with 5 ml of methylene chloride. The organic layer was separated, washed with 10 ml of saturated sodium bicarbonate solution, dried over magnesium sulfate, and filtered. The precipitate was washed with 1 ml of methylene chloride and the combined filtrate and washings were analyzed by glpc. For the runs that contained amides, 0.800 g of acrylamide or acetamide was dissolved in the water-glycol mixture before the addition of the lead(IV).

Relative thermal conductivity and extraction ratios for the product to standard for the three types of lead(IV) reactions were determined in a fashion similar to that used for the cerium(IV) reactions.

The yields of cyclohexanone were calculated by the method used for the cerium(IV) runs and are reported in Table I. The B/B' ratios were based on at least two runs and were found to be 0.777 ± 001, 0.774 ± 0.033, and 0.765 ± 0.002 with no addend, in the presence of acrylamide and in the presence of acetamide, respectively.

Registry No.—Bicyclohexyl-1,1′-diol, 2888-11-1.

Factors Influencing Episulfonium Ion Formation. The Reactivity of Unsaturated Aliphatic Hydrocarbons toward Methanesulfenyl Chloride

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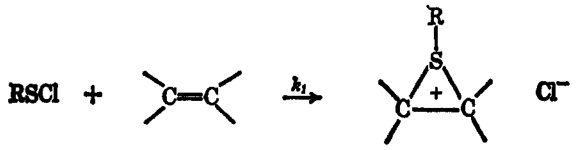
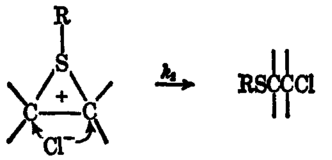
The reaction of methanesulfenyl chloride with a series of unsaturated hydrocarbons has been utilized to measure relative rates of episulfonium ion formation. The structure-reactivity correlation obtained in this fashion contrasts with other electrophilic additions such as chlorination in that the methanesulfenyl chloride additions appear to be significantly less sensitive to the nucleophilicity of the unsaturated hydrocarbon and quite sensitive to steric factors. The data have been interpreted in terms of transition states in which the positive charge resides essentially on sulfur, and consequently alkyl substituents about the double bond contribute relatively little toward delocalization of the positive charge. The observed reactivities reflect the opposing steric and electronic factors.

Early studies pertaining to the mechanism of electrophilic sulfenyl halide reactions with olefins utilized 2,4-dinitrobenzenesulfenyl chloride[1] as a convenient model reagent due to its unusual stability. More recent discoveries of novel aspects of the mechanism of sulfenyl chloride addtions[2] indicate that only limited generalizations can be drawn from this model. The addition of sulfenyl halides to olefins evidently proceeds *via* episulfonium ion intermediates, the substituents both on carbon and sulfur exerting profound directive influences controlling the structure of the β-chloro thioether products. Recent studies[3,4] correlating episulfonium ion structure with product geometry have provided considerable insight into the nature of episulfonium ions and have demonstrated that simple alkyl- (and aryl-) sulfenyl chlorides frequently behave quite differently from 2,4-dinitrobenzenesulfenyl chloride. Although examination of product structures has provided data concerning episulfonium ring opening in the second reaction step, there is a paucity of information on the formation of these species during the first reaction step, especially in systems involving unsaturated aliphatic hydrocarbons and simple alkylsulfenyl halides. The object of the present investigation is a correlation between structure and reactivity for episulfonium ion formation from unsaturated aliphatic hydrocarbons and alkanesulfenyl halides.



(1)



(2)

Results

The relative rates of reaction of pairs of unsaturated hydrocarbons with methanesulfenyl chloride in dilute paraffin solution at −70° was measured by means of vapor phase chromatography. Initial experiments utilizing dropwise addition of CH_3SCl and analysis at frequent intervals demonstrated that relative reactivities were independent of conversion. The relative rates reported in Table I are the mean values of dupli-

TABLE I

COMPETITION OF OLEFIN PAIRS FOR METHANESULFENYL CHLORIDE

Olefin A	Olefin B	Solvent	Mean k_A/k_B
Cyclopentene	*cis*-Pentene-2	*n*-Heptane	$1.76^a \pm 0.05^b$
Pentene-1	3-Methyl-1-butene	*n*-Heptane	1.17 ± 0.04
cis-Pentene-2	Pentene-1	*n*-Heptane	7.94 ± 0.28
Cyclopentene	2-Methyl-2-butene	*n*-Heptane	5.06 ± 0.52
2-Methyl-2-butene	3-Methyl-1-butene	*n*-Heptane	4.22 ± 0.49
3-Methyl-1-butene	*trans*-2-Pentene	*n*-Heptane	1.18 ± 0.02
3-Methyl-1-butene	Isobutylene	Cyclopentane	2.62 ± 0.18
Butene-1	*trans*-2-Butene	*n*-Pentane	1.40 ± 0.03
cis-2-Butene	Butene-1	*n*-Pentane	13.04 ± 1.40
Isobutylene	1,3-Butadiene	*n*-Pentane	4.86 ± 0.31
trans-2-Butene	Isobutylene	*n*-Pentane	0.96 ± 0.04
1,3-Butadiene	1-Butyne	Cyclopentane	6.11 ± 0.68
Isobutylene	2-Butyne	Cyclopentane	4.63 ± 0.13
2,3-Dimethyl-2-butene	2-Methyl-2-butene	*n*-Heptane	1.56 ± 0.02
Vinylcyclohexane	Styrene	*n*-Pentane	1.17 ± 0.09

[a] Mean value of four runs. [b] Mean deviation.

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[1] N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, 1961, pp 375–396.

[2] (a) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966). (b) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[3] W. A. Thaler, W. H. Mueller, and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2069 (1968).

[4] W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968).

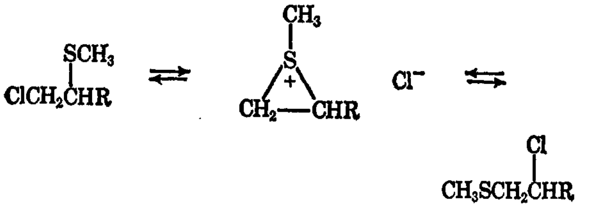
TABLE II

RELATIVE RATES OF EPISULFONIUM ION FORMATION FOR THE REACTION OF CH_3SCl WITH UNSATURATED HYDROCARBONS

Hydrocarbon	k_1[a]
1-Butyne	0.034 ± 0.001[b]
1,3-Butadiene	0.206 ± 0.013
2-Butyne	0.216 ± 0.006
trans-2-Butene	0.96 ± 0.04
Isobutylene	1.00[c]
1-Butene	1.34 ± 0.09
trans-2-Pentene	2.22 ± 0.18
3-Methyl-1-butene	2.60 ± 0.18
1-Pentene	3.04 ± 0.31
2-Methyl-2-butene	11.0 ± 2.0
2,3-Dimethyl-2-butene	17.2 ± 3.3
cis-2-Butene	17.4 ± 3.0
cis-2-Pentene	24.1 ± 1.1
Cyclopentene	42.4 ± 3.1

[a] Relative to isobutylene. [b] Mean deviation. [c] Arbitrary standard.

cate runs, each measured at 40 and 60% total conversion. Relative reactivities were calculated using the expression $k_A/k_B = \log (A_0/A)/\log (B_0/B)$ where A_0/A and B_0/B represent the ratio of initial to final concentrations of each of two competing olefins. If eq 1 is rate determining, then k_A/k_B is the ratio of the rate constants (k_1) for the formation of episulfonium ions from olefin A and B. Several factors support the assumption that the over-all reaction is irreversible. Observed rearrangements of anti-Markovnikov to Markovnikov isomers which proceed *via* the episulfonium ions are very much slower than the formation of episulfonium ions from the reaction of the sulfenyl halide with the olefins, indicating that during the course of CH_3SCl addition the β-chloro sulfide products are not reverting to episulfonium ions. Furthermore, the failure to observe any regeneration of olefins by heating alkanesulfenyl chloride adducts under conditions where episulfonium ions are regenerated indicates that such episulfonium ions do not decompose back to RSCl and olefin under considerably more vigorous reaction conditions than experienced during this study.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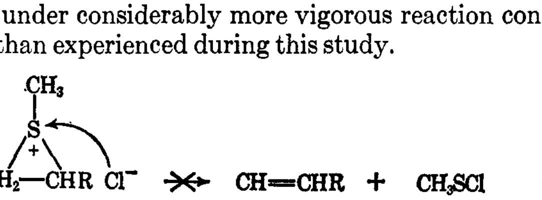
(4)

A precipitate was observed during low-temperature reaction in paraffin solvents which was not formed in more polar media such as CH_2Cl_2, and it has been suggested[5] that this material may be the chloride salt of the episulfonium ion. The precipitate dissolved on warming to ambient temperature and did not reform on recooling. In order to ensure uniform sampling, analyses were performed (after consumption of the sulfenyl chloride increment) upon samples withdrawn from the liquid phase of the heterogeneous mixture at −70° and the homogeneous mixture at ambient. In all cases the determined values were within the random error of the vpc measurement. Apparently, the precipitate does not selectively entrain any of the unsaturated hydrocarbons.

The data obtained in this fashion have been utilized to calculate the reactivity sequence shown in Table II. Examination of Table II reveals some unusual features of CH_3SCl additions which will be discussed presently.

Discussion

The reactions of 2,4-dinitrobenzenesulfenyl chloride with olefins[6] and acetylenes[7] exhibit second-order kinetics consistent with an episulfonium ion mechanism.[8] The rate is enhanced by polar solvents and a correlation with Hammett σ values for reaction with *para*-substituted styrenes ($\rho = -2.20$, 25°, acetic acid) indicates that the α carbon is electron deficient in the transition state.[9] The reaction of *para*-substituted *o*-nitrobenzenesulfenyl chlorides with cyclohexene correlates well with Brown σ^+ values ($\rho = -0.714$, 25°, acetic acid) suggesting a mesomeric stabilization of electron-deficient sulfur.[10] The *trans* stereochemistry of the addition of sulfenyl chlorides to olefins and the insensitivity of the stereochemistry to wide temperature ranges[11] are again consistent with a cyclic intermediate. However, the marked differences in reactivity as well as in kinetically controlled isomer orientations[2] (Markovnikov *vs.* anti-Markovnikov) between nitrobenzenesulfenyl chloride reactions and those of the simple aliphatic (and aromatic) sulfenyl chlorides indicates that the corresponding episulfonium ions differ significantly. The reactivities in Table II provide some additional insight regarding the formation of episulfonium ions with an alkyl substituent on sulfur.

A direct comparison of sulfenation with electrophilic chlorination (Table III) free from competing radical chlorination[12] is possible since data on both reactions in nonpolar media are now available. The two processes are significantly different both qualitatively and quantitatively, apparantly precluding the involvement of chloronium ion intermediates in CH_3SCl additions. Both the reactivity sequence and the magnitude of the

TABLE III

RELATIVE REACTIVITIES OF OLEFINS TOWARD ELECTROPHILIC ATTACK IN NONPOLAR MEDIA

Olefin	Cl_2[b]	CH_3SCl[c]
1-Butene[a]	1.0	1.0
cis-2-Butene	63	13.0
trans-2-Butene	58	0.72
Isobutylene	50	0.75
Trimethylethylene	11,000	8.26
Tetramethylethylene	430,000	12.9

[a] Arbitrary standard. [b] M. L. Poutsma, *Science*, **157**, 997 (1967); nonpolar media, −9 to 25°. [c] Paraffin media, −70°.

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(5) P. S. Skell, private communication.

(6) (a) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **75**, 6030 (1953). (b) D. R. Hogg and N. Kharasch, *ibid.*, **78**, 2728 (1956).

(7) N. Kharasch and C. N. Yiannios, *J. Org. Chem.*, **29**, 1190 (1964).

(8) N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949).

(9) W. L. Orr and N. Kharasch, *ibid.*, **78**, 1201 (1956).

(10) C. Brown and D. R. Hogg, *Chem. Commun.*, 357 (1965).

(11) G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **41**, 1338 (1966).

(12) See Table III, footnote *b*.

difference in reactivity of olefins toward positive chlorine suggests that chloronium ion formation is quite sensitive to the nucleophilicity of the π electrons. Thus the successive accumulation of alkyl groups about a double bond causes dramatic increases in reactivity. In contrast, the differences in reactivity toward sulfenyl chloride are much smaller and considerably less sensitive to olefin nucleophilicity, indicating that, in the transition state for episulfonium ion formation, a good deal of the positive charge residues on sulfur. The relatively small magnitude of these differences is quite remarkable when one considers that the temperature for the sulfenyl chloride reactions was 60–95° lower than the corresponding chlorinations which would serve to enhance further selectivity by taking advantage of changes in activation energy due to structural differences.

The rather unique reactivity sequence suggests that factors in addition to electronic considerations are also important. Examination of the reactivity sequence (highlighted in Figure 1) reveals that dienes are less reactive than simple olefins, and *cis* olefins are significantly more reactive than other unsaturates. One plausible explanation is that, although alkyl substituents facilitate reaction by increasing the nucleophilicity of the π electrons, they also exert an unfavorable steric influence, and the reactivity represents a compromise between these two opposing factors. The *cis* olefins are the most reactive because the alkyl substituents can be oriented away from the incoming sulfenyl chloride in a fashion which minimizes the unfavorable steric interaction of the substituents on sulfur with the substituents on the ethylenic bond.

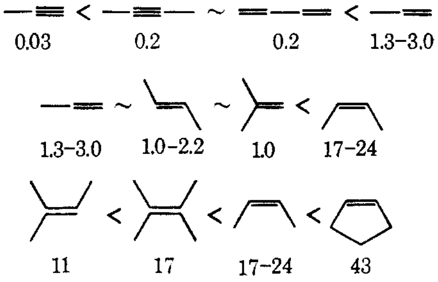

Figure 1.—Structural features influencing the reactivity toward episulfonium ion formation (CH_3SCl).

The similarity of the reactivities of *cis* and *trans* olefins toward 2,4-dinitrobenzenesulfenyl chloride[13] contrasts sharply with these results, but is consistent with other observations that electronic rather than steric factors are generally more important in reactions of 2,4-dinitrobenzenesulfenyl chloride[1,14] than with simple alkylsulfenyl chlorides.[2] Dienes are less reactive than one might anticipate because they behave as isolated olefins bonded to an electron-withdrawing vinyl group. Since most of the positive charge resides on sulfur, there is little stabilization from allyl carbonium ion structures.

The reactivities of acetylenes and tri- and tetramethylethylenes are consistent with this interpretation. Acetylenes are less nucleophilic than olefins and are, therefore, less reactive. Since acetylenes are linear, an additional alkyl substituent increases the nucleophilicity without significantly increasing steric interactions with the result that internal acetylenes are nearly an order of magnitude more reactive than terminal acetylenes. Both isobutylene and *trans*-butene are significantly less reactive than *cis*-butene, and, since each has two methyl substituents about the double bond, the unfavorable feature appears to be the presence of alkyl substituent on both sides of the plane of the double bond. Apparently the presence of a single group on both sides of the double bond causes a marked steric deactivation. This is also apparent from the absence of any increase in reactivity in going from a terminal olefin to a disubstituted olefin. The presence of additional alkyl substituents, as for example in trimethylethylene and tetramethylethylene, promotes reactivity by increasing the basicity of the π electrons to a greater extent than the increase in steric deactivation. Evidently, there exists a saturation effect wherein a third and fourth alkyl substituent do not contribute as significantly to steric deactivation as the

TABLE IV

ANALYTICAL CONDITIONS

Olefin pair	Vpc standard	Solvent	Chromatograph	Column	Temp, °C
Cycloopentene, *cis*-pentene-2	Cyclopentane	*n*-Heptane	P & E 154D[a]	4-m DMS[b]	25
Pentene-1, 3-methyl-1-butene	Cyclopentane	*n*-Heptane	P & E 154D	4-m DMS	25
cis-Pentene-2, pentene-1	Cyclopentane	*n*-Heptane	P & E 154D	4-m DMS	25
Cyclopentene, 2-methyl-2-butene	Cyclopentane	*n*-Heptane	F & M 810[c]	12-ft DMS	25
2-Methyl-2-butene, 3-methyl-1-butene	Cyclopentane	*n*-Heptane	F & M 810	12-ft DMS	25
3-Methyl-1-butene, *trans*-pentane-2	Cyclopentane	*n*-Heptane	F & M 810	12-ft DMS	25
3-Methyl-1-butene, isobutylene	Freon 114	Cyclopentane	F & M 810	12-ft DIP[d]	25
Butene-1, *trans*-butene-2	Freon 114	*n*-Pentane	F & M 810	12-ft DIP	25
cis-Butene-2, isobutylene	Freon 114	*n*-Pentane	F & M 810	12-ft DIP	25
Isobutylene, 1,3-butadiene	Freon 114	*n*-Pentane	F & M 810	12-ft DIP	25
trans-Butene-2, isobutylene	Freon 114	*n*-Pentane	F & M 810	12-ft DIP	25
1,3-Butadiene, butyne-1	Freon 114	Cyclopentane	F & M 810	12-ft DIP	25
Isobutylene, butyne-2	Freon 114	Cyclopentane	F & M 810	12-ft DIP	25
2,3-Dimethyl-2-butene, 2-methyl-2-butene	Cyclopentane	*n*-Heptane	F & M 810	6-ft DIP	25
Vinylcyclohexane, styrene	Ethylbenzene	*n*-Pentane	P & E 154D	2-m PPG[e]	100

[a] Perkin-Elmer Model 159D gas chromatograph. [b] Dimethylsulfolane. [c] F & M Model 810 gas chromatograph. [d] Diisodecylphthalate. [e] Polypropylene glycol.

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(13) N. R. Slobodkin and N. Kharasch, *J. Amer. Chem. Soc.*, **82**, 5837 (1960).

(14) G. M. Beverly and D. R. Hogg, *Chem. Commun.*, 138 (1966).

introduction of a second alkyl group. Thus the presence of four alkyl groups activates the double bond to the point where reactivity approaches that of the *cis* olefin.

An alternative argument based on relative ground state stabilities can hardly be used to rationalize the greater reactivity of *cis* olefins relative to *trans* olefins, since it is difficult to envisage the significance of such a factor when the transition state is a cyclic structure with the positive charge primarily on sulfur. It would seem that in such circumstances there would be little lowering of the potential energy barrier due to the relief of *cis* interactions.

Experimental Section

Competitive rate determinations were conducted in the manner of the following example. A volumetric 250-ml *n*-heptane solution containing 3-methyl-1-butene (0.1 mol) and *trans*-2-pentene (0.1 mol), together with 0.05 mol of cyclopentane as an inert internal standard was subjected to three replicate vapor phase chromatographic analyses to determine the area ratio of each olefin to cyclopentane. A 100-ml aliquot was withdrawn, cooled to −70° and a quantity of methanesulfenyl chloride equivalent to 40 mol % of the initial unsaturation added slowly with stirring. After the CH_3SCl was consumed (starch–iodide test) the solution was reanalyzed in triplicate, withdrawing samples at −70, 0, and 25°. The ratio of initial to final concentrations provided sufficient data to utilize the expression

$$k(\text{3-methyl-1-butene})/k(\textit{trans}\text{-2-pentene}) = \log\frac{(\text{methylbutene})_0}{(\text{methylbutene})} \bigg/ \log\frac{(\text{pentene})_0}{(\text{pentene})}$$

to calculate the relative reaction of the two olefins.

A second increment of CH_3SCl sufficient for 60% total conversion of the initial unsaturation was then added and the reaction mixture reanalyzed in the same fashion. This procedure was duplicated on a second 100-ml aliquot of the standard solution, thus providing four values for each relative rate. Analytical conditions are tabulated in Table IV, p 873.

Registry No.—Methanesulfenyl chloride, 5813-48-9.

Acknowledgment.—The technical assistance of Mr. J. J. Werner is gratefully acknowledged.

Synthetic Approaches to Dibenzo-1,2,6,7-bisdehydro[10]annulene

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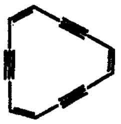
Several reactions designed to produce 1,5-dibenzo-3,8-bisdehydro[10]annulene were investigated. Evidence is presented for formation of derivatives of this π system as reactive intermediates in the reactions investigated.

By the principle of "ethynylogy" one may slice up [*n*]annulenes, insert *m* triple bonds and reclose to form 2*m*-dehydro[*n* + 2*m*]annulenes.[1] The benzene ethynologs 1 and 2 have been prepared recently.[2–5] The present paper details some work of ours on the dibenzo derivative (4) of 1,2,6,7-bisdehydro[10]annulene (3).



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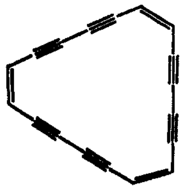

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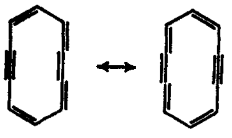

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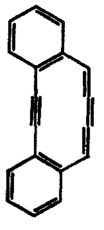
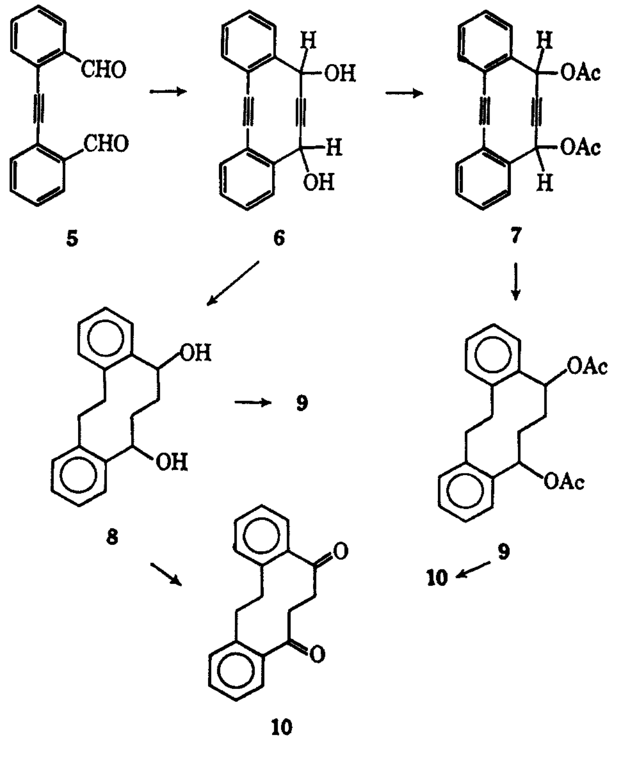


4

Results and Discussion

Construction of the ten-membered-ring system related to 4 was accomplished by a novel addition of acetylenedimagnesium bromide to 2,2′-diformyldiphenylacetylene (Scheme I). Reaction of a suspension of

Scheme I



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(1) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(2) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5991 (1967).

(3) K. G. Untch and D. C. Wysocki, *ibid.*, **88**, 2608 (1966).

(4) R. Wolovski and F. Sondheimer, *ibid.*, **87**, 5720 (1965).

(5) F. Sondheimer, R. Wolovski, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966).