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

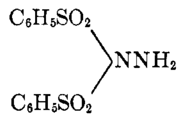
Received August 29, 1966

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



$(C_6H_5SO_2)_2NNH_2$

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).

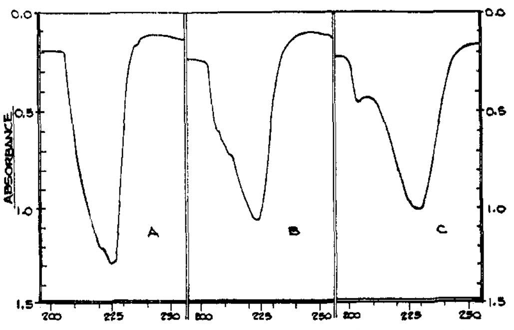
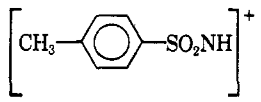


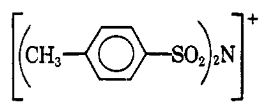
Figure 1.

a clear distinction was possible between the symmetrical and unsymmetrical formulations of the structure of this product. Figure 2 presents that portion of the mass spectrum obtained for the interval from *m/e* 50 to the parent peak at 340. Expectedly, the masses below 200 are far more abundant (the scale *m/e* 190–340 has been magnified ten times).

This spectrum must be examined in terms of what masses could be anticipated to appear in greater relative abundance for each of the structural alternatives. Thus, for the (homologous) structure **1**, the fragment **5**, arising from symmetrical cleavage at the N–N bond, could have been anticipated (or some related fragment possessing several hydrogens more or less). For the unsymmetrical homolog of **2**, the fragment **6** representing the cleavage of the N–N bond could be anticipated (or some related fragment possessing one or more additional hydrogens).



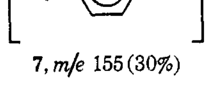
5, *m/e* 170



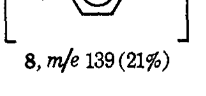
6, *m/e* 324

However, the actual findings are not in clear-cut, exclusive agreement with either expectation, and cannot therefore be regarded as a decisive basis for distinction between the alternative structures **1** and **2**. Thus, peaks are found at *m/e* 172 (relative abundance 15%) and *m/e* 326 (0.1%). The *m/e* 326 peak could be construed to be in support of both alternatives since it could also have arisen as a rearrangement product of structure **1**.

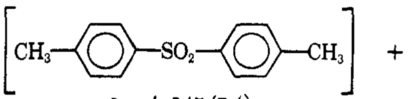
Other peaks that are to be noted in the spectrum can be reconciled as fragmentation products of either structure. For instance, the relatively intense peaks at *m/e* 155 and 139 are to be correlated with the fragments **7** and **8**, sulfone and sulfoxide moieties. Peaks at *m/e* 245 and 310 can be identified with the fragments **9** and **10** which could conceivably have originated from either precursor (**1** or **2**).



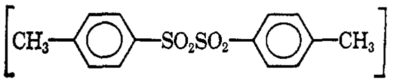
7, *m/e* 155 (30%)



8, *m/e* 139 (21%)



9, *m/e* 245 (7%)



10, *m/e* 310 (1%)

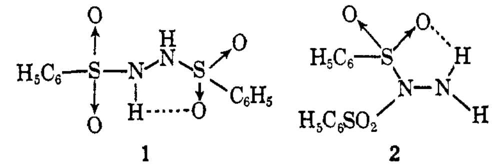
Nmr Spectroscopy.—In acetone solution in the A-60 the hydrazine derivative from benzenesulfonyl chloride displayed a multiplet of relative area 5 centered near 7.75 ppm (phenyl protons) and a poorly resolved peak near 8.82 ppm of relative area 1 (N–H protons). The corresponding *p*-tolyl derivative, examined in the 100-Mc instrument, showed the aromatic protons as a clearly defined AB quartet and the N–H protons appeared downfield as a relatively sharp singlet.

These observations would suggest that the true structure of the Curtius compound possesses a highly acidic N–H proton. This is confirmed by measurement of the pK_a (6.45), but, again, it is not possible to deduce with any confidence whether this fact is in better agreement with either of the alternatives being considered.

Hydrogen Bonding.—In dilute carbon tetrachloride solution it was possible to identify both an intramolecularly bonded N–H at 3300 and a free N–H at 3390 cm^{-1}. In dilute tetrahydrofuran the intramolecular bond disappeared (as usual) and an intermolecular bond (to the THF) at 3350 cm^{-1} replaced it. A $\Delta\nu$ value of 90 cm^{-1}, however, can be reconciled with either of the hydrogen bonded versions of **1** or **2**, as seen in Scheme I.

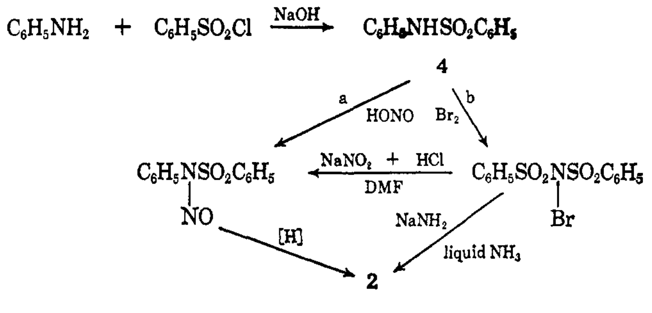
SCHEME I

INTRAMOLECULAR H BONDING



Structure Proof *via* Synthesis.—Two approaches were undertaken in the effort to establish the structure of the Curtius product through the use of common preparative procedures and structural transformations. The first attempt was directed toward an independent synthesis of structure **2** through the route outlined in Scheme II.

SCHEME II



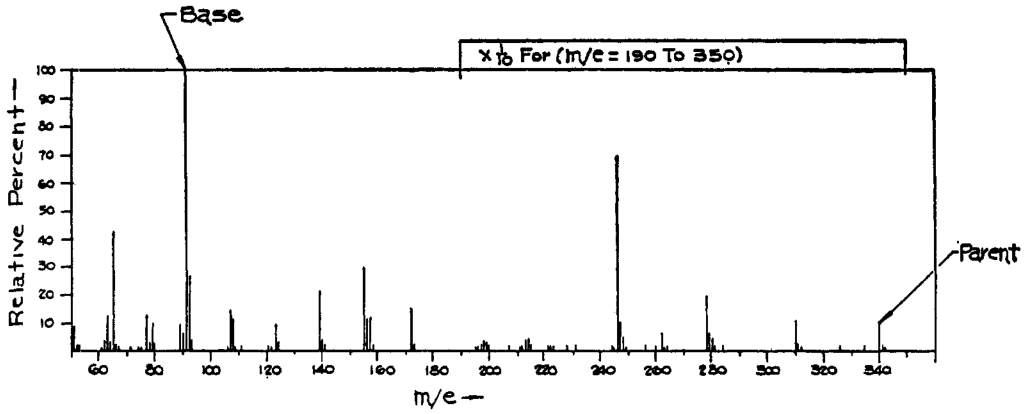


Figure 2.—Mass spectrum of dibenzenesulfonylhydrazine.

TABLE I

Reacn no.	Nitrosating agent	Compd reacted	Solvent	Temperature, °C	Product	Ref
1	HNO_2 + HCl	$(C_6H_5SO_2)_2NH$	Water	0	$(C_6H_5SO_2)_2NH$	*a*
2	HNO_2 + dry HCl	$(C_6H_5SO_2)_2NH$	C_2H_5OH	0	$(C_6H_5SO_2)_2NH$	*a*
3	HNO_2 + dry HCl	$(C_6H_5SO_2)_2NH$	DMSO[b]	0	$(C_6H_5SO_2)_2NH$	*c*
4	HNO_2 + dry HCl	$(C_6H_5SO_2)_2NH$	DMF[d]	0	$(C_6H_5SO_2)_2NH$	*c*
5	HNO_2 + dry HCl	$(C_6H_5SO_2)_2NBr$	DMSO	0	$(C_6H_5SO_2)_2NH$	*c*
6	HNO_2 + dry HCl	$(C_6H_5SO_2)_2NBr$	DMF	0	$(C_6H_5SO_2)_2NH$	*c*
7	Isoamyl nitrite + dry HCl	$(C_6H_5SO_2)_2NBr$	Ether	40	$(C_6H_5SO_2)_2NH$	*e*
8	Isoamyl nitrite + dry HCl	$(C_6H_5SO_2)_2NH$	Ether	0–40	$(C_6H_5SO_2)_2NH$	*e*
9	Nitrosyl sulfuric acid	$(C_6H_5SO_2)_2NH$	Water	0	$(C_6H_5SO_2)_2NH$	*a, e*

[a] W. W. Hartman and L. J. Roll, "Organic Syntheses," Coll Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 460. [b] DMSO was dried over a molecular sieve and distilled under vacuum. [c] N. Kornblum, *et al.*, *J. Amer. Chem. Soc.*, **78**, 1497 (1956); N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957). [d] DMF was dried over calcium hydride and distilled. [e] N. Levin and W. H. Hartung, "Organic Syntheses," Coll Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 191; W. H. Hartung and J. C. Munch, *J. Amer. Chem. Soc.*, **51**, 2262 (1929); W. H. Hartung and F. Crossley, "Organic Syntheses," Coll Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 363.

Dibenzenesulfonimide (**4**) was prepared by a method analogous to that of Dykhanov.[10] The structure of **4** was in complete agreement with its nmr spectrum showing a phenyl proton multiplet of relative area 10 at 7.42–8.25 ppm and an N–H peak of relative area 1 at 11.1 ppm. However, all attempts to convert it into the N-nitroso derivative through route a or b failed. The various attempts, both successful and unsuccessful, made to carry out each of the steps in Scheme II summarized in Table I (see Experimental Section).

The second effort was directed at transforming the Curtius compound to a product which could be unequivocally identified, and its structure related to that of the starting material by means of the nature of the transforming reaction. It has been pointed out[2] that other investigators have attempted to oxidize the hydrazine derivative **1** in the effort to obtain the corresponding azo compound and have reported decomposition of the presumed reaction product even at −50°. In our hands, however, this objective could be accomplished in ideal fashion through the use of bromine at refluxing ethanol temperatures.

The proof of the structure of **11** then clearly establishes the structure **1** for its hydrazine precursor, unless the obtuse assumption be made that structure **2** could be transformed to **11** *via* oxidative rearrangement of a benzenesulfonyl group in the unsummetrical hydrazine. The migration of groups, which normally show high migration tendency in passing from one nitrogen to the other in unsymmetrically disubstituted hydrazines, has recently been reviewed by Lemal.[11] However, the substrates and reaction conditions under which such rearrangements can be effected are quite different than those which bring about formation of **11**. Moreover, the rearrangement of a benzenesulfonyl group in a 1,2 shift of this nature will be recognized as quite unprecedented.[11]

$$1 \xrightarrow[\text{ETOH}]{Br_2} \underset{11}{C_6H_5SO_2N{=}NSO_2C_6H_5} + 2HBr$$

Proof of Structure and Characterization of Di(phenylsulfonyl)diimide. A. Analysis.—The elemental analysis involving direct determination of the elements (C, H, O) and ebullioscopic determination of molecular weight (mol wt, 299 *vs.* 310 calcd) are completely consistent with a dehydrogenation product of **1**, rather than some dimeric oxidation product. The possibility that the oxidation of **1** may have proceeded to the *azoxy* stage is ruled out by the direct determination of the oxygen content of **11** (see Experimental Section).

B. Nmr Data.—The spectrum consisted of only phenyl protons in the usual multiplet relationship at *ca.* 7.7–8.0 ppm. This is again in accord with the assigned structure **11**.

C. Ir Data.—The spectrum was devoid of an –N–H absorption and had instead a prominent and very

---

(10) N. N. Dykhanov, *Zh. Obshch. Khim.*, **29**, 3602 (1959); *Chem. Abstr.*, **54**, 19577*h* (1960).

(11) D. M. Lemal, F. Menger, and E. Coats, *J. Amer. Chem. Soc.*, **86**, 2395 (1964).

TABLE II
ELEMENTS OF COMPARISON AND CONTRAST IN THE MASS SPECTRA[a] OF THE SUBSTRATE HYDRAZINE AND ITS OXIDATION PRODUCT

Dibenzenesulfonylhydrazine (1)			Di(phenylsulfonyl)diimide (11)		
Relative[b] approximate intensity	m/e	Possible identity	Possible identity	m/e	Relative[b] approximate intensity
0.3	313	Ion molecule reaction of P		Missing	. . .
0.4	312	P		Missing	. . .
0.2	282	P − $(NH)_2$	P − N_2	282	48
4	250	P − (2N + 2O + 2H)	P − (2N + 2O)	250	7
. . .	Missing		P − (SO + 2N)	234	99
0.7	218	P − (SO_2NHNH)		Missing	. . .
3	171	Cleavage ($C_6H_5SO_2NHNH^+$; $C_6H_5SO_2NN$ + 2H) or rearrangement product	Ion–molecule reaction?	171	29
100	142	$C_6H_5SO_2H^+$	Ion–molecule reaction	142	15
14	141	$C_6H_5SO_2^+$		141	100
43	125	$C_6H_5SO^+$		125	36

[a] Spectra were obtained with a direct injection probe on the CEC 21-103C mass spectrometer. For compound 1 the results recorded are from runs with probe temperatures of 180–210°. For compound 11 which was thermally (relatively) unstable the probe temperature was approximately 100°. The usual isotope peaks are not listed in this comparison table. [b] The peaks of compounds 1 and 11 are not to be compared to each other in any absolute sense since their recorded spectra were not run under precisely the same conditions. For instance, under exactly the same conditions the 142 peak of 11 is only *ca.* 1/20 as intense as that from 1.

sharp band at 1575 cm^{-1} known[12] to be characteristic of the disubstituted azo grouping.

The presence of this band, which we and others[12] have shown to be absent in the ir spectrum of azobisdiformamide, azobisisobutyronitrile, and diisopropyl azobisdiformate, would suggest that at least part of the composition of **11** has the *cis* structure about the —N=N— bond; otherwise, as in the cases of the other symmetrically substituted *azo* compounds, the —N=N— (unconjugated) stretch would be infrared inactive. (See Raman spectra below). The occurrence of an attractive sulfone–sulfone interaction stabilizing the *cis* configuration (**11a**) is apparently quite unique. The analogous carbonyl and cyano bearing substituents on the azo group are mutually repulsive and exist exclusively in the *trans* configuration.[12c]

It must also be noted that the ir spectrum of **11** does not of itself exclude an azoxy structure, but the intense 1575-cm^{-1} band makes this structure much less probable in consideration of the great variety of unsymmetrical azo compounds correlated with this absorption by LeFevre and coworkers.[12]

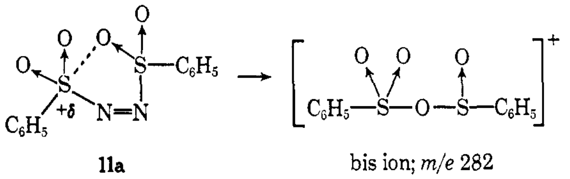
D. Raman Spectrum.—The azo (unconjugated) stretch in **11** is also strongly active in the Raman spectrum at 1576 cm^{-1}. This observation affords direct support for the presence of *trans* configuration material in the composition of the oxidation product. Furthermore, azobisdiformamide and diisopropyl azobisdiformate also show very strong absorptions at 1575 cm^{-1} in the Raman spectrum, which establish for both of these structures the symmetrical *trans* configuration about the double bond arrived at tentatively by LeFevre and coworkers[13c] on the basis of other measurements.

Judging roughly from the ratio of intensities of the $-SO_2-$ band at 1150 cm^{-1} and the 1576-cm^{-1} absorption, the oxidation product was comprised of two-thirds *trans* and one-third *cis*. This is further born out by direct petrographic microscope examination of the oxidation product, showing two types of crystals in the approximate ratio confirmed by these Raman band intensities.

E. Mass Spectrum.—In seeking verification of the structure of **11** a comparison of its spectrum with that of the precursor hydrazine proved to be most informative (see Table II).

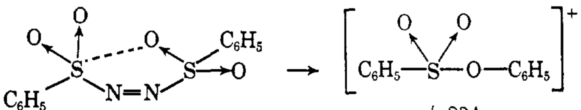
The relatively weak intensity peak at m/e 282 in **1** is explained as the product of extrusion of -NH-NH-, as commented on earlier in connection with the spectrum of di-*p*-toylsulfonylhydrazine (see above). This is one of the strongest peaks in the spectrum of **11** in the same mass range. The ready expulsion of nitrogen from the parent ion of azobisarylsulfone to give the bis ion (see Scheme III) accounts for the total absence of P in the spectrum of **11** and represents just what one would have expected of a molecule of its structure. That is to say, in view of the ir and Raman spectral evidence demonstrating the interaction that stabilizes the *cis* structure **11a**, the large extent of formation of the bis ion is made understandable.

SCHEME III



11a bis ion; m/e 282

The second most abundant peak of **11** in this mass range is actually missing in the spectrum of **1**, namely, m/e 234. This must represent the alternative manner of recombination of radical ion fragments produced in the nitrogen extrusion from **11a** accompanied by expulsion of SO.



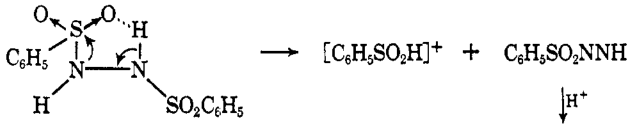
11a m/e 234

The most abundant peak of **1** may be correlated with the occurrence of intramolecular hydrogen bonding (identified above for **1**) which cannot occur in **11**.

---

(12) (a) R. J. W. LeFevre, M. F. O'Dwyer, and R. L. Werner, *Chem. Ind.* (London), 378 (1953); (b) R. J. W. LeFevre, M. F. O'Dwyer, and R. L. Werner, *Aust. J. Chem.*, **6**, 341 (1953); (c) R. J. W. LeFevre, C. G. LeFevre, and W. T. Oh, *ibid.*, **10**, 218 (1957).

Thus, with the formation of m/e 142, a cleavage product can also be regarded as a rearrangement result. Azo compound **11** forms this ion at only $^1/_{20}$th the relative intensity under very similar spectrometer conditions. In all likelihood what is presumably the same (but much less abundant) peak derived from **11** is formed as the result of a molecule–ion interaction involving the unusually abundant peak m/e 141 ($C_6H_5SO_2^+$). The ready thermal decomposition which **11** undergoes, a property shared by most azo compounds, could be responsible for its observed facility in forming ion–molecule interaction products.



1 m/e 171

Finally, it must be mentioned that many of the fragment ions supporting the assigned azo structure of **11** are the same as those observed for the hydrazine **1**. However, it must also be emphasized that the large difference in the abundance of the m/e 142 ion (a factor of 20 under similar spectrometer conditions) eliminates the presence of the hydrazine as an impurity in any significant amounts, as does the absence of the 312 and P ions.

F. Other Lines of Evidence.—It seemed desirable to test the proposed structure of **11** by means of chemical reactivity studies. Efforts were made to reduce it to the parent hydrazine **1** without success. When **11** was subjected to hydrogenation with finely divided platinum or platinum on charcoal, at 3 atm in alcoholic solvent, the starting material was recovered unchanged. Evidently the bulky sulfonyl substituents on the azo center of unsaturation prevents its adsorption on the catalyst, the necessary preliminary step to heterogeneous hydrogenation.

The attempt to reduce **11** to **1** by purely chemical means, such as zinc in acid solution, failed to produce the desired reaction and resulted instead in products representing sulfone–nitrogen cleavage. The ir spectrum of this product mixture showed neither an N–H band at *ca.* 3430 cm^{-1} to identify the hydrazine, nor the —N=N— band at 1575 cm^{-1}, characteristic of the starting material. It is also clear from this result that the unsymmetrically substituted hydrazine **2** was not present in the complex reduction product obtained.

A further indication of the steric hindrance to reactivity of the azo group in **11** that is afforded by the bis sulfone substituents was realized in attempts to utilize it as a Diels–Alder dienophile. Analogous azobisdiformate esters have been shown to undergo reaction rather readily, using typical dienes such as cyclopentadiene. However, using reaction conditions (see Experimental Section) which usually yielded good conversions with azobisdiformates, the reaction of **11** with cyclopentadiene failed completely. The unconverted starting material was recovered nearly quantitatively.

To the best of our knowledge **11** is a new composition of matter and is the first example of a stable class of compounds possessing the azobisdisulfone structure. Further studies of the properties, methods of preparation and reactions of this class of substances are currently in progress in these laboratories.

Experimental Section

All melting points were taken with a Fisher-Johns hot-stage apparatus and are essentially uncorrected.

N,N′-Bisbenzenesulfonylhydrazine (1) was prepared according to the method of Hinsberg.[6] Recrystallization from glacial acetic acid gave white needles, mp 236–237° (lit.[5] *ca.* 245°).

Dibenzenesulfonimide (4).—Benzenesulfonyl chloride (1.1 mol) was added dropwise over a period of 2 hr to a solution of benzenesulfonamide (1.0 mol) in 880 ml of 5% NaOH in water. The pH of the reacting solution was maintained throughout at *ca.* 7.2 by discreet additions of 5% NaOH. When addition was completed, stirring was continued for 30 min and 100 ml of 40% NaOH run into the mixture. The charge was then stirred and cooled to 15° and the sodium salt of **4** permitted to precipitate under stirring. In various runs, between 0.6 and 0.9 mol of the sodium salt was obtained in several runs by filtration. After taking up in water, boiling, and cooling, a sample of the salt melted above 260° with decomposition. Addition of slightly more than 1 equiv of 36% HCl at 25° to a solution of 1 mol of sodium salt in 300 ml of H_2O gave the free imide **2**, which is nearly insoluble in water at pH 2. On recrystallization from ethanol–water solution, a white crystalline product was obtained, mp 157–159° (lit.[9] 157–158°).

N-Bromodibenzenesulfonimide.—A solution of 20 g of **4** (*ca.* 0.10 mol) in 4 g of NaOH and 30 ml of H_2O was cooled by addition of 20 g of ice. The flask was surrounded by an ice bath and under vigorous (magnetic) stirring 6 ml of bromine was added all at once. Stirring was continued for 5 min longer and the precipitate collected on a fritted-glass filter. It was washed with cold water until free of bromide. The product (25-g yield) after drying in a desiccator at 40° melted at 120–122°.

Anal. Calcd for $C_{12}H_{10}S_2O_4NBr$: Br, 21.27; Found: Br, 20.34.

The infrared spectrum showed no N–H bands in the characteristic frequency regions.

Attempted Preparations of N-Nitrosodibenzenesulfonimide.—The experiments are summarized in Table I.

Di(phenylsulfonyl)diimide.—A solution of 0.2 g of **1** in 25 ml of ethanol was brought to reflux with stirring and 3 ml of bromine was added dropwise over 1 hr. Reflux was continued for 1 hr after addition was completed. The reflux condenser was then removed and the solvent permitted to boil away until the volume wa reduced to less than 5 ml. When a few drops of water was added to the cooled residue, a crystalline product separated, mp 188–193°. On recrystallization from ethanol–H_2O, the pure product resulted, mp 193–194° with fuming and decomposition. Upon infrared analysis (KBr pellet) of the product, the most characteristic band was observed at 1575 cm^{-1} (—N=N—).

Anal. Calcd for $C_{12}H_{10}N_2S_2O_4$: C, 46.15; H, 3.20; N, 8.97; S, 20.51; O, 21.07. Found: C, 46.21; H, 3.12; N, 8.92; S, 20.31; O, 21.04.

Reaction of N-Bromodibenzenesulfonimide in Liquid Ammonia.—Anhydrous liquid NH_3 (100 ml) was introduced into a 500-ml, three-necked flask equipped with mechanical stirrer and a Dry Ice condenser. Freshly cut sodium (4.72 g) was converted into sodamide in the usual fashion through use of a small amount of ferric nitrate. When the blue color had disappeared, the N-bromodibenzenesulfonimide (35.0 g) was added portionwise. After addition was completed, the mixture was stirred for 6 hr, the cooling condenser was removed, and the excess ammonia was vented. On working up the residue only dibenzenesulfonimide could be isolated.

N,N′-Bis-*p*-toluenesulfonylhydrazine (1a) was prepared according to the directions of Jennings.[5] Recrystallization from acetone–water solution afforded a product of mp 217–218° as white needles (lit.[5] 219–220°).

Reduction of 11.—A solution of 0.2 g of **11** in 15 ml of ethanol was charged in a round-bottom, three-necked flask equipped with reflux condenser and magnetic stirrer. To this was added in small portions at 30–40° powdered zinc (0.1 g, total) and concentrated HCl (4 ml, total) allowing sufficient time between additions of both of these reagents for foaming to subside. After addition was completed, the temperature was raised to reflux and held there for 0.5 hr. The solution was now cooled and filtered, and the solvent was stripped under reduced pressure, leaving a viscous liquid residue which resisted repeated attempts at crystallization. The ir spectrum of this residue showed neither a band at *ca.* 3430 nor at 1575 cm^{-1}, and thus contained neither **1** or **11** in significant amounts.

Attempted Condensation of 11 with Cyclopentadiene.—A solution of 0.6 g (*ca.* 0.002 mol) of **11** and 0.150 g (*ca.* 0.002 mol) of freshly prepared cyclopentadiene in anhydrous ether was maintained at 15–20° for 24 hr under nitrogen with magnetic stirring.[3] Upon stripping all volatiles at the water pump up to steam bath temperatures slightly more than 0.6 g of a solid remained which had an ir spectrum nearly identical with that of the starting compound **11**.

Mass Spectra.—That of N,N′-bis-*p*-toluenesulfonylhydrazine was taken on an Atlas double focus high resolution instrument (Atlas Mess and Analysentechnik GMBH Bremen) through the courtesy of Dr. C. Djerassi at Stanford University, Stanford, California, while one of us (H. K.) was in residence as visiting professor of Chemistry in 1964. Direct introduction of the sample was possible with this instrument and consequently pyrolytic decomposition could be avoided. The spectra of N,N′-bisbenzenesulfonylhydrazine and of compound **11** were recorded under conditions specified in Table II through the courtesy of Dr. W. B. Askew, for which we are most grateful.

Nmr spectra were determined with either a Varian A-60 or Varian HR-100 instruments.

H bonding data were taken with a Perkin-Elmer Model 337 grating infrared spectrometer.

pK_a measurements were obtained by use of a Sargeant Model D recording titrator.

Ebullioscopic determinations of the molecular weight of **11** were carried out in benzene solution with benzyl as a standard and using an instrumental design described in the literature.[13] Four determinations were made with the results ranging from 298–299, compared to calculated 310.

Registry No.—**1**, 6272-36-2; **3**, 98-10-2; **4**, 2618-96-4; **11a**, 15815-54-0; **11b**, 15815-55-1; N-bromodibenzenesulfonimide, 15815-56-2.

---

[13] R. V. Bonnar, M. Dimbal, and F. H. Strass, "Number Average Molecular Weight," Interscience Publishers, Inc., New York, N. Y., 1958.

The Hydrohalogenation and Deuteriohalogenation of 7-Norbornenone

Ronald Caple, Han Wan Tan, and Fu Mei Hsu

Department of Chemistry, University of Minnesota, Duluth, Minnesota 55812

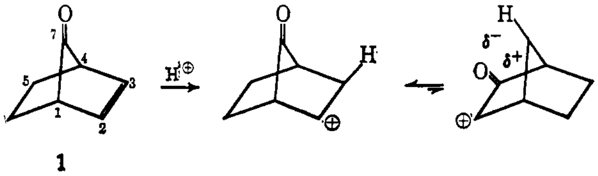
Received September 15, 1967

The polar addition of hydrogen bromide, hydrogen chloride, and the corresponding deuterio halides to 7-norbornenone (**1**) has been carried out. The products cannot be reconciled with an intermediate involving interaction between the protonated carbonyl group and the π electrons of the ethylenic system. The major product is the result of *cis-exo* addition with the rearranged *exo* product occurring to a much smaller extent. The importance of steric, bridging, and torsional effects in controlling the stereochemistry are considered.

The stereochemistry of the electrophilic addition of hydrogen halides to olefins has received considerable attention.[1-8] It has become apparent that the *trans* addition of a hydrogen halide to an α,β-unsaturated carboxylic acid is the result of a 1,4 addition and is not related mechanistically to the reaction of an isolated olefin.[9] It has also become apparent that the stereochemical course of addition to an isolated olefin is not a simple function of π complexes and steric effects. The occurrence of ion pairs or complexes leading to a preference for *cis* addition, unless torsional strain effects are unfavorable, is now recognized.[3,7]

The norbornene system has occupied a place by itself in these investigations owing to the importance, if any, of the delocalized "nonclassical" carbonium ion or the "windshield wiper effect"[10] in determining the stereochemistry of electrophilic additions. Steric effects alone cannot account for all of the *exo* products[2,4,5] since the hydrochlorination of bornylene and apobornylene also produces *exo* adducts.[6] The occurrence of a delocalized structure in the transition state of the proton-addition step also seems unlikely in view of the recent results of Brown[6] and Schleyer.[7]

We have investigated the hydrohalogenation, and deuteriohalogenation, of 7-norbornenone (1) in the hopes that we would be able to examine the stereochemical course of addition when a classical secondary norbornyl cation was involved. Attack of a proton on the double bond of 7-norbornenone (1) should produce a carbonium ion which is reluctant to rearrange as the rearranged carbonium ion involves a juxtaposition of positive changes. Likewise delocalization of the σ electrons of the C-1, C-6 bond in the transition state of the proton-addition step would seem less important here as compared to the norbornyl cation. If this is true, then it is possible that neither the nonclassical carbonium ion nor the equilibrating classical ions would be involved in the product-controlling attack of the halide ion.



1

Results

The polar hydrobromination, and deuteriobromination, of 7-norbornenone (1) was carried out in methylene chloride saturated with hydrogen bromide, or deuterium bromide, at 0°. The reaction was complete within

---

[1] P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **29**, 1625 (1964).

[2] S. J. Cristol, J. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719, 2726, 2733, 2738 (1966), and previous papers; S. J. Cristol and R. Caple, *ibid.*, 31, 2741 (1966).

[3] M. J. S. Dewar and R. C. Fahey, *Angew. Chem., Intern. Ed. Engl.*, **3**, 245 (1964), and references cited therein.

[4] H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

[5] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

[6] H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466, 3898, 3900 (1967), and references cited therein.

[7] P. von R. Schleyer, *ibid.*, **89**, 3901 (1967).

[8] R. C. Fahey, *Chem. Commun.*, **18**, 936 (1967), and previous papers.

[9] R. Caple, and W. R. Vaughan, *Tetrahedron Lett.*, 4067 (1966), and references cited therein.

[10] H. C. Brown, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21, 1961, p 2-O; "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept 5, 1962.