The Reaction of Sulfenyl Chlorides with Allene

W. H. MUELLER[1] AND P. E. BUTLER[2]

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

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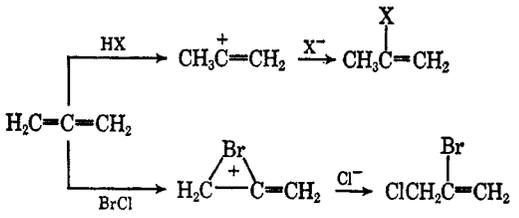
The reaction of either methane-, benzene-, or acetylthiosulfenyl chloride with allene was studied. In all cases allylic chlorides of the general structure I, $CH_2{=}C(SR)CH_2Cl$, were found to be the primary monoadducts. Diadducts of the general structure IV, $RSCH_2(Cl)C(SR)CH_2Cl$, were formed. With the exception of the acetylthiosulfenyl chloride adducts, the monoadducts rearranged to the vinylic chlorides II, $ClHC{=}C(SR)CH_3$; the diadducts IV decomposed rapidly with the loss of HCl. As a consequence of this decomposition, products of the general structure III, $CH_3(Cl)C(SR)CH_2Cl$, were produced. From the reaction of acetylthiosulfenyl chloride and tetramethylallene only the dehydrohalogenated product VI, 2,4-dimethyl-3-acetylthiosulfenyl-1,3-pentadiene, was isolated.

The mechanistic course of electrophilic additions to allene seems to follow one of two paths depending on the nature of the reactant.[3] Addends such as hydrogen halides add with the formation of a vinylic carbonium ion intermediate, resulting in Markovnikov oriented addition products. In contrast, a completely reversed adduct orientation has been observed with interhalogen compounds, *i.e.*, BrCl. Apparently the formation of a bromonium ion and subsequent nucleophilic attack of the chlorode ion on the terminal sp^3 carbon takes place (Scheme I).

SCHEME I



The episulfonium ion intermediate postulated for sulfenyl chloride additions to olefins[4] suggests *a priori* a similar intermediate in additions to allene. Thus, the addition mechanism would be expected to be analogous to that of interhalogens (Scheme I). Indeed, the addition of 2,4-dinitrobenzenesulfenyl chloride to allene has been reported to give 2-(2,4-dinitrobenzenethio)-3-chloro-1-propene.[5] However, similar additions to 1,2-cyclononadiene or 1,2-cyclodecadiene apparently resulted in the opposite adduct orientation, *i.e.*, the vinylic chloride.[6] This discrepancy and the recently recognized strong dependence of sulfenyl chloride–olefin adduct orientation on steric[7] as well as electronic effects[8,9] initiated the present study.

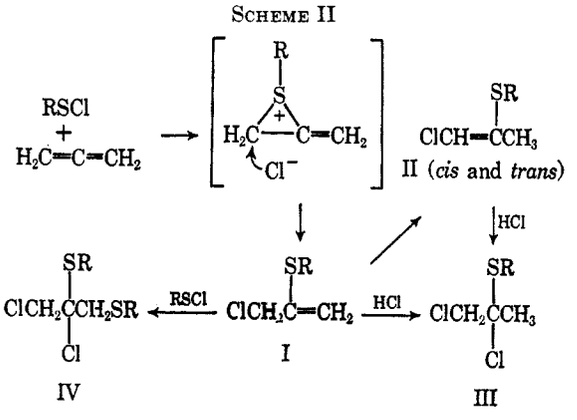
Results and Discussion

Methane-, benzene-, or acetylthiosulfenyl chloride were slowly added to a five- to tenfold excess of allene in methylene chloride. Methane- and benzenesulfenyl chloride reacted spontaneously at −30°, whereas reaction times up to 2 hr were necessary with acetylthiosulfenyl chloride at the same temperature. After it was recognized that the primary products from methane- and benzenesulfenyl chloride were quite labile at ambient temperature, the solvent was removed under vacuum at −10° and the residue analyzed immediately by nmr spectroscopy. This was less critical with acetylthiosulfenyl chloride adducts.

Sulfenyl Chloride–Allene Adducts.—The above described additions afforded four principal products (I–IV). Their relative product distributions obtained are summarized in Table I.

The data show an initial product distribution, *i.e.*, analyzed within 30 min after the addition was completed; values in brackets represent the "final" product distribution. This latter distribution was reached at −20° within 72 hr with the methanesulfenyl chloride adducts and after several weeks with the benzene- and acetylthiosulfenyl chloride adducts. From these data it becomes apparent that there are two primary products, the monoadduct I and the diadduct IV (Scheme II). Both compounds are quite stable if R represents an acetylthio group. In fact, the stability increases depending on R in the following order: $CH_3 < C_6H_5 << CH_3C(O)S$.

SCHEME II



The structure of adduct I is consistent with a product formed by nucleophilic ring opening of the episulfonium ion by the chloride.[7] The possibility of an allylic carbonium ion intermediate cannot be ruled out; however, a significant contribution by a carbonium ion appears unlikely in view of the recently observed 1,2 addition of sulfenyl chlorides to 1,3-dienes[8] and, more importantly, the exclusive *trans* addition to acenaphthylene.[7]

(1) To whom inquiries should be directed.
(2) Analytical Research Division.
(3) K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, **5**, 933 (1966), and references therein.
(4) N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 375–396.
(5) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960).
(6) W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).
(7) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966).
(8) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).
(9) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **32**, 2925 (1967).

TABLE I
SULFENYL CHLORIDE–ALLENE ADDUCTS

Reactants: RSCl, R	Mole ratio, C_3H_4/RSCl	% product distribution[a,b]: $ClCH_2C(SR)=CH_2$ I	$ClHC=C(SR)CH_3$ II *cis* and *trans*	$ClCH_2C(Cl)(SR)CH_3$ III	$ClCH_2C(Cl)CH_2SR$ IV
CH_3–	10	67 [6]	8 [70]	9 [20]	10 [0]
C_6H_5–	5	75 [9]	0 [64]	3 [15]	17 [2]
$CH_3C(O)S$–	10	85 [78]	0 [3]	0 [5]	10 [10]

[a] From semiquantitative nmr analysis within 30 min after reaction; the balance (*ca.* 5%) to 100% remains unidentified. [b] The values in brackets are obtained after postisomerization at −20°.

TABLE II
NMR PARAMETERS OF ALLENE–SULFENYL CHLORIDE PRODUCTS

No.	Structure	R	Chemical shift,[a] ppm: H_a	H_b	H_c	R	Coupling constant, cps: $J_{a,b}$	$J_{a,c}$	$J_{b,c}$
I	$H_bC(H_a)(SR)=C(H_c)CH_2Cl$	CH_3	4.87dt[b]	5.40qt	4.16bd	2.25s	1.60	~0.6	1.92
		C_6H_5	5.25t	5.58t	4.02dd	7.25m	<0.3	0.48	1.20
		$CH_3C(=O)S$–	5.65dt	5.73m	4.23dd	2.48s	0.63	0.60	1.25
II	$H_aC(Cl)=C(SR)CH_3$ (*trans*)	CH_3	5.72qt	1.99d		2.24s	1.20		
		C_6H_5	5.93qt	1.89d		7.18m	1.37		
	$H_aC(Cl)=C(SR)CH_3$ (*cis*)	CH_3	5.91qt	1.97d		2.27s	1.50		
		C_6H_5	6.24qt	1.62d		7.18m	1.47		
	$H_aC(SR)=C(Cl)CH_3$[d]	CH_3	6.04qt	2.10d		2.24s	1.00		
III	$CH_3C(Cl)(SR)CH_2Cl$	CH_3	3.92s	1.92s		2.25s			
		C_6H_5	3.77s	1.85s		~7.2m			
		$CH_3C(=O)S$	3.77s	1.94s		2.48s			
IV	$RSCH_2C(SR)(Cl)CH_2Cl$	CH_3	4.12s	3.28s		2.27s			
		C_6H_5	3.93s	3.68s		~7.2m			
		$CH_3C(=O)S$	4.18s	3.57s		2.48s			
VI	$HC(H_a)(SR)=C(C(=O)CH_3)C(CH_3)_2$	$CH_3C(=O)S$	4.57dqt	5.02dqt	2.10bs[c] 1.82*s	2.33s	2.45	0.90	1.45

[a] Abbreviations are s = singlet, d = doublet, t = triplet, qt = quartet, m = multiplet. [b] Since $J_{a,b} = J_{b,c}$, proton H_a appears as a quartet. The small magnitude of $J_{a,c}$ results in partially resolved signals for H_b and H_c. H_a appears as a double triplet and H_c as a broadened doublet. [c] H_c appears as a broad singlet owing to unresolved coupling with H_a and H_b. [d] Registry no.: 15893-18-2.

The formation of diadduct IV from I may not involve an episulfonium ion. In any case, the adduct orientation is electronically controlled and in accord with similar additions of sulfenyl chlorides to vinyl ethers[10] or vinyl sulfides.[11] If R represents methyl or phenyl then diadduct IV is quite labile and decomposes with elimination of HCl. While its characteristic nmr signals disappear those of adduct III increase at a proportional rate. Its formation is due to HCl addition to compounds I and II (Scheme II).

The structural assignments of compounds I, III, and IV are based on nmr evidence primarily. In several cases, particularly in the S-methyl series, structural confirmation was obtained by subsequent independent synthesis.

The nmr spectrum of the methanesulfenyl chloride adduct I is typical of the series (Table II) and gives strong support for the assigned adduct orientation. The terminal methylene group bearing chlorine is a partially resolved double doublet at 4.16 ppm and is coupled allylically to the strongly deshielded terminal olefin protons at 4.87 and 5.40 ppm. The field position of the methylene protons is strong evidence for the terminal chlorine group. A terminal methylene group bearing an S-methyl group would be expected to resonate at *ca.* 0.8 ppm upfield.[12]

Further support for the terminal disubstituted olefinic structure is supplied by characteristic infrared bands at 1605 (C=C stretching[13a]), 3105 (=CH_2

(10) A. Senning and S. O. Lawesson, *Tetrahedron*, **19**, 695 (1963); *Acta Chem. Scand.*, **15**, 1203 (1961); M. J. Baldwin and R. K. Brown, *Can. J. Chem.*, **45**, 1195 (1967).

(11) W. H. Mueller, unpublished data.

(12) P. E. Butler and W. H. Mueller, *Tetrahedron Lett.*, **19**, 2179 (1966).

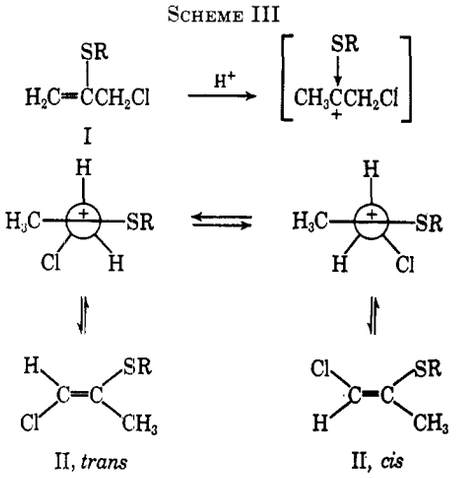
(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p 35; (b) p 51; (c) p 36.

stretching[13b]), and 862 cm^{-1} (=CH_2 out-of-plane hydrogen deformation[13b]).

The nmr spectra of the S-methyl compounds III and IV consist of three singlets (Table II) with intensities and field positions identical with those of independently synthesized samples. Product IV was obtained from the reaction of 2 equiv of either methane- or acetylthiosulfenyl chloride with allene. The diadduct formed from the latter sulfenyl chloride proved quite stable at ambient temperature, whereas the methanesulfenyl chloride diadduct decomposed rapidly even at −20° with the evolution of gaseous HCl and black tar. Hydrogen chloride addition to the S-methyl analog of II, whose independent synthesis is described below, produced a product identical with III.

Rearrangement of Monoadduct I.—As indicated above, there is a correlation between the stability of adducts I and IV with the electronic character of R. A similar relationship had been found previously for the propensity for rearrangement of sulfenyl chloride adducts from olefins[7,9] and conjugated dienes.[8] This has been attributed to the relative electron availability on the sulfur atom toward SNi displacement of the respective β-chlorides. The same factors may be envoked to provide a rationale for the stability or ease of formation of the intermediate carbonium ion (Scheme III) postulated for the rearrangement of adduct I to compound II.

SCHEME III



The kinetically controlled product of this acid-catalyzed rearrangement is the *cis* isomer of II. At a low conversion level (*ca.* 20% rearranged), compound *cis* II was the exclusive product if R was phenyl. When R = methyl, a 4:1 *cis/trans* ratio was observed at the same conversion. When adduct I, however, had rearranged to the extent of >90% a 1:1 and 3:2 *trans/cis* isomer ratio was observed with R being phenyl and methyl, respectively. This represents the equilibrium mixture of the two isomers since the same ratio was obtained independently from the acid-catalyzed isomerization of the pure *trans*-S-methyl compound, II. This compound was available from the addition of methanesulfenyl chloride to methylacetylene.

Infrared analysis indicated the trisubstituted olefin for II. Characteristic peaks are at 1605 (C=C stretching) and 795 cm^{-1} (=CH— out-of-plane hydrogen deformation).[13c]

The nmr data confirmed this structural assignment. The allylic methyl hydrogens of the *trans* isomer II exhibit a doublet at 1.99 ppm coupled *trans* to the vinylic proton (J = 1.20 cps) which appears as a quartet at 5.72 ppm. The *cis* isomer shows a doublet for its methyl hydrogens at 1.97 ppm which is coupled to the *cis* oriented vinylic hydrogen (J = 1.50 cps). Its signal appears as a quartet at 5.91 ppm.

The anti-Markovnikov adduct orientation and *trans* stereochemistry are assigned by analogy to similar additions with dimethylphosphorylsulfenyl chloride[14] or dimethylaminosulfenyl chloride.[15] The dependence of product orientation on solvent has recently been reported.[16] In general, *trans* addition of sulfenyl chlorides to acetylenes has been assumed.[16,17]

Acetylthiosulfenyl Chloride–Tetramethylallene Adduct.—To our knowledge the reaction of 2,4-dinitrobenzenesulfenyl chloride with cyclic allenes[6] is the only previously reported example of such additions to substituted allenes. It is quite surprising that this addition should result in Markovnikov oriented monoadducts, *i.e.*, the opposite adduct orientation as now observed in several cases with allene. Ring opening of an episulfonium ion intermediate on the vinylic carbon or a vinyl carbonium ion as postulated for hydrogen halide additions (Scheme I) does not offer an attractive explanation, particularly since little evidence for the occurrence of carbonium ion intermediates was found throughout our previous work on sulfenyl chloride additions to olefins[7] and dienes.[8]

Tetramethylallene was thought to provide a convenient model reagent to study the effect of terminal substituents on the adduct orientation. Acetylthiosulfenyl chloride was chosen as the addend since it had afforded the most stable adducts with allene. Although the addition reaction appeared to proceed in a normal fashion, the subsequent product elucidation became unexpectedly complicated. The reaction mixture rapidly evolved HCl at ambient temperature. Compound VI (Scheme IV) was the sole identifiable product and was isolated in *ca.* 80% yield.

The structure of the diene VI was revealed by its nmr spectrum (Table II). A singlet at 2.10 ppm appears for the vinylic methyl group, and a more shielded singlet at 1.82 ppm of twice the intensity represents the two terminal methyl groups. Two double quartets at 4.57 and 5.02 ppm are characteristic for the nonequivalent terminal methylene protons.

The nmr spectrum of the crude product mixture at low temperature is quite complex containing a number of methyl group signals. Signals pertinent for compound VI indicate its presence in this crude product and some of the additional methyl group singlets are consistent with structure V; however, a definite assignment was not possible. In view of the questionable intermediacy of the expected primary adduct V, an additional pathway for the formation of product VI has to be considered (Scheme IV). Expulsion of a proton from either an episulfonium ion or carbonium ion inter-

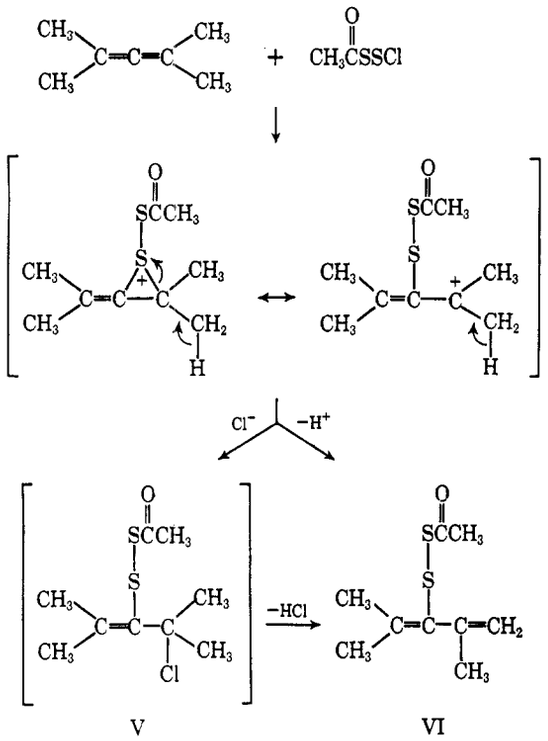
(14) W. H. Mueller, R. M. Rubin, and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).

(15) W. H. Mueller and P. E. Butler, β-Chloroalkylsulfenamides, *ibid.*, in press.

(16) V. Calò, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Lett.*, **49**, 4399 (1965), and references therein.

(17) N. Kharasch and C. N. Yianios, *J. Org. Chem.*, **29**, 1190 (1964).

SCHEME IV



mediate provides an alternate mechanism for the formation of VI. A significant contribution of an allylic carbonium ion structure to the intermediate in this special case is conceivable, particularly in view of previous work with acetylthiosulfenyl chloride.[9] It had been found that the withdrawing effect of the acetyl group tends to destabilize a positive charge on the sulfur atom in an episulfonium ion, thus contributing to the development of an electron deficient center on an alkyl-substituted carbon atom. This resulted in predominant Markovnikov addition to isobutylene.

Although the present result in the case of tetramethylallene does not rigorously exclude the possibility of Markovnikov addition (*i.e.*, vinylic chloride) to alkyl-substituted allenes, it is consistent with the normal adduct orientation observed with the parent allene.

Experimental Section

Method of Analysis.—Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Neat samples containing tetramethylsilane as an internal standard were used unless stated otherwise.

Infrared spectra were recorded on a Beckman Model IR-10 infrared spectrophotometer.

Starting Materials. Unsaturates.—The allene used was a Matheson product of +99% purity. It contained *ca.* 0.8% propene and traces of propane. Tetramethylallene (*ca.* 98% pure) was obtained from Columbia Organic Chemicals Co.

Methanesulfenyl Chloride.—Its previously reported preparation[18] from dimethyl disulfide and sulfuryl chloride was slightly modified by omitting tetrachloroethane as a solvent. The distilled methanesulfenyl chloride was obtained in *ca.* 90% yield and +98% purity. Its nmr spectrum shows a singlet at 2.91 ppm.

Benzenesulfenyl Chloride.—Freshly distilled sulfuryl chloride (20.3 g, 0.15 mol) was slowly added at ambient temperature to a solution of 32.7 g (0.15 mol) of diphenyl disulfide in 100 ml of CH_2Cl_2 (dry) containing 3 ml of pyridine.[19] After completion of the addition, the solution was stirred for an additional hour and then the solvent was removed at ambient temperature (12 mm). Subsequent distillation of the residue afforded 33 g (76% yield) of the dark red benzenesulfenyl chloride: bp 49° (4 mm); $n^{20}D$ 1.613 [lit.[20] $n^{20}D$ 1.610).

Acetylthiosulfenyl Chloride.—The chlorination of diacetyl disulfide afforded acetylthiosulfenyl chloride of *ca.* 99% purity.[9] The only impurity present was the starting disulfide.

General Method of Addition of Sulfenyl Chlorides to Unsaturates.—To an approximately 50% solution of the unsaturate in methylene chloride, the sulfenyl chloride was slowly added at such a rate to keep the reaction mixture at −30 to −40°. Anhydrous conditions and a nitrogen atmosphere were maintained. Approximately a 9 *M* excess of the unsaturate was used for the selective synthesis of monoadducts. Diadducts were obtained from stoichiometric amounts of reactants. Addition of methane- and benzenesulfenyl chloride to the unsaturates was strongly exothermic and instantaneous. After removal of most of the solvent at *ca.* −10° (2 mm) the crude product mixtures were analyzed immediately by nmr spectroscopy. Similar additions using acetylthiosulfenyl chloride were found to be much slower. In case the reaction mixtures were kept for 2 hr at −30° after the addition was completed. The reaction mixtures were then allowed to warm to room temperature, and the solvent was removed on a rotary evaporator.

The crude product mixtures were analyzed by nmr. Essentially quantitative consumption of the sulfenyl chlorides was observed. Product distributions and nmr parameters of the individual adducts are summarized in Tables I and II, respectively.

1-Chloro-2-methylthio-1-propene (*trans* **II**).—Addition of methanesulfenyl chloride to methylacetylene according to the above procedure afforded the *trans* adduct II in >95% selectivity together with <5% of the isomeric 1-methylthio-2-chloro-1-propene. Distillation under vacuum yielded the *trans* adduct II, bp 58° (32 mm).

Anal. Calcd for C_4H_7SCl: C, 39.18; H, 5.71; S, 26.15. Found: C, 39.09; H, 5.98; S, 26.04.

1,2-Dichloro-2-methylthiopropane (**III**).—Gaseous HCl was bubbled through 1-chloro-2-methylthio-1-propane (II) and the conversion was followed by nmr analysis. After the reaction was completed, the product was briefly degassed at reduced pressure. The tan, liquid compound slowly darkened (24 hr at room temperature); however, no sign of decomposition was observed in its nmr spectrum.

Anal. Calcd for $C_4H_8SCl_2$: C, 30.20; H, 5.09; S, 20.16. Found: C, 30.31; H, 5.18; S, 19.95.

***trans–cis* Isomerization of 1-Chloro-2-methylthio-1-propene** (**II**).—Gaseous HCl was introduced into pure *trans* adduct II until 5–10% of II was converted into the HCl adduct III. The isomerization of *trans* into *cis* adduct II was then followed by nmr analysis. Within 8 hr at room temperature, equilibrium was reached at a *cis/trans* ratio of 2:3.

2-Acetylthiosulfenyl-3-chloro-1-propene (I).—Acetylthiosulfenyl chloride was added to allene as described in the general procedure. Distillation of the crude product under vacuum afforded pure monoadduct I, bp 64–65° (0.02 mm).

Anal. Calcd for $C_5H_7S_2OCl$: C, 32.87; H, 3.86; S, 35.10. Found: C, 32.59; H, 3.79; S, 35.63.

1,2-Diacetylthiosulfenyl-2,3-dichloropropane (**IV**).—Addition of 2 equiv of acetylthiosulfenyl chloride to allene according to the general procedure resulted in the diadduct IV. It was not possible to distil the oily product, however, small amounts of volatile impurities were removed with nitrogen bubbling at room temperature (*ca.* 10^{-4} mm).

Anal. Calcd for $C_7H_{10}S_4O_2Cl_2$: C, 25.84; H, 3.01; S, 39.42. Found: C, 25.67; H, 3.01; S, 40.01.

2,4-Dimethyl-3-acetylthiosulfenyl-1,3-pentadiene (**VI**).—The addition of acetylthiosulfenyl chloride to tetramethylallene was carried out as described in the general procedure. The crude product evolved HCl at room temperature which was facilitated by decreased pressure and moderate heating (*ca.* 60°). Once a constant vacuum could be maintained distillation became possible. The dehydrohalogenated product VI was attained in *ca.* 80% yield at bp 63–64° (5×10^{-3} mm).

(18) H. Brintzinger, K. Pfannstiel, H. Koddebusch, and K. Kling, *Ber.*, **83**, 87 (1950).

(19) N. Kharasch, U. S. Patent 2,929,820 (1960); *Chem. Abstr.*, **54**, 15318 (1960).

(20) I. B. Douglass, K. R. Brower, and P. I. Murrin, *J. Amer. Chem. Soc.*, **74**, 5770 (1952).

Anal. Calcd for $C_9H_{14}S_2O$: C, 53.42; H, 6.97; S, 31.69. Found: C, 52.96; H, 6.90; S, 31.90.

Registry No.—Allene, 463-49-0; methanesulfenyl chloride, 5813-48-9; benzenesulfenyl chloride, 931-59-9; acetylthiosulfenyl chloride, 3250-24-3; I (R = CH_3), 15893-05-7; I (R = C_6H_5), 15893-06-8; I (R = CH_3COS), 15893-07-9; II (R = CH_3) (*trans*), 15893-08-0; II (R = C_6H_5) (*trans*), 15893-09-1; II (R = CH_3) (*cis*), 15893-10-4; II (R = C_6H_5) (*cis*), 15893-11-5; III (R = CH_3), 15893-12-6; III (R = C_6H_5), 15893-13-7; III (R = CH_3COS), 15893-14-8; IV (R = CH_3), 15893-15-9; IV (R = C_6H_5), 15893-16-0; IV (R = CH_3COS), 15893-17-1; VI, 15822-80-7.

Acknowledgment.—The authors thank Mr. W. C. Whitlock for excellent technical assistance.

The Structure of Di(benzenesulfonyl)hydrazines and the Synthesis and Characterization of Di(phenylsulfonyl)diimide, a New Azo Compound[1-3]

HAROLD KWART AND A. A. KHAN

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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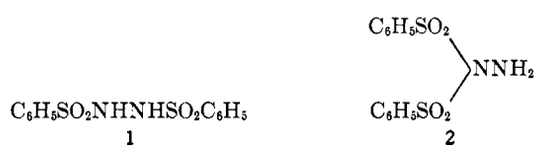
Evidence provided by nmr, mass spectrometry, ultraviolet, infrared, and pK_a measurements on dibenzenesulfonylhydrazine has been evaluated in the effort to distinguish between the symmetrical and unsymmetrical formulations possible for this substance. A clear-cut distinction on the basis of these physical lines of evidence alone has not been found possible. However, on mild oxidation it is shown that di(phenylsulfonyl), **11**, is produced in good yield. The formation of this oxidation product, which could not have arisen from the unsymmetrical structure **2** except by an unprecedented rearrangement of a benzenesulfonyl group, is regarded as proof of the originally proposed structure **1**. The structure proof for **11**, based on elemental analysis, molecular weight determination, nmr, ir, Raman, and mass spectral evidence, appears to contradict earlier statements in the literature that such azo compounds are synthetically unstable.

Several groups of workers[4-6] have reported a preparation alleged by Curtius[4] to be **1**, the summetrically substituted N,N′-bisbenzenesulfonylhydrazine, by reacting benzenesulfonyl chloride with hydrazine in alkaline solution.[5,6] However, the only evidence presented in support of their proposed structure was an elemental analysis and a molecular weight determination. The possibility that the unsymmetrical isomer **2** had been formed was not considered by these early workers.



$C_6H_5SO_2NHNHSO_2C_6H_5$ (**1**)

(**2**)

Recent results reported by Smith and Hein[6] for analogous sulfone–hydroxamic acid reactions suggest the need to consider the alternative structure **2**. A clear distinction in the behavior of corresponding sulfonyl and carbonyl derivatives undergoing acylation reactions has been demonstrated. Thus, Smith and Hein[7] showed that, whereas acylation of sulfonehydroxamic acids proceeded by oxygen substitution, further substitution occurred at nitrogen faster than O-acylation of the unsubstituted hydroxamic acid. Finally, in these laboratories,[8] it has been established that the reaction of sulfonehydroxamic acids with toluenesulfonyl chlorides results exclusively in the N,N-bis(toluenesulfonyl)hydroxylamine.

The only basis for a choice between structures **1** and **2** has been proposed by Grammaticakis[9] in studies of the absorption of α,β-disubstituted hydrazines in the visible and ultraviolet. He has claimed, in effect, that uv spectral similarities between benzenesulfonamide and the Curtius product, dibenzenesulfonylhydrazine, can be construed to support structure **1**.

Results and Discussion

Ultraviolet Spectra.—In reexamining the basis of Grammaticakis' deduction, the spectral characteristics of dibenzenesulfonylhydrazine were compared with those of benzenesulfonamide (**3**) and dibenzenesulfonimide (**4**) (see Figure 1). It will be noted that all three spectra possess a shoulder on the short wave length side of λ_{max}. Furthermore, the λ_{max} positions and intensities are almost identical in all three cases. Clearly the strong similarity in the spectral features of the imide **4** and the amide **3** tends to vitiate the Grammaticakis argument in support of structure **1**. His interpretation, which makes the implicit assumption that the presence on the nitrogen atom of only a single acyl or sulfonyl group is responsible for the observed relationship in the uv characteristics of the Curtius product and benzenesulfonamide (**3**), is obviously unfounded. Thus, formula **2** is still admissible on the basis of the uv evidence as a possible structure of dibenzenesulfonylhydrazine.

Mass Spectroscopy.—For this purpose the homologous di-*p*-toluenesulfonylhydrazine (**1a**) was employed. The objective again was to determine whether

(1) This name is chosen to be consistent with the nomenclature usage set forth in *Chemical Abstracts*. However, the common name azobisdiarenesulfones appears to be somewhat established in the literature.[2]

(2) H. Bock, *Angew. Chem.*, **77**, 472 (1965), see ref 3. This reference was kindly supplied by a very knowledgeable referee.

(3) These reaction conditions were very similar to those employed commonly in the Diels–Alder condensation reactions of cyclopentadiene with azobisdiformate esters. See for examples (a) J. G. Kuderna, U. S. Patent 2,802,012 (1957); (b) J. G. Kuderna, J. W. Sims, J. F. Wikstrom, and S. B. Soloway, *J. Amer. Chem. Soc.*, **81**, 382 (1959); (c) O. Diels, J. H. Blum, and W. Koll, *Ann.*, **443**, 242 (1925); (d) J. C. J. Mackenzie, A. Rodgman, and G. F. Wright, *J. Org. Chem.*, **17**, 1666 (1952); (e) A. Rodgman and G. F. Wright, *ibid.*, **18**, 465 (1953).

(4) T. Curtius and F. Lorenzen, *J. Prakt. Chem.*, **58**, 166 (1898).

(5) K. F. Jennings, *J. Chem. Soc.*, 1172 (1957).

(6) O. Hinsberg, *Ber.*, **27**, 601 (1894).

(7) P. A. S. Smith and G. E. Hein, *J. Amer. Chem. Soc.*, **82**, 5731 (1960).

(8) B. E. J. Schultz, M. S. Thesis, University of Delaware, 1963.

(9) P. Grammaticakis, *Bull. Soc. Chim. Fr.*, 93 (1953).