	CCl_4	2137 (m-w)	2089 (w)	2059 (s), 2041 (s)	2024 (m)
	$CHCl_3$	2141 (m-w)	2093 (w)	2061 (s), 2049 (s)	2035 (m, sh)
	CH_3CN	2142 (m-w)	2089 (w)	2057 (s)	2047 (m, sh)

[a] Recorded on a Beckman Model IR-9 spectrophotometer. Abbreviations: s, strong; m, medium; m-w, medium weak; w, weak; sh, shoulder.

The infrared carbonyl stretching frequencies of the derivatives are listed in Table I, and the spectrum of $Mn(CO)_5(SO_2CH_3)$ in $CHCl_3$ in the 2200–1900-cm^{-1} region is given in Figure 2. These data clearly indicate appreciable distortion from regular C_{4v} molecular symmetry, the effect becoming more pronounced as the size of the perturbing sulfinate group increases. Accordingly, the splitting of the E band, not discernible for $Mn(CO)_5(SO_2CH_3)$ in $CHCl_3$, is clearly apparent for $Mn(CO)_5(SO_2CH_2C_6H_5)$ in the same solvent. In both cases, the B_1 absorption is easily detectable.

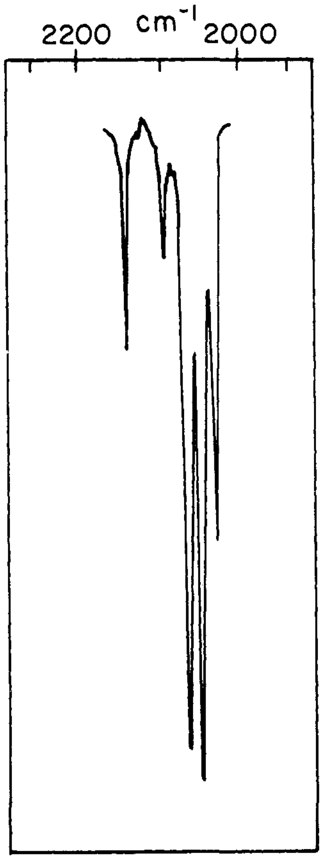

Figure 3. The infrared spectrum of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in CCl_4 in the CO stretching region.

The splitting becomes easier to detect as the polarity of the solvent decreases; this is illustrated by the carbonyl stretching region spectrum of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in CCl_4, given in Figure 3. It may be seen from Table I that the separation of the two components of the E absorption amounts to 18 cm^{-1}, much larger than any of the splittings reported by Wilford and Stone.[7] However, no splitting of the E band is discernible in the polar acetonitrile because of broadening of the peaks.

The absorptions due to the $A_1^{(1)}$ mode occur at much higher wavenumbers (*ca.* 20–35 cm^{-1}) than those reported for the halogeno- and alkylmanganese pentacarbonyls,[8,9] but at frequencies comparable to those found in the acyl and perfluoroacyl derivatives.[7] The values indicate an appreciable π-bonding capacity of the sulfinate ligands, which is consistent with the proposed manganese–sulfur linkage in the complexes.

A study is now in progress on reactions of $Mn(CO)_5(SO_2CH_2C_6H_5)$ with several neutral ligands. Of interest will be to determine whether, as with the thiocyanato complexes,[10] replacement of carbon monoxide by ligands of much lesser π-bonding ability might lead to a linkage rearrangement from $Mn-SO_2CH_2C_6H_5$ to $Mn-OS(O)CH_2C_6H_5$. Preliminary results indicate that the reactions with triphenylphosphine and pyridine proceed very slowly.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

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(7) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(8) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *ibid.*, **1**, 933 (1962).

(9) F. A. Cotton, *ibid.*, 3, 702 (1964).

(10) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

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Bicyclo[2.1.0]pent-2-ene

Sir:

We wish to describe the preparation, isolation, and identification of bicyclo[2.1.0]pent-2-ene ("homocyclobutadiene") (I), valence bond isomer of cyclopentadiene

I

and the smallest unsaturated polycycle yet secured in the organic laboratory.[1]

The new hydrocarbon can be generated by ultraviolet irradiation of cyclopentadiene, either in a basic or a neutral ethanolic medium. One of the more satisfactory preparations involves a 1–2 hr photolysis (450-w Hanovia high-pressure mercury arc lamp) of an approx-

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(1) For a recent review of small-ring compounds, see D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).

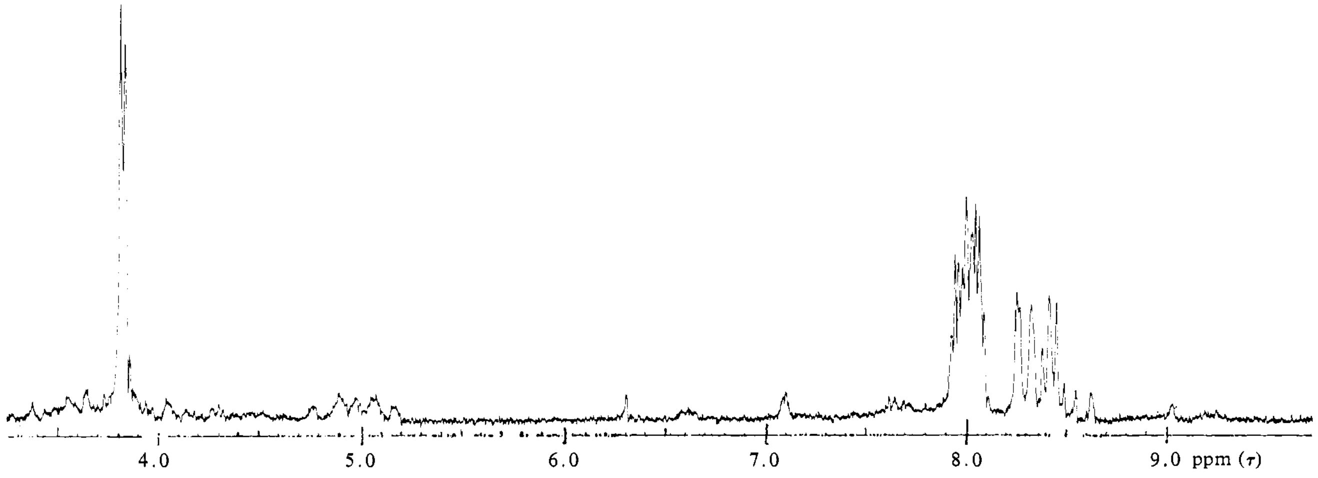


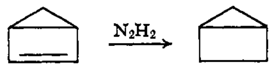
Figure 1.

imately 0.3 M ice-cooled solution of cyclopentadiene in ethanol, under which circumstances as high as 10% of the starting material is converted to the valence bond isomer I. After introduction into a vacuum line, the reaction mixture is degassed and then transferred, while being stirred at 0°, into a receiver cooled in liquid nitrogen. Bicyclopentene is concentrated in the first few drops of distillate, and almost all of the hydrocarbon formed is collected in the first 5 ml of distillate. Final isolation of solvent-free I is achieved by preparative vpc, carried out with a $^1/_4$ in. Ucon polar column 2 m in length (helium pressure 15 psi) and a collection tube kept at −80°. At 50°, the vpc retention time of bicyclopentene is 4.25 min, as compared with 5.25 min for cyclopentadiene under similar conditions.[2]

Figure 1 depicts the 100-Mc nmr spectrum, measured in carbon tetrachloride solution at room temperature (tetramethylsilane = τ 10.0). The slightly split olefinic hydrogen peak at τ 3.8 compares favorably with that in cyclobutene (τ 4.03, $J = \mp 0.2$ cps).[3] As expected, the splitting exhibited by the methine and (nonequivalent) cyclopropyl methylene hydrogens is extensive, while the marked downfield shift of the latter type, and overlapping with the former, is consistent with trends noticeable in bicyclo[2.1.0]pentane[4a] and certain vinylcyclopropanes.[4b-c] As revealed by mass spectral analysis, the photohydrocarbon is monomeric, with mol wt 66.[5]

That cyclopentadiene is the primary, but not the sole, thermolysis product of I was indicated by the change in the nmr spectrum with time. Although products other than cyclopentadiene were not identified, appearance of high-field cyclopropane methylene signals connotes formation of polymers derived at least in part from bicyclopentene. At room temperature in dilute carbon tetrachloride solution, bicyclopentene possesses a half-life of approximately 2 hr.[6]

In order to confirm chemically the structure of the photohydrocarbon, diimide reduction to the known[7] bicyclo[2.1.0]pentane (II) was carried out. With ex-



II

cess disodium azodicarboxylate–acetic acid as the diimide source and under conditions previously described,[8] bicyclopentene in ethanol was converted almost quantitatively (vpc) to the saturated bicycle II, identified by vpc, nmr, and infrared comparison with an authentic specimen prepared by pyrolysis of 1,3-diazocyclopentane.[7]

In view of the failure of previous workers to observe bicyclopentene (I),[9,10] brief comment on synthesis routes and stability factors is in order at this point. Aside from other photochemical events,[11] light-induced ring closure of cyclopentadiene to the bicyclic valence bond isomer could reasonably be expected, since the stereochemistry of this isomerization would provide the requisite *cis* ring fusion.[12] On the other hand, thermal reversion of the cyclobutene moiety to 1,3-diene would, by the stereoelectronic pathway of normally lowest energy, generate a *cis,trans* isomer, in this case an impossibly strained ground-state system.[13] Overruling the normal thermal stability of the cyclobutene nucleus, the considerable internal strain of the bicyclic system forces the new hydrocarbon either to polymerize or, through circumvention of the normal orbital symmetry requirements[14] for ring opening,

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(2) The very volatile bicyclopentene can be stored conveniently in ethanol at Dry Ice temperatures.

(3) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(4) Chemical shifts (tetramethylsilane = τ 10) of cyclopropyl ring methylene hydrogens in (a) bicyclo[2.1.0]pentane, τ 9.3–9.6, (b) thujene, τ 9.2 and 10.0, one of several examples in D. Forbess, Ph.D. Dissertation, Stanford University, 1965; (c) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(5) A mass 68 band indicates the presence of some cyclopentene, undoubtedly formed by photoreduction of excited state cyclopentadiene or possibly bicyclopentene.

(6) Compare the half-life of bicyclo[2.2.0]hexa-2,5-diene (parent "Dewar benzene"), *ca. 2 days* at room temperature in pyridine: E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

(7) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(8) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961). Diimide chemistry was most recently reviewed by S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Intern. Ed. Engl.*, **4**, 271 (1965).

(9) D. H. R. Barton, *Helv. Chim. Acta*, 42, 2604 (1959).

(10) L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

(11) N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962), reported that *sensitized* ultraviolet irradiation of cyclopentadiene produced equal amounts of three dimers: *endo*-dicyclopentadiene, *exo*-dicyclopentadiene, and *trans*-[3.0.3.0]tricyclo-2,8-decadiene.

(12) For the first precedent, see W. G. Dauben and G. J. Fonken, *ibid.*, **81**, 4060 (1959).

(13) E. Vogel, *Ann.*, **615**, 14 (1958); R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959).

(14) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

isomerize under mild conditions to cyclopentadiene. With the information presently available, it seems likely that the dehalogenation of 1,1-dibromo-2-vinylcyclopropane does not involve, as proposed,[10] intermediary formation of I and spontaneous isomerization at −78° to cyclopentadiene, the isolated product, but rather cyclopentadiene formation by one of several alternative direct routes not involving (ground-state) I.

Acknowledgment. The authors are grateful to Professor R. LaLonde (State University College of Forestry at Syracuse University) for a gift of 1,3-diazocyclopentane; Dr. Lois Durham for consultation on nmr spectra; and ARO(D) (Project No. CRD-AA-5227-C) for financial assistance.

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(15) National Science Foundation Predoctoral Fellow, 1964–present.

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The Sulfur Isotope Effect in the E2 Reaction of 2-Phenylethyldimethylsulfonium Bromide with Hydroxide Ion. A Correction[1]

Sir:

Some time ago, two of us[2] reported that the reaction of 2-phenylethyldimethylsulfonium bromide with hydroxide ion in water at 59° occurred with a very small sulfur isotope effect, the S^{32} compound reacting only 0.15% faster than the S^{34} compound. We recently had occasion to repeat this work, and we are now convinced that the original result is wrong.

The reactions were carried out essentially as before.[2] Table I gives the new results. In the experiments at Zagreb (series 1 and 2), the methyl sulfide was flushed from the reaction mixture by pure oxygen and the gas mixture was passed through a furnace at 1000° to obtain sulfur as sulfur dioxide, which was examined in a mass spectrometer. Series 2 utilized the same samples as series 1 after removal of all but 5% of the carbon dioxide produced in the combustion.[3] There is no significant difference except for the improved precision in series 2.

Table I. Sulfur Isotope Effects in the Reaction of 2-Phenylethyldimethylsulfonium Bromide with Hydroxide Ion in Water at 59°

Series	$((k_{32}/k_{34}) - 1)100$[a]	
1[b]	0.85, 0.60, 0.60, 0.64, 0.56	Av 0.65 ± 0.052[d]
2[c]	0.61, 0.60, 0.62, 0.58, 0.67	Av 0.62 ± 0.015[d]
3[e]	0.68, 0.65, 0.70, 0.64, 0.65, 0.61, 0.71	Av 0.66 ± 0.015[d]
4[e]	0.63,[f] 0.62,[g] 0.61[h] 0.58[i]	Av 0.61 ± 0.11[d]

[a] Except where otherwise noted, k_{32}/k_{34} is the ratio of S^{32}/S^{34} at 3% reaction (20 min) to S^{32}/S^{34} at 100% reaction (150–180 min). [b] Methyl sulfide combusted to $SO_2 + CO_2$. Samples contained *ca.* 70% CO_2. [c] Same as *b*, but samples contained <5% CO_2 (see ref 3 for method of removal). [d] Standard deviation of mean. [e] Isotope ratio measured directly on methyl sulfide from mass 62/mass 64. [f,g,h,i] S^{32}/S^{34} ratios determined at 10, 15, 20 and 30% reaction, respectively, and the isotope effect calculated from the formula of Stevens and Attree (ref 4).

In the experiments at Rochester, the only departure from the original procedure was to quench the reaction at the desired percentage completion by acidification with hydrochloric acid rather than by cooling. The methyl sulfide was expelled by nitrogen and purified, and the isotope ratio was determined as before. Series 3 utilized samples collected up to 3% reaction, but four runs from 10 to 30% reaction (series 4) were also done, and the isotope effect was calculated from the formula of Stevens and Attree.[4] The average of all of the results of series 3 and 4 is 0.64%, with a standard deviation of the mean of 0.012.

The excellent agreement of the values obtained by two different groups using two different methods is a gratifying demonstration of the precision with which isotope effects can be determined and makes it virtually certain that the original value[2] is erroneous. The two most probable reasons for the error are incomplete formation or collection of methyl sulfide in the "100%" runs and/or trace impurities in the reactants which could affect more strongly the samples taken at low completion. We favor the first explanation, for we noted no significant trend in the figures in series 4 as the extent of reaction increased.

The new value of the sulfur isotope effect makes it evident that the carbanion character in the transition state for the sulfonium salt is less extreme than formerly believed, for the effect is now *ca.* 30–40% of the experimental[2] and theoretical[5] maximum values.

A formerly puzzling situation is now cleared up. A comparison of the Hammett ρ values for the 2-phenylethyldimethylsulfonium and -trimethylammonium salts (+2.6[6] and +3.8,[7] respectively, at 30° in ethanol) indicates a transition state with higher carbanion character for the latter. In contrast to these facts was the nitrogen (N^{14}/N^{15}) isotope effect of about 1%[8] for reaction of the ammonium salt, a value which is much larger relative to the theoretical maximum[5] than was the old figure of 0.15% for the sulfonium salt relative to its theoretical maximum. The sulfonium salt is now seen to have a transition state with an extent of bond weakening to the leaving group at least as large as that for the ammonium salt, and the greater carbanion character with the ammonium salt is largely the result of more complete proton transfer to base.[9]

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(1) That part of this work done at Rochester was supported by the National Science Foundation.

(2) W. H. Saunders, Jr., and S. Ašperger, *J. Am. Chem. Soc.*, 79, 1612 (1957).

(3) W. A. Sheppard and A. N. Bourns, *Can. J. Chem.*, 32, 4 (1954).

(4) W. H. Stevens and R. W. Attree, *Can. J. Res.*, B27, 807 (1949).

(5) W. H. Saunders, Jr., *Chem. Ind.* (London), 1661 (1963), and unpublished results.

(6) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, 79, 3712 (1957).

(7) W. H. Saunders, Jr., and D. G. Bushman, unpublished results.

(8) A. N. Bourns and P. J. Smith, *Proc. Chem. Soc.*, 366 (1964), report 0.9% at 97°. About 1.0–1.1% would be expected at 59°.

(9) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, 82, 138 (1960), report k_H/k_D values consistent with this conclusion, provided the proton is more than half transferred.

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