the unchanged enol ester, m.p. 98.6–99.6°, was recovered; the recovery amounted to 225 mg. (90%) of the unaltered enol benzoate, m.p. 98.6–99.4°, when ether was the solvent used. Both samples were identified by mixing melting point determinations with the authentic enol benzoate.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Unsaturated Sulfonic Acids. V.[1] Addition of Diazomethane and Phenyl Azide to Derivatives of Ethylenesulfonic Acid and its Homologs[2]

BY CHRISTIAN S. RONDESTVEDT, JR., AND PAULINE K. CHANG

RECEIVED JUNE 21, 1955

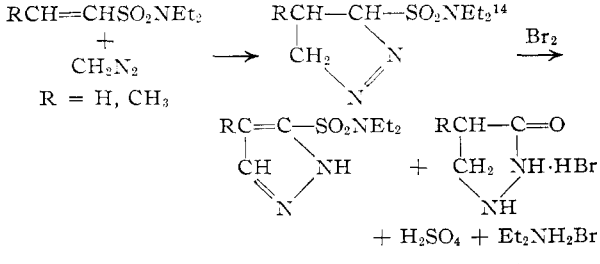
Diazomethane adds to derivatives and homologs of ethylenesulfonic acid to form pyrazoline-3-sulfonic acid derivatives. Pyrazoline-3-diethylsulfonamide on bromination gives pyrazole-3-diethylsulfonamide and 3-pyrazolidone in 2:1 ratio. *n*-Butyl pyrazoline-3-sulfonates on bromination give pyrazole-3-sulfonic acids and butyl bromide. Pyrazoline-3-sulfonyl chloride is unstable and appears to lose sulfur dioxide, forming 3-chloropyrazoline which undergoes conjugate addition to a second mole of ethylenesulfonyl chloride. Phenyl azide adds to N,N-diethylethylenesulfonamide normally to form 1-phenyl-1,2,3-triazoline 4-diethylsulfonamide. Phenyl azide reacts with *two* moles of ethylenesulfonyl chloride or propene-2-sulfonyl chloride, even in the presence of excess phenyl azide, to form 2-(1-phenyl-1-prototriazol-3-yl)-ethanesulfonate (VIa) or its 4,α-dimethyl homolog VIb. VIa was also formed quantitatively by addition of 1-phenyltriazole to ethylenesulfonyl chloride. These reactions are interpreted as a novel form of conjugate addition of a dipolar form of the triazoline or triazole. α-Bromoethylenesulfonyl chloride adds phenyl azide to form the unstable 1-phenyl-4-bromotriazoline-4-sulfonyl chloride which aromatizes promptly by loss of sulfur dioxide and hydrogen chloride to 1-phenyl-4-bromotriazole.

α,β-Unsaturated sulfonic acid derivatives add many nucleophilic reagents readily.[3–5] Diazomethane behaves as a nucleophilic reagent when adding to unsaturated systems,[6,7] and azides appear to react in a similar manner.[7–9] It was therefore of interest to explore the addition of diazomethane and phenyl azide to unsaturated sulfonic acid derivatives. These additions would afford convenient syntheses of derivatives of the unfamiliar pyrazoline-3-sulfonic acids and 1-phenyl-1,2,3-triazoline-4-sulfonic acids. A similar reaction, addition of diazomethane to vinyl *p*-tolyl sulfone, furnished 3-*p*-toluenesulfonylpyrazoline.[10]

Reactions of Diazomethane.—Ethylenesulfonic acid derivatives and homologs were selected for study, since preliminary experiments[11] had shown that derivatives of β-phenylethylenesulfonic acid added diazomethane at an inconveniently slow rate. Derivatives of ethylenesulfonic acid have been described previously[1,12] and the corresponding derivatives of propene-1-sulfonic acid were prepared similarly. It was more convenient to prepare propene-2-sulfonyl chloride by low-temperature dehydrochlorination[1] of 1-chloropropane-2-sulfonyl chloride than by the previously published method.[13]

Addition to Sulfonamides.—N,N-Diethylethylenesulfonamide and N,N-diethylpropene-1-sulfonamide absorbed a molar equivalent of diazomethane slowly (1–4 days) at room temperature. The crude pyrazolines were formed in quantitative yields but, since they could not be purified by distillation or crystallization, they were characterized by aromatization to the corresponding pyrazoles. Jacobs[6] noted that the most satisfactory method for converting pyrazolines to pyrazoles was bromination.

The action of bromine upon crude pyrazoline-3-diethylsulfonamide produced pyrazole-3-diethylsulfonamide in 57% yield, together with 3-pyrazolidone hydrobromide in 30% yield and comparable amounts of sulfuric acid and diethylamine hydrobromide, plus about 4% of hydrazine sulfate. Similarly, 4-methylpyrazoline-3-diethylsulfonamide yielded 4-methylpyrazole-3-diethylsulfonamide in 57% yield, together with diethylamine hydrobromide and sulfuric acid in 18% yield, and 4% of hydrazine sulfate. Only a trace of 4-methylpyrazolidone hydrobromide was isolated, probably because its physical properties render it more difficult to separate from other products of the reaction. The pyrazolidone salts were identified by comparison with authentic samples.



Addition to Sulfonate Esters.—*n*-Butyl ethylenesulfonate and *n*-butyl propene-1-sulfonate absorbed a molar equivalent of diazomethane in 3–5 hr. at room temperature. The pyrazolines were formed in quantitative yield, but they could not be purified

(1) Paper IV, C. S. Rondestvedt, Jr., THIS JOURNAL, **76**, 1926 (1954).

(2) Abstracted from the Ph.D. Dissertation of P. K. Chang, University of Michigan, June, 1955.

(3) C. S. Rondestvedt, Jr., and J. C. Wygant, THIS JOURNAL, **73**, 5785 (1951); *J. Org. Chem.*, **17**, 975 (1952).

(4) H. R. Snyder, H. V. Anderson and D. P. Hallada, *ibid.*, **73**, 3258 (1951).

(5) A. Lambert and J. D. Rose, *J. Chem. Soc.*, 46 (1949).

(6) T. L. Jacobs, chapter on Pyrazoles in R. C. Elderfield, Editor, "Heterocyclic Compounds," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1956. We are indebted to Prof. Elderfield for making the manuscript of this chapter available prior to publication.

(7) L. I. Smith, *Chem. Revs.*, **23**, 193 (1938).

(8) J. H. Boyer and F. C. Canter, *ibid.*, **54**, 41 (1954).

(9) F. R. Benson and W. L. Savell, *ibid.*, **46**, 1 (1950).

(10) L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, **15**, 824 (1950).

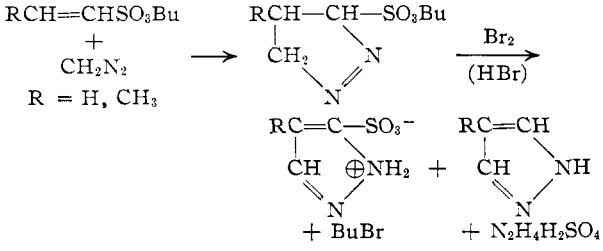
(11) Unpublished experiments with T. Y. Yu in this Laboratory.

(12) W. F. Whitmore and E. F. Landau, THIS JOURNAL, **68**, 1797 (1946).

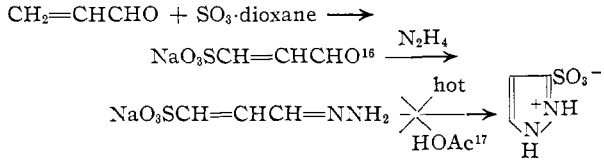
(13) J. M. Stewart and H. P. Cordts, *ibid.*, **74**, 5880 (1952).

(14) No attempt is made to assign the Δ¹- or Δ²-structure to the pyrazolines. A discussion of isomerism in pyrazolines is given by Jacobs.[6] See also reference 10.

as such. Bromination of crude *n*-butyl pyrazoline-3-sulfonate gave pyrazole-3-sulfonic acid (as the inner salt) in 72% yield, together with an approximately equivalent amount of butyl bromide. A trace of pyrazole also was isolated, together with a small amount of an unidentified product (see Experimental). *n*-Butyl 4-methylpyrazoline-3-sulfonate, upon bromination, gave the corresponding 4-methylpyrazole-3-sulfonic acid (as the inner salt) in 53% yield, together with butyl bromide and traces of hydrazine sulfate and 4-methylpyrazole. In neither reaction could a pyrazolidone be detected.



The structures of the sulfonic acids have been written as pyrazole-3-sulfonic acids by analogy to the 3-substituted pyrazolines and pyrazoles obtained when diazomethane adds to unsaturated ketones, esters and nitro compounds.[6,15] Although it seemed very unlikely that the 4-sulfonic acids were the products, an attempt was made to synthesize pyrazole-3-sulfonic acid independently by the following scheme. The synthesis failed, however, at the last step.

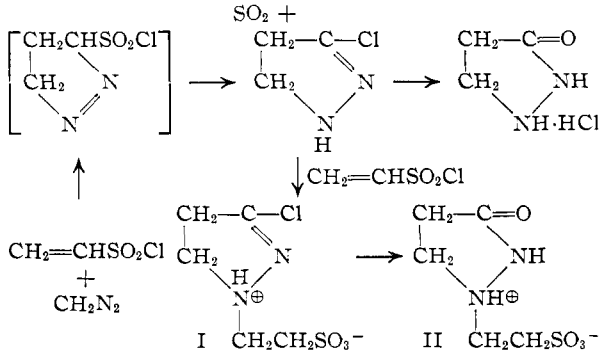


The problem was then attacked by independent synthesis of the isomeric pyrazole-4-sulfonic acid. Since pyrazole undergoes electrophilic substitution in the 4-position,[6] direct sulfonation of pyrazole should yield the 4-isomer. The procedure of Morgan and Ackerman[18] applied to pyrazole gave pyrazole-4-sulfonic acid[19] which was definitely different from the supposed 3-sulfonic acid obtained in this work. The available evidence, therefore, supports the contention that addition of diazomethane to unsaturated sulfonic acid derivatives gives derivatives of pyrazole-3-sulfonic acid, in keeping with the general pattern of addition of diazomethane to activated olefins.

Addition to Sulfonyl Chlorides.—Ethylenesulfonyl chloride reacted with two moles of diazomethane instantaneously at room temperature. An unstable amorphous solid (50%) precipitated from the ether solution, but it became oily on standing. It could not be purified as such. Titration with base showed an equivalent weight of 690, and microanalysis indicated that a substantial fraction of the sulfur had been lost. Ultimately 3-pyrazolidone hydrochloride was isolated from the oil in 20% yield. Arndt[20] has shown that although sulfonyl chlorides do not react with diazomethane, they catalyze its decomposition to nitrogen and polymethylene. Therefore, it appears that the oil may contain polymethylene in addition to pyrazoline (or pyrazolidone or pyrazole) rings combined in some form of a low polymer.

When ethylenesulfonyl chloride reacted with *one* mole of diazomethane, the principal product was a 2:1 adduct. The structure of 2-(3-chloro-1-proto-Δ^2-pyrazoline-1-yl)-ethanesulfonate[21] (I) was assigned on the basis of its analysis, physical properties and its facile hydrolysis to 2-(1-proto-3-pyrazolidone-1-yl)-ethanesulfonate (II). The infrared spectrum of the latter compound was practically identical with that of 2-(4-methyl-1-proto-3-pyrazolidone-1-yl)-ethanesulfonate prepared independently by addition of 4-methyl-3-pyrazolidone to *n*-butyl ethylenesulfonate, followed by hydrolysis. The attachment of the side chain at N-1 of the pyrazolidone ring is probable because the terminal nitrogen of a hydrazide is the more basic and more likely to undergo conjugate addition.

The corresponding reactions of diazomethane with propene-1-sulfonyl chloride and propene-2-sulfonyl chloride appeared to be similar, but they were investigated only briefly.



Reactivities.—The reactivities of derivatives of ethylenesulfonic acid toward diazomethane decrease in the order $-SO_2Cl > -SO_2OR > -SO_2NR_2$, judging from reaction times. This is in keeping with the reactivities observed when unsaturated sulfonic acid derivatives function as dienophiles in the Diels–Alder reaction,[3,4] and it provides additional evidence for the formulation of diazomethane addition as a nucleophilic attack on the double bond.

Furthermore, derivatives of propene-1-sulfonic acid were less reactive than the corresponding derivatives of ethenesulfonic acid, in line with the usual retarding influence of a β-methyl group to the addition of diazomethane.[6] N,N-Diethylpropene-1-sulfonamide requires four days to react with diazomethane while N,N-diethylethylenesul-

(15) W. E. Parham, *et al.*, THIS JOURNAL, (a) **72**, 3843 (1950); (b) **73**, 4664 (1951); (c) **76**, 799 (1954).

(16) A. V. Dombrovskiĭ, *Doklady Akad. Nauk U.S.S.R.*, **81**, 411 (1951); *C. A.*, **46**, 7998 (1952).

(17) K. von Auwers and K. Müller, *Ber.*, **41**, 4230 (1908).

(18) J. T. Morgan and I. Ackerman, *J. Chem. Soc.*, 1308 (1923).

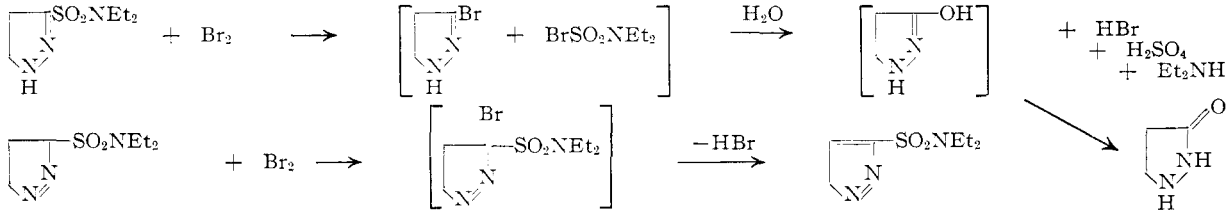
(19) Pyrazole-4-sulfonic acid has been referred to by Eppler, *Z. Krist.*, **29**, 233, but no melting point was given.

(20) F. Arndt and H. Schloz, *Ber.*, **41**, 4230 (1933).

(21) For a discussion of this nomenclature, see F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., THIS JOURNAL, **76**, 3945 (1954), footnote 7.

fonamide reacts in one day. *n*-Butyl propene-1-sulfonate reacts in five hours, compared to three hours for *n*-butyl ethylenesulfonate. The sulfonyl chlorides react almost instantaneously, so that a rate comparison is not possible.

Chemistry of Pyrazoline-3-sulfonic Acid Derivatives.—An unexpected feature of the present study is the unusual lability of the sulfonyl derivative attached to C-3 of the heterocyclic ring. Upon bromination of the pyrazoline-3-sulfonamides, about 60% aromatizes normally, but the remainder undergoes cleavage of the carbon–sulfur bond. The formation of a pyrazolidone, rather than a pyrazolone, shows that cleavage occurs prior to aromatization. The cleavage may be explained by proposing that in the Δ^2-form, the sulfonamido group undergoes electrophilic brominolysis to 3-bromo-Δ^2-pyrazoline (an imidyl bromide) which is hydrolyzed by moisture present to 3-hydroxy-Δ^2-pyrazoline, tautomeric with 3-pyrazolidone. Brominolysis of sulfo groups attached to aromatic rings is quite common,[22] particularly when the ring holds electron-releasing groups; this type of reaction often can be generalized to groups attached to olefinic bonds, as well as to aromatic rings. It may be that the extent of cleavage observed is a measure of the amount of Δ^2-pyrazoline present, since the Δ^1-isomer would not be expected to undergo electrophilic brominolysis but rather to aromatize.



The spontaneous loss of sulfur dioxide from pyrazoline-3-sulfonyl chloride is not unexpected, particularly if the Δ^1-isomer is regarded as formally analogous to an allylic sulfonyl chloride. Again, the 3-chloropyrazoline should be rapidly hydrolyzed to the pyrazolidone.

The facile cleavage of sulfonate esters by hydrogen bromide was unexpected. However, the carbon–sulfur bond resists cleavage, either because the Δ^2-isomer is not present in sufficient amount or because cleavage at the ester linkage is rapid and the resulting dipolar ion is not subject to carbon–sulfur cleavage. It may be that aromatization of the ester is much more rapid than that of the amide, for pyrazole-3-sulfonic acids are not cleaved readily by bromine, as shown by the formation of not more than trace amounts of pyrazole and 4-methylpyrazole.

The formation of hydrazine sulfate appeared surprising at first. However, as early as 1888, Büchner[23] had found hydrazine upon acid hydrolysis of ethyl pyrazoline-3,4,5-tricarboxylate. Later, Franke[24] found a trace of hydrazine on acid hydrolysis of 4,4-dimethyl-5-isopropylpyrazoline.

(22) For references, see C. S. Rondestvedt, Jr., and J. C. Wygant, THIS JOURNAL, **76**, 509 (1954).

(23) E. Büchner, *Ber.*, **21**, 2637 (1888).

(24) A. Franke, *Monatsh.*, **20**, 865 (1899).

Infrared Spectra of Pyrazole Derivatives.—Pyrazole, pyrazole-3-diethylsulfonamide, 4-methylpyrazole-3-diethylsulfonamide and methyl pyrazole-3-carboxylate all have peaks at 6.8 and 10.7 μ which appear to be characteristic of the pyrazole ring system. A peak in the spectrum of 3,5-dimethylpyrazole at 6.74 μ has been observed[25] but not assigned; Mirone and Vampiri also found a strong peak at 6.28 μ assigned to the "carbon–nitrogen double bond" and weak peaks at 6.03 and 6.44 μ assigned to the "carbon–carbon double bond." We observed that pyrazole itself has a weak peak at 6.25 μ and 4-methylpyrazole-3-diethylsulfonamide has a weak peak at 6.40 μ. In the sulfonamides, the peaks arising from the sulfonyl group are at 7.50 and 8.70 μ.[26]

Pyrazole-3-sulfonic acid, 4-methylpyrazole-3-sulfonic acid and pyrazole-4-sulfonic acid show infrared peaks between 6.34 and 6.45 μ. This appears to be the characteristic pyrazole frequency (6.8 μ, above) shifted somewhat to shorter wave lengths by inner salt formation. The peaks characteristic of the sulfonate ion are found at 8.43–8.45 and 9.58–9.70 μ.

The salts of 3-pyrazolidone and 4-methyl-3-pyrazolidone have very similar spectra. They all show a strong peak characteristic of the carbonyl group in cyclic amides at 5.8 μ.[27]

The infrared spectra of II and its 4-methyl homolog exhibit the carbonyl frequency at 5.80 and 5.74 μ, respectively. Moreover, they have the sulfonyl peaks at 8.5 and 9.7 μ.

The ultraviolet spectra of the above compounds were examined but, with the exception of 4-methylpyrazole-3-diethylsulfonamide, none exhibited a maximum above 220 mμ, the limit of the Cary instrument.

Reactions of Phenyl Azide. Addition to Sulfonamides.—N,N-Diethylethylenesulfonamide added phenyl azide slowly in refluxing benzene to form 1-phenyl-1,2,3-triazoline-4-diethylsulfonamide (III) in 30% yield. The structure is assigned on the basis of elementary analysis, a comparison of the ultraviolet and infrared spectra with those of model compounds, and the known course of the addition of phenyl azide to unsaturated systems.[7–9]

Attempts were made to aromatize III to the triazole. Although certain fused-ring 1,2,3-triazolines have been aromatized by the action of quinones,[28] *p*-benzoquinone was without effect

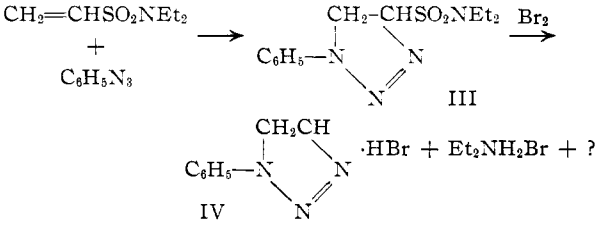
(25) P. Mirone and M. Vampiri, *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **12**, 583 (1952); *C. A.*, **46**, 9423*g* (1952).

(26) An analysis of the infrared spectra of sulfonamides has been given recently by J. N. Baxter, J. Cymerman-Craig and J. B. Willis, *J. Chem. Soc.*, 669 (1955).

(27) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 176.

(28) L. Wolffe, *Ann.*, **394**, 23 (1912); **399**, 274 (1913).

upon III. N-Bromosuccinimide likewise did not produce a triazole. Bromination, as used above with pyrazolines, converted III into a 12% yield of 1-phenyl-1,2,3-triazoline hydrobromide (IV), 60% of diethylamine hydrobromide and a trace of sulfuric acid. The triazoline structure was tentatively assigned to IV on the basis of elementary analysis and a study of the ultraviolet spectrum.



N,N-Diethylpropene-1-sulfonamide did not form a recognizable product with phenyl azide when refluxed in tetrahydrofuran solution for 48 hours. About half of the phenyl azide was recovered by distillation,[29] and the residue was tarry.

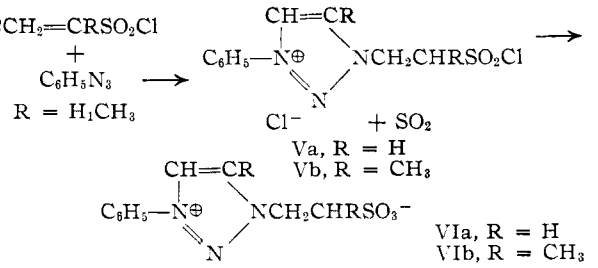
Addition to Sulfonate Esters.—Neither *n*-butyl ethylenesulfonate nor *n*-butyl propene-1-sulfonate formed identifiable products when heated with phenyl azide. Considerable decomposition occurred, and half of the phenyl azide was the only material which could be recovered from the tarry mixtures [29]

Addition to Sulfonyl Chlorides.—Ethylenesulfonyl chloride reacted spontaneously at room temperature with phenyl azide to give a quantitative yield of a 2:1 adduct. Even with an excess of phenyl azide, the same product was obtained. The primary adduct appears to be 2-(1-phenyl-1-proto-1,2,3-triazol-3-yl)-1-chlorosulfonylethane chloride (Va) judging from its analysis and ultraviolet and infrared spectra. It was relatively unstable, and standing or attempted recrystallization transformed it into 2-(1-phenyl-1-proto-1,2,3-triazol-3-yl)-ethanesulfonate (VIa). The structure of VIa was assigned because of its salt-like properties, its analysis, and the correspondence of its ultraviolet and infrared spectra with those of 1-phenyl-3-methyl-1,2,3-triazolium iodide and 1-phenyl-3-methyltriazolium methanesulfonate which were prepared as model compounds. The attachment of the side chain at N-3 was suggested by the fact that 1-alkyl-1,2,3-triazoles are alkylated at N-3 by alkyl halides.[30] Further evidence for the ring system present in VIa was adduced from synthesizing VIa by heating 1-phenyl-1,2,3-triazole with ethylenesulfonyl chloride.

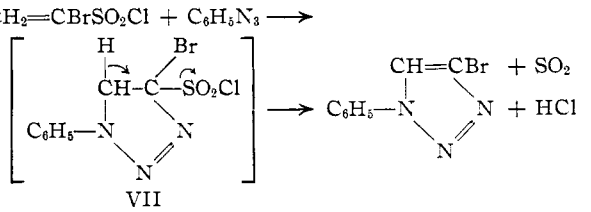
Propene-2-sulfonyl chloride reacted similarly with phenyl azide. The intermediate sulfonyl chloride (Vb) was not isolated, but the dipolar ion VIb was obtained in 45% yield. On the other hand, propene-1-sulfonyl chloride did not appear to add phenyl azide. Much of the phenyl azide was recovered,[29] but the sulfonyl chloride apparently decomposed during the heating.

(29) The fact that *half* of the phenyl azide was recovered may mean that an unstable 2:1 adduct (see below) was formed rapidly, but that it decomposed as it was formed.

(30) R. H. Wiley and J. Moffat, THIS JOURNAL, **77**, 1703 (1955).



α-Bromoethylenesulfonyl chloride reacted differently with phenyl azide. Apparently the expected 1-phenyl-4-bromo-1,2,3-triazoline-4-sulfonyl chloride (VII) aromatized promptly by loss of hydrogen chloride and sulfur dioxide, since the product isolated was 1-phenyl-4-bromo-1,2,3-triazole in 45% yield.

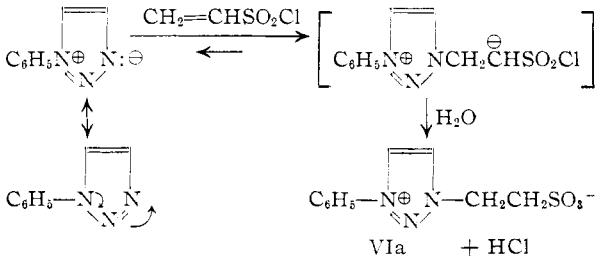


Aromatization of 1-Phenyl-4-bromo-1,2,3-triazoline-4-sulfonyl Chloride (VII).—When VII is formed during addition of phenyl azide to α-bromoethylenesulfonyl chloride, it may aromatize either by loss of hydrogen bromide or sulfur dioxide and hydrogen chloride; experimentally the latter was observed. VII is formally analogous to 4-phenyl-3-nitro-3-bromopyrazoline (XI), which was observed to eliminate nitrous acid in the presence of acid to form 4-phenyl-3-bromopyrazole.[15b] Parham and Bleasdale suggested that the proton of the acid catalyst attacked the nitro group of XI rather than the bromine atom; the nitro group has the greater proton affinity as shown by the fact that the solubility of nitroalkanes in sulfuric acid is greater than that of bromoalkanes. The same argument applies to the aromatization of VII, since it was found that methanesulfonyl chloride dissolved readily in sulfuric acid. Although no acid was added deliberately to VII, aromatization of a portion of the compound by either path would have produced enough acid to catalyze aromatization of the remainder to 1-phenyl-4-bromo-1,2,3-triazole. Base-catalyzed elimination was not tested since VII could not be isolated.

Reactivities.—The various unsaturated sulfonic acid derivatives exhibit the same order of reactivity toward phenyl azide that they did toward diazomethane, although the data are incomplete because of the failure of several reactions. Phenyl azide is less reactive than diazomethane. A β-methyl group retards phenyl azide addition much more strongly than diazomethane addition, since no heterocyclic compound could be isolated from phenyl azide and any of the derivatives of propene-1-sulfonic acid. On the other hand, an α-substituent (methyl or bromo), has a much smaller effect.

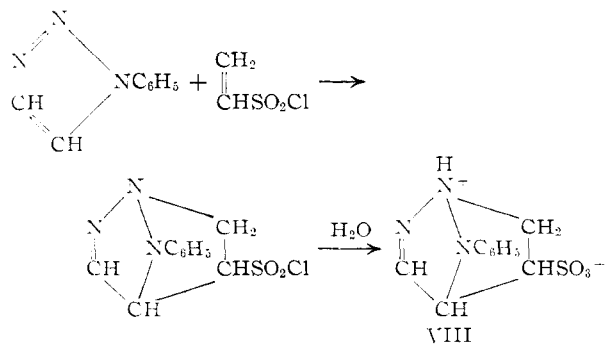
"Michael Additions" of 1-Phenyl-1,2,3-triazole Derivatives.—1,2,3-Triazole itself and benzotriazole add in the Michael fashion in the presence of bases

to typical acceptors,[31] but these compounds possess an imino hydrogen. It was most unusual to find that 1-phenyltriazole added fairly rapidly to ethylenesulfonyl chloride in the absence of a base,[32] despite the absence of imino hydrogen. Preliminary attempts to add 1-phenyl-1,2,3-triazole to acrylonitrile and acrylic acid under the same conditions returned the unreacted triazole quantitatively. We are investigating this unique reaction further; at present, it appears to be limited to unsaturated sulfonyl chlorides and possibly esters.[29] The reaction is thought to involve the steps



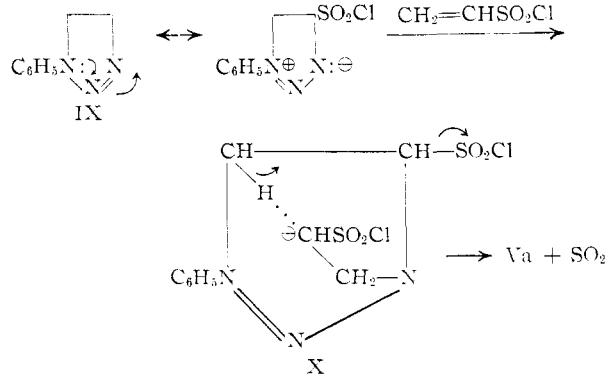
VIa + HCl

It is unlikely that there is an initial reaction of the triazole with the sulfonyl chloride function, since it was demonstrated that methanesulfonyl chloride did not react with the triazole. It was suspected at first that the product might have resulted from a Diels–Alder reaction with the "diene" system present in the triazole. It would then have the structure VIII in which the location of the sulfonate group on the ethano bridge is uncertain. VIII, however, is the inner salt of a tertiary amine, and it should be titratable with base. The product actually obtained behaves like a quaternary salt and cannot be titrated. Furthermore, structure VIII does not possess the triazolium ring system; the ultraviolet spectrum of VIII should resemble that of a triazoline salt (see below). However, the ultraviolet spectrum of the product is virtually identical with that of an authentic triazolium salt; the infrared spectra are likewise very similar.



VIII

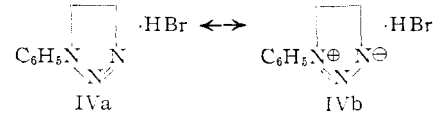
In the reaction of phenyl azide with ethylenesulfonyl chloride, the formation of Va may be explained by the following steps. First, normal addition to form 1-phenyl-1,2,3-triazoline-4-sulfonyl chloride (IX). Second, reaction of the polarized form of IX with a second mole of ethylenesulfonyl chloride to give a new dipolar ion X. The negative charge on the side chain is then neutralized by abstraction of hydrogen from C-5 on the ring. (The possibility of *inter*molecular hydrogen transfer cannot be excluded.) Simultaneously with the loss of the hydrogen at C-5, sulfur dioxide and chloride ion are lost with aromatization of the triazoline. Since Va is formed so readily, even in the presence of excess phenyl azide, it is attractive to consider that the driving force of the reaction from IX to Va arises from telescoping of the various processes into a single concerted mechanism, perhaps through an intermediate complex.



The timing of the various steps is not certain. However, it is unlikely that the formation of Va from phenyl azide and ethylenesulfonyl chloride involves aromatization of IX to 1-phenyl-1,2,3-triazole before reaction with the second mole of ethylenesulfonyl chloride. This conclusion was reached by considering that Va is formed rapidly without external heating, while the addition of 1-phenyl-1,2,3-triazole to ethylenesulfonyl chloride required 6 hr. in refluxing benzene.

Ultraviolet and Infrared Spectra of 1,2,3-Triazole Derivatives.—The ultraviolet maxima of the 1,2,3-triazole derivatives studied in this work are presented in Table I, together with the spectra of model compounds.

The 1-phenyl-1,2,3-triazoles exhibit a maximum in the region from 243-254 mμ, those with 4-substituents absorbing at the longer wave lengths; 4-phenyltriazole also absorbs here. The sole absorption appears to arise from the interaction of the phenyl group with the "aromatic" triazole ring. In the triazoline III, this interaction is absent, and its spectrum resembles that of aniline with additional contributions from an excited state similar to that in azo compounds. Compound IV, the supposed triazoline hydrobromide, has absorption maxima almost exactly like those of aniline, except for the reduced intensity which may be attributed to salt formation.



IVa IVb

The virtual identity of the ultraviolet absorption of VIa and the authentic triazolium salt is strong

(31) R. H. Wiley, N. R. Smith, D. M. Johnson and J. Moffat, THIS JOURNAL, **76**, 4933 (1954).

(32) Triazoles and triazolines are weak bases, as shown by the formation of salts.

TABLE I

ULTRAVIOLET SPECTRA OF DERIVATIVES OF 1,2,3-TRIAZOLE AND RELATED COMPOUNDS[a]

Compound	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$
1-Phenyl-1,2,3-triazole	243	10.31[b]
4-Phenyl-1,2,3-triazole	247	15.8[c]
1-Phenyl-4-bromo-1,2,3-triazole	253	9.2
1-Phenyl-1,2,3-triazole-4-carboxylic acid	247	11.9
1-Phenyl-1,2,3-triazoline-4-diethylsulfonamide (III)	310	8.45
	289[d]	6.28
	225	10.80
1-Phenyl-1,2,3-triazoline hydrobromide (IV)	285	0.50
	234	5.08
Aniline[e]	288	1.82
	234	9.12
Azobenzene[f]	313	20.0
$C_6H_5N{=}N{-}N(CH_2)_5$	290	16.0
$C_6H_5N{=}N{-}NHCH_3$[g]	304	7.58
	276	12.88
VIa	252.5	8.77
1-Phenyl-3-methyltriazolium iodide	251.6	8.41

[a] Taken in ethanol on a Cary recording spectrophotometer, except for literature values. [b] Reported as 12.02 by P. Ramart-Lucas and M. J. Hoch, *Bull. soc. chim. France*, 447 (1949). [c] L. W. Hartzel and F. R. Benson, THIS JOURNAL, **76**, 667 (1954). [d] Shoulder. [e] American Petroleum Institute Research Project 44, "Ultraviolet Spectral Data," Carnegie Institute of Technology, Pittsburgh, Pa., 1953, Spectrum No. 106. [f] A. Burawoy, *J. Chem. Soc.*, 1865 (1937). [g] Given in ref. *b*.

evidence for the formulation of VIa as a triazolium salt also.

The infrared spectra of 1-phenyl-1,2,3-triazole and 1-phenyl-4-bromo-1,2,3-triazole are very similar, both showing strong peaks at 9.6 and 10.1 μ. Benson[33] has reported that 4-alkyl-1,2,3-triazoles have common peaks in the 8.8–9.2 and 9.8–10.3 μ regions which he ascribed to the triazole ring.

The infrared spectra of 1-phenyl-3-methyl-1,2,3-triazolium methanesulfonate (and iodide) and compounds VIa and VIb were very similar. All had a strong peak at 13.2 μ and a weak peak at 6.30 μ; these, perhaps are associated with the vibrations of the triazolium ring. The peaks from the sulfonyl vibrations appear at 8.25 and 9.64 μ.

Experimental[34]

Ethylenesulfonyl chloride, α-bromoethylenesulfonyl chloride and N,N-diethylethylenesulfonamide have been described previously.[1] *n*-Butyl ethylenesulfonate was prepared by the procedure of Whitmore and Landau,[12] although the yield was only 40–45%; dry ether was usually used as solvent.

Propene-1-sulfonyl Chloride.—2-Chloropropane-1-sulfonyl chloride was prepared in 40% yield, b.p. 55° (1.5 mm.), by the modified[1] procedure of Goldberg[35] from sodium 2-hydroxypropane-1-sulfonate.[36] The low-temperature dehydrochlorination procedure[1] was modified by using triethylamine as base at −25°, since 2,6-lutidine at −50° gave inferior yields. The yield of propene-1-sulfonyl chloride was 80%, b.p. 32–34° (0.3 mm.), $n^{24.5}D$ 1.4775. This sulfonyl chloride is not as objectionable a lachrymator as ethylenesulfonyl chloride.

Anal. Calcd. for $C_3H_5ClO_2S$: Cl, 25.22. Found: Cl, 25.40 (by alkaline hydrolysis followed by Volhard titration).

To verify the position of the double bond, a sample was ozonized in ethyl acetate solution at −80°. Acetaldehyde was isolated as the dimedon derivative. The infrared spectrum of ethylenesulfonyl chloride has a sharp peak at 10.20 μ associated with the terminal methylene group. This peak was completely absent from the spectrum of propene-1-sulfonyl chloride.

N,N-Diethylpropene-1-sulfonamide.—A solution of 8.0 g. (0.057 mole) of propene-1-sulfonyl chloride in 50 ml. of dry ether was cooled to −70°, and a solution of 6.5 g. (0.057 mole) of triethylamine and 4.2 g. (0.057 mole) of diethylamine in 25 ml. of ether was added at such a rate that the temperature did not exceed −50°. The mixture was stirred while it warmed to room temperature, and it was then washed with ice-water, dilute acid, dilute sodium carbonate solution and water, dried over sodium sulfate and distilled. The liquid sulfonamide (4.7 g., 46%) was collected at 72–74° (0.2 mm.), $n^{25}D$ 1.4661.

Anal. Calcd. for $C_7H_{15}NO_2S$: C, 47.43; H, 8.53; N, 7.70. Found: C, 47.19; H, 7.84; N, 7.63.

***n*-Butyl Propene-1-sulfonate.**—The procedure of Whitmore and Landau[12] was followed, except that dry ether was used as solvent. The yield was 58%, b.p. 85–87° (0.5 mm.) or 95–99° (1.0 mm.), $n^{25}D$ 1.4461.

Anal. Calcd. for $C_7H_{14}O_3S$: C, 47.17; H, 7.91. Found: C, 47.54; H, 7.90.

Propene-2-sulfonyl Chloride.—1-Chloropropane-2-sulfonyl chloride[13] (30.8 g., 0.175 mole) in 100 ml. of dry ether was cooled to −30° and a solution of 17.5 g. (0.175 mole) of triethylamine in 25 ml. of dry ether was added between −25 and −20°. After one hour at −25° and one hour at −10°, the solution was washed with acid and water, dried and distilled. Propene-2-sulfonyl chloride was collected from 40–45° (1.5 mm.), $n^{22}D$ 1.4729, yield 14.6 g. (50%); reported[13] b.p. 70–75° (10 mm.), $n^{20}D$ 1.4740. In earlier runs using 2,6-lutidine as the base, poorer yields were obtained.

Diazomethane was prepared and standardized by the method of Arndt.[37] Phenyl azide was prepared by the method of Smith and Boyer.[38]

N,N-Diethylethylenesulfonamide and Diazomethane.—An equimolar amount of diazomethane was added to a solution of 6 g. (0.036 mole) of N,N-diethylethylenesulfonamide in ether. The color disappeared in 24 hr. at room temperature. Evaporation of the ether left 6.8 g. (92%) of the oily pyrazoline. It could not be distilled nor induced to crystallize from various solvents.

A solution of bromine (2.7 g., 0.0168 mole) in 10 ml. of chloroform was added dropwise to a vigorously stirred solution of 3.0 g. (0.147 mole) of the above crude pyrazoline in 35 ml. of chloroform at such a rate that the temperature did not rise. The orange solution was stirred for 6 hr. and allowed to stand overnight. The fine precipitate of 3-pyrazolidone hydrobromide (1.2 g.) was collected; m.p. 188–190°. After recrystallization from 95% ethanol, it melted at 206–207°, mixture m.p. 205–207°, yield 0.8 g. (32%). Sodium fusion showed bromine and nitrogen, but no sulfur.

Anal. Calcd. for $C_3H_7BrN_2O$: C, 21.57; H, 4.22; N, 16.39; Br, 47.85; neut. equiv., 167. Found: C, 21.49; H, 4.32; N, 16.98; Br, 47.8 (Volhard); neut. equiv., 160.

When the crude pyrazolidone hydrobromide was dissolved in ethanol for recrystallization, there remained 0.08 g. (4%) of ethanol-insoluble hydrazine sulfate. After two recrystallizations from aqueous methanol, it melted at 254°, not depressed upon admixture of authentic hydrazine sulfate. Microanalysis agreed with this identification.

The chloroform filtrate from the pyrazolidone hydrobromide was washed with three 20-ml. portions of water. The organic layer was evaporated, leaving 2.2 g. (74%) of crude pyrazole-3-diethylsulfonamide which crystallized on standing; m.p. 95–105°. When recrystallized from benzene–petroleum ether, it melted at 112–113°, yield 1.7 g. (57%). Sodium fusion showed the presence of sulfur and nitrogen, absence of bromine.

Anal. Calcd. for $C_7H_{12}N_3O_2S$: C, 41.36; H, 6.45; N, 20.67. Found: C, 41.57; H, 6.41; N, 20.38.

(33) L. W. Hartzel and F. R. Benson, THIS JOURNAL, **76**, 667 (1954).

(34) Melting points are uncorrected. Microanalyses are by Geller Microanalytical Laboratories, Hackensack, N. J., by Spang Microanalytical Laboratory, Plymouth, Mich., and by Anna Griffin and Goji Kodama in this Laboratory.

(35) A. Goldberg, *J. Chem. Soc.*, 464 (1945).

(36) Generously supplied by Wyandotte Chemical Co.

(37) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166.

(38) P. A. S. Smith and J. H. Boyer, *Org. Syntheses*, **31**, 16 (1951).

The combined aqueous extracts of the chloroform layer were concentrated, acidified and treated with barium chloride. The precipitated barium sulfate weighed 0.72 g. (21%). The filtrate was evaporated to dryness and extracted with 95% ethanol. The diethylamine hydrobromide thus obtained weighed 0.5 g. (22%), m.p. 213–214°, identified by mixture m.p. and microanalysis.

N,N-Diethylpropene-1-sulfonamide and Diazomethane.—An equimolar amount of diazomethane was added to a solution of 6.25 g. (0.035 mole) of N,N-diethylpropene-1-sulfonamide in ether. The color disappeared in 4 days at room temperature. Evaporation of the ether left 7.63 g. (99%) of the oily pyrazoline. It could not be distilled nor induced to crystallize from methanol, nitromethane, acetonitrile, dioxane, chloroform or petroleum ether.

A solution of bromine (3.2 g., 0.0202 mole) in 10 ml. of chloroform was added dropwise to a vigorously stirred solution of 4.43 g. (0.0202 mole) of the above crude pyrazoline in 35 ml. of chloroform at room temperature. The orange solution was stirred for 6 hr. and allowed to stand overnight. A trace of hydrazine sulfate separated from the chloroform solution. The filtrate was washed with three 20-ml. portions of water, and the organic layer was evaporated. The crude 4-methylpyrazole-3-N,N-diethylsulfonamide (3.0 g., 66%) was sublimed at 110° (0.1 mm.), giving 2.6 g. (57%) of material which melted at 127° after crystallization from acetonitrile–water.

Anal. Calcd. for $C_8H_{14}N_3O_2S$: C, 44.10; H, 6.93; N, 19.06. Found: C, 44.20; H, 6.96; N, 19.34.

The combined water extracts were concentrated, acidified and treated with barium chloride. The precipitated barium sulfate weighed 0.4 g. (12%). The filtrate was evaporated to dryness and the residue was extracted successively with chloroform and ethanol. The chloroform extract yielded 0.58 g. (18%) of diethylamine hydrobromide which melted at 213–214° after one crystallization from 95% ethanol, mixture m.p. not depressed. The ethanol extract of the residue was evaporated to dryness and sublimed, giving a trace of 4-methylpyrazolidone hydrobromide, m.p. 166–169°, mixture m.p. 166–168°.

3-Pyrazolidone and Its Salts.—The sole report of 3-pyrazolidone is von Rothenberg's claim that he obtained it by the reaction of hydrazine hydrate and acrylic acid.[39] Several attempts to repeat his procedure were unsuccessful. The reaction of β-bromopropionic acid with hydrazine also failed. The following method was successful, though yields were low.

Methyl acrylate (29.0 g., 0.338 mole) was cautiously mixed with 11.0 g. (0.34 mole) of *anhydrous* hydrazine. The mixture was kept at 80° for 24 hr. until the characteristic odor of the ester disappeared. The viscous liquid remaining after removal of methanol was distilled, giving 10.52 g. (27%) of acrylhydrazide, b.p. 136–140° (0.4 mm.). It gave positive tests for unsaturation and condensed with acetone to yield (presumably) N-acrylyl acetone hydrazone, m.p. 78–81°. An attempt to cyclize acrylhydrazide by boiling with glacial acetic acid gave only acethydrazide, identified as N-acetyl acetone hydrazone, m.p. 133° (reported[40] 133°). However, after standing for several days, the acrylhydrazide had cyclized, as evidenced by its failure to condense with acetone.

A sample of the "aged" acrylhydrazide (4.0 g.) was dissolved in concd. hydrochloric acid and the mixture was evaporated to dryness. The residue was extracted with absolute ethanol in a Soxhlet apparatus for 4 hr. The extract was evaporated to dryness and the residue (1.1 g.) was sublimed at 100° (0.05 mm.). The white needles of 3-pyrazolidone hydrochloride weighed 0.20 g., 4% based on hydrazide, m.p. 199–200°. No attempt was made to improve the yield, since the objective was preparing comparison samples.

Anal. Calcd. for $C_3H_7ClN_2O$: C, 29.40; H, 5.75; N, 22.85; Cl, 29.01; neut. equiv., 122.5. Found: C, 29.60; H, 5.66; N, 23.05; Cl, 29.02; neut. equiv., 126.0.

By a similar procedure, hydrobromic acid converted the "aged" hydrazide into 3-pyrazolidone hydrobromide in 3% yield, m.p. 205–206°.

Anal. Calcd. for $C_3H_7BrN_2O$: Br, 47.85; neut. equiv., 167. Found: Br, 47.68 (Volhard); neut. equiv., 163.

(39) R. von Rothenberg, *J. prakt. Chem.*, [2] **51**, 72 (1895).

(40) T. Curtius and T. S. Hofmann, *ibid.*, [2] **53**, 524 (1896).

4-Methyl-3-pyrazolidone and Its Salts.—4-Methyl-3-pyrazolidone was prepared by the method of Lieser and Kemmner[32] in 72% yield, b.p. 114–117° (0.2 mm.), reported[41] b.p. 162° (12 mm.). The hydrochloride prepared as above was recrystallized twice from absolute alcohol, m.p. 177–179°, reported[41] 178°. 4-Methyl-3-pyrazolidone hydrobromide was prepared by the above method; it melted at 168–169° after crystallization from alcohol.

Anal. Calcd. for $C_4H_{10}BrN_2O$: Br, 43.90; neut. equiv., 182. Found: Br, 43.56 (Volhard); neut. equiv., 187.

***n*-Butyl Ethylenesulfonate and Diazomethane.**—An equimolar amount of diazomethane was added to a solution of 10 g. (0.061 mole) of *n*-butyl ethylenesulfonate in dry ether. The color disappeared in 2 hr. Evaporation of the ether left 13.3 g. of oily pyrazoline which could not be crystallized nor distilled.

A solution of bromine (2.4 g., 0.015 mole) in 10 ml. of chloroform was added dropwise to a stirred solution of 3.1 g. (0.015 mole) of crude pyrazoline in 35 ml. of chloroform at room temperature. The orange solution was stirred for 5 hr. and allowed to stand overnight. The oily precipitate, 2.04 g. (92%), was dissolved in absolute methanol, leaving 0.13 g. of an insoluble material (compound A). The methanol solution was evaporated in an air jet, and the crystalline residue was recrystallized from methanol–acetonitrile to give 1.6 g. (72%) of pyrazole-3-sulfonic acid, m.p. 257° dec. Sulfur and nitrogen were present, bromine was absent.

Anal. Calcd. for $C_3H_4N_2O_3S$: C, 24.32; H, 2.72; neut. equiv., 148. Found: C, 24.42; H, 2.74; neut. equiv., 151.6.

Pyrazole-3-sulfonic acid formed a pyridine salt instantly when pyridine was dropped on the crude compound. The salt melted at 169–170° after crystallization from methanol–acetonitrile.

Anal. Calcd. for $C_8H_9N_3O_3S$: C, 42.28; H, 3.99; N, 18.49; neut. equiv., 227. Found: C, 41.85; H, 4.06; N, 18.28; neut. equiv., 225.2.

The methanol-insoluble compound A was recrystallized from aqueous methanol, m.p. 238° dec. Sodium fusion showed sulfur and nitrogen present, bromine absent.

Anal. Calcd. for $C_6H_{10}N_4O_3S$: C, 32.98; H, 4.61; N, 25.77; neut. equiv., 228. Found: C, 33.80; H, 4.67; N, 24.85; neut. equiv., 219.

The analysis is in fair agreement with pyrazolinium pyrazole-3-sulfonate or pyrazolium pyrazoline-3-sulfonate, but none of these components could be isolated by treatment with acid or base. No further work was done with compound A.

The chloroform filtrate from the crude pyrazole-3-sulfonic acid was extracted with three 20-ml. portions of water. The organic layer was evaporated and the residue was taken up in ether and again evaporated. The oil remaining (1.5 g.) was identified as butyl bromide by formation of the isothiuronium picrate.

The aqueous extracts were acidified and concentrated. Addition of barium chloride gave 1.00 g. (30%) of barium sulfate. The filtrate was basified and extracted with ether. Addition of picric acid gave 0.17 g. of pyrazole picrate, m.p. 160° after recrystallization from ethanol, m.p. not depressed upon admixture with an authentic sample.

In an early experiment with methyl ethylenesulfonate, the ester decolorized diazomethane rapidly to form a yellow amorphous solid which could not be purified. It contained sulfur and nitrogen.

***n*-Butyl Propene-1-sulfonate and Diazomethane.**—An equimolar amount of diazomethane was added to 5.3 g. (0.03 mole) of *n*-butyl propene-1-sulfonate in dry ether at room temperature. The color disappeared in 5 hr. When the ether was evaporated, there remained 6.18 g. (95%) of oily pyrazoline which could not be crystallized from ethanol, petroleum ether, acetonitrile, ethyl acetate or dioxane, nor could it be distilled.

When 3.1 g. (0.014 mole) of crude pyrazoline in chloroform was brominated as above with 2.2 g. (0.014 mole) of bromine, 1.5 g. of crude 4-methylpyrazole-3-sulfonic acid separated. After recrystallization from methanol–chloroform, 1.2 g. (53%) of pure material was obtained, m.p. 275° dec. It contained sulfur and nitrogen, but not bromine.

(41) T. Lieser and K. Kemmner, *Ber.*, **84**, 10 (1951).

Anal. Calcd. for $C_4H_6N_2O_3S$: C, 29.62; H, 3.73; N, 17.28; neut. equiv., 162. Found: C, 29.55; H, 3.66; N, 17.52; neut. equiv., 163.

When the crude 4-methylpyrazole-3-sulfonic acid was dissolved in methanol for crystallization, there remained 0.08 g. (4%) of insoluble hydrazine sulfate.

The original chloroform filtrate was washed with water. The above procedure with the water washes produced 1.2 g. (36%) of barium sulfate and 0.2 g. of 4-methylpyrazole picrate, m.p. 142° (EtOH), reported[42] 142°. The chloroform solution yielded 1.5 g. of butyl bromide identified as the isothiuronium picrate.

Ethylenesulfonyl Chloride and Diazomethane. A.—A solution of 4.7 g. (0.037 mole) of ethylenesulfonyl chloride in 10 ml. of ether was treated with ethereal diazomethane until a slight excess was present; 0.074 mole was added. A white amorphous deposit (4.0 g.) formed in the reaction flask. No gas evolution was observed. The solid became oily on standing and could not be purified. A sample gave a neut. equiv. of 690. It contained nitrogen, sulfur and chlorine. After several months standing, the oil deposited 1.0 g., 22%, of white needles of 3-pyrazolidone hydrochloride, which after sublimation melted at 199–200°. Its melting point was not depressed by an authentic sample, and microanalysis supported the identification.

B.—A solution of 2.26 g. (0.0179 mole) of ethylenesulfonyl chloride in ether was treated dropwise during one hr. with 0.009 mole of ethereal diazomethane at room temperature. The color was discharged instantly, and 0.55 g. of ether-insoluble oil settled to the bottom of the flask. It could not be crystallized, and when it was dissolved in water and the solution was evaporated to dryness on the steam-bath, there remained a taffy-like residue which could not be purified by crystallization or sublimation.

The supernatant ether solution was evaporated at reduced pressure, leaving 1.98 g. of a viscous oil which could not be redissolved in ether. On standing overnight, 0.94 g. of oily solid separated. It was recrystallized from methanol–ethyl acetate, m.p. 168–169° dec. It contained sulfur, nitrogen and chlorine. It is assigned the structure I.

Anal. Calcd. for $C_5H_9ClN_2O_3S$: C, 28.25; H. 4.27; N, 13.18; S, 15.07; Cl, 16.67. Found: C, 29.09; H, 4.39; N, 13.21; S, 14.72; Cl, 16.28.

The analysis indicates that it may be contaminated by II.

A solution of 0.74 g. of the above oily solid in 5 ml. of water was evaporated to dryness. The residue crystallized when treated with ethanol; 0.38 g., m.p. 258–259° dec. after crystallization from water–methanol. It contained sulfur and nitrogen, but not chlorine. Structure II is assigned.

Anal. Calcd. for $C_5H_{10}N_2O_4S$: C, 30.93; H, 5.17; N, 14.44; S, 16.51; neut. equiv., 194. Found: C, 31.04; H, 5.16; N, 14.27; S, 16.41; neut. equiv., 196.

Reaction of 4-Methyl-3-pyrazolidone with *n*-Butyl Ethylenesulfonate.—A mixture of 1.0 g. (0.01 mole) of 4-methyl-3-pyrazolidone and 1.65 g. (0.01 mole) of *n*-butyl ethylenesulfonate in 20 ml. of absolute ethanol was refluxed for 2 hr. The ethanol-insoluble precipitate, 0.60 g. (29%), m.p. 271–272° dec., was recrystallized from acetonitrile–water; m.p. 275° dec.

Anal. Calcd. for $C_6H_{12}N_2O_3S$: C, 34.61; H, 5.80; N, 13.45; neut. equiv., 208. Found: C, 34.39; H, 5.72; N, 13.23; neut. equiv., 211.

The structure 2-(4-methyl-1-proto-3-pyrazolidone-1-yl)-ethanesulfonate is assigned.

Propene-1-sulfonyl Chloride and Diazomethane.—Propene-1-sulfonyl chloride (4.8 g., 0.034 mole) reacted instantaneously with 0.068 mole of diazomethane in ether solution at room temperature. A yellow deposit, 2.7 g., formed on the walls of the flask, but it became oily in contact with the atmosphere. It was soluble in polar solvents, insoluble in non-polar solvents, and partially soluble in dioxane, chloroform, ethyl acetate, acetone, nitrobenzene and propanol. A solid was obtained by stirring the oil with chloroform, then scratching the insoluble material with petroleum ether; m.p. 65° dec.

Anal. Calcd. for $C_{11}H_{20}ClN_5O_2S$: C, 41.05; H, 6.26; N, 21.76; S, 9.96; Cl, 11.01; neut. equiv., 322. Found: C, 41.97, 42.64, 43.97; H, 6.28, 6.87, 6.57; N, 20.94, 19.00, 18.22; S, 10.24; Cl, 11.63; neut. equiv., 590, 550.

This material could not be purified further, as shown by the above erratic analyses obtained on different samples. Attempts were made to form derivatives with phenyl isocyanate,[43] acetyl chloride, benzenesulfonyl chloride and picric acid. Acidic and basic hydrolysis gave no identifiable product. On sublimation, it decomposed. Pyrolysis liberated a little nitrogen, but again no product.

Propene-2-sulfonyl Chloride and Diazomethane.—Two moles of diazomethane reacted rapidly. The ether-insoluble material could not be purified. Evaporation of the ether gave a dark orange oil which was soluble in acetone, acetonitrile and pyridine, but it could not be crystallized nor distilled.

N,N-Diethylethylenesulfonamide and Phenyl Azide.—A mixture of 4.32 g. (0.0266 mole) of N,N-diethylethylenesulfonamide and 3.59 g. (0.0292 mole) of phenyl azide in 25 ml. of benzene was refluxed for 16 hr. The mixture was distilled, giving 1.1 g. (30% recovery) of phenyl azide. The residue in the distilling flask crystallized on cooling, giving 1.77 g., 31% based on unrecovered azide, of 1-phenyl-1,2,3-triazoline-4-diethylsulfonamide, m.p. 87–91°. It was recrystallized from dioxane–water; m.p. 92.5–93.5°.

Anal. Calcd. for $C_{12}H_{18}N_4O_2S$: C, 51.05; H, 6.43; N, 19.85. Found: C, 51.29; H, 6.40; N, 19.35.

When the above triazoline was refluxed in benzene for 7 hr. with an equimolar amount of *p*-benzoquinone, it was recovered unchanged. N-Bromosuccinimide with benzoyl peroxide converted it into an intractable tar.

The triazoline (0.82 g., 0.00284 mole) in 15 ml. of chloroform was stirred vigorously while 0.5 g. (0.003 mole) of bromine in 6 ml. of chloroform was added dropwise at room temperature. The mixture became dark red, and solid separated. After 2.5 hr. of stirring, the mixture was allowed to stand overnight. The crystalline product, 0.08 g., 12%, of 1-phenyl-1,2,3-triazoline hydrobromide was collected, m.p. 270° dec. After two recrystallizations from methanol–ethyl acetate, it melted at 278° dec. It contained bromine and nitrogen but not sulfur.

Anal. Calcd. for $C_8H_{10}BrN_3$: C, 42.12; H, 4.42; Br, 35.04; neut. equiv., 228. Found: C, 41.63; H, 4.89; Br, 35.60 (Volhard); neut. equiv., 220.

The chloroform filtrate above was extracted with water and evaporated to dryness. The black, tarry residue weighed 0.70 g. and contained nitrogen, sulfur and bromine. No pure material could be obtained from the tar.

The water extract of the chloroform solution was treated with barium chloride to give 0.014 g. of barium sulfate, 2.1%. The filtrate was evaporated to dryness and the residue was extracted with chloroform. Evaporation left 0.26 g. (60%) of impure diethylamine hydrobromide, identified by recrystallization (ethanol) to m.p. 213–214°, and mixture m.p.

N,N-Diethylpropene-1-sulfonamide and Phenyl Azide.—A mixture of 3.0 g. (0.017 mole) of N,N-diethylpropene-1-sulfonamide and 2.02 g. (0.017 mole) of phenyl azide in 20 ml. of peroxide-free tetrahydrofuran was refluxed for 48 hr. Vacuum distillation led to the recovery of 1 g. of phenyl azide. The residue, 2.9 g., could not be crystallized nor sublimed, and it appeared to be polymeric.

Sulfonate Esters and Phenyl Azide.—A mixture of 4.62 g. (0.03 mole) of *n*-butyl ethylenesulfonate and 4.5 g. (0.03 mole) of phenyl azide in 30 ml. of benzene was refluxed gently for 3.5 hr. The mixture turned dark and 20 mg. of dark precipitate separated. It did not melt, but charred near 300°. The filtrate yielded 2 g. of unreacted phenyl azide on vacuum distillation. The residue could not be crystallized nor sublimed.

A mixture of 2 g. (0.011 mole) of *n*-butyl propene-1-sulfonate and 1.5 g. (0.01 mole) of phenyl azide was allowed to stand at room temperature for 6 months. The mixture turned dark and slowly deposited a black precipitate. After one crystallization from methanol–acetonitrile, the dark brown material (0.5 g.) melted at 245°. It became insoluble in water and methanol on standing and could not be purified further.

Ethylenesulfonyl Chloride and Phenyl Azide.—Ethylenesulfonyl chloride (6.0 g., 0.05 mole) was added in small portions to a solution of 3.0 g. (0.025 mole) of phenyl azide in 10 ml. of benzene. Heat was liberated, and after 0.5 hr. a precipitate appeared. The reaction was complete in

(42) H. von Pechmann and E. Burkhard, *Ber.*, **33**, 3590 (1900).

(43) L. I. Smith and K. L. Howard, THIS JOURNAL, **65**, 159 (1943).

about 5 hr. The crude product weighed 6.7 g., 98%, m.p. 120–127°. After three recrystallizations from methanol–ethyl acetate, it melted at 129–130°. It contained sulfur, nitrogen and chlorine. Structure Va was assigned to this compound.

Anal. Calcd. for $C_{10}H_{11}ClN_3O_2S$: C, 38.87; H, 3.76; N, 13.60; S, 10.35; Cl, 22.95; neut. equiv., 154. Found: C, 38.67; H, 5.01; N, 14.05; S, 10.66; Cl, 15.90; neut. equiv., 140, 170, 180.[44]

In several other experiments, the mole ratios of phenyl azide and ethylenesulfonyl chloride were varied from 1:2 to 2:1, and inverse addition also was tried. In every case, Va was formed in quantitative yield based on ethylenesulfonyl chloride.

Repeated crystallization converted Va to VIa. The latter was most conveniently prepared (91% yield from crude Va) by dissolving Va in water and evaporating to dryness. It was recrystallized from methanol–ethyl acetate, m.p. 215–216°. It contained nitrogen and sulfur but no chlorine, and could not be titrated.

Anal. Calcd. for $C_{10}H_{11}N_3O_3S$: C, 47.43; H, 4.38; N, 16.59; S, 12.66. Found: C, 47.49; H, 4.61; N, 16.62; S, 13.04.

Addition of 1-Phenyl-1,2,3-triazole to Ethylenesulfonyl Chloride.—A mixture of 1.45 g. (0.01 mole) of 1-phenyl-1,2,3-triazole and 1.26 g. (0.01 mole) of ethylenesulfonyl chloride in 15 ml. of benzene was refluxed for 6 hr. The precipitated VIa, 2.7 g., 99%, m.p. 195–202°, was recrystallized (Norit) from methanol–ethyl acetate; m.p. 215–216°, not depressed by VIa obtained previously.

Propene-1-sulfonyl Chloride and Phenyl Azide.—A mixture of 3.5 g. (0.025 mole) of propene-1-sulfonyl chloride and 3.0 g. (0.02 mole) of phenyl azide in 25 ml. of benzene was refluxed for 6 hr. On distillation of the dark solution, 1.5 g. of phenyl azide was recovered. The dark viscous residue was soluble in methanol and ethanol, partially soluble in acetone and water, but it could not be crystallized nor sublimed.

Propene-2-sulfonyl Chloride and Phenyl Azide.—Propene-2-sulfonyl chloride (1.2 g., 0.0085 mole) was added in small portions to a solution of 0.5 g. (0.0042 mole) of phenyl azide in 15 ml. of chloroform. The mixture was refluxed for 6 hr. Upon removal of the solvent, there remained 1.4 g. of dark oil which yielded 0.5 g. (45%) of solid on chilling. After three crystallizations from ethanol, the compound VIb melted at 268° dec. It contained sulfur and nitrogen but no chlorine, and it could not be titrated.

Anal. Calcd. for $C_{12}H_{15}N_3O_3S$: C, 51.23; H, 5.37; N, 14.93. Found: C, 51.08; H, 5.62; N, 14.61.

α-Bromoethylenesulfonyl Chloride and Phenyl Azide.—α-Bromoethylenesulfonyl chloride (1.02 g., 0.005 mole) was added in small portions to a solution of 0.6 g. (0.005 mole) of phenyl azide in 15 ml. of chloroform. After 1 hr. of reflux, the solvent was removed in an air jet, leaving 0.50 g. (45%) of 1-phenyl-4-bromo-1,2,3-triazole, m.p. 117–120°. It contained nitrogen and bromine, but no sulfur. The analytical sample was crystallized several times from aqueous methanol; m.p. 121.5–122.5°, 0.38 g.

Anal. Calcd. for $C_8H_6BrN_3$: C, 42.88; H, 2.69; N, 18.75. Found: C, 42.94; H, 2.74; N, 18.87.

The reaction of two moles of α-bromoethylenesulfonyl chloride with one mole of phenyl azide was not attempted.

Attempted Addition of 1-Phenyl-1,2,3-triazole to Acrylonitrile and Acrylic Acid.—When 1-phenyl-1,2,3-triazole was refluxed in benzene with an equimolar amount of acrylonitrile for 7 hr., 94% of the former was recovered. When it was refluxed with an equimolar amount of glacial acrylic acid in benzene for 11 hr., 93% was recovered.

Pyrazole-4-sulfonic Acid.—A mixture of 0.7 g. (0.0104 mole) of pyrazole[45] in 3.3 ml. of 20% fuming sulfuric acid was heated on a steam-bath for 5 hr. It was then diluted with water and the solution was neutralized with barium carbonate and filtered. The filtrate was evaporated to dryness and the residue was extracted with hot water. The water extracts were treated carefully with just sufficient dilute sulfuric acid to remove any barium, filtered and concentrated until pyrazole-4-sulfonic acid crystallized; 1.1 g., 73%, m.p. 345° dec. after one crystallization from water.

Anal. Calcd. for $C_3H_4N_2O_3S$: C, 24.32; H, 2.72; N, 18.91; neut. equiv., 148. Found: C, 24.16; H, 2.85; N, 18.96; neut. equiv., 154.

1-Phenyl-3-methyl-1,2,3-triazolium Salts.—1-Phenyl-1,2,3-triazole was prepared by the method of Dimroth.[46] A mixture of 1.05 g. of 1-phenyl-1,2,3-triazole, 1 ml. of methyl iodide, 6 ml. of acetone and 5 ml. of dry ether was allowed to stand at room temperature.[23] Crystals began to separate after 24 hr. and continued to form during 2.5 weeks, m.p. 130–135°. After two crystallizations from acetone–ethyl acetate, 1-phenyl-3-methyl-1,2,3-triazolium iodide melted at 134.5–135.5°, total yield 1.71 g., 84%.

Anal. Calcd. for $C_9H_{10}IN_3$: C, 37.65; H, 3.55; N, 14.63. Found: C, 37.84; H, 3.52; N, 14.71.

The methanesulfonate salt was prepared by metathesis between silver methanesulfonate (from silver oxide and methanesulfonic acid) and the triazolium iodide in aqueous solution. The filtrate from the silver iodide was evaporated leaving an oil which was dissolved in methanol and allowed to stand in an open flask while the methanol evaporated. The solid, m.p. 144–148°, which separated was obtained in 73% yield. After two crystallizations from methanol–ethyl acetate, 1-phenyl-3-methyl-1,2,3-triazolium methanesulfonate melted at 148–149.5°.

Anal. Calcd. for $C_{10}H_{13}N_3O_3S$: C, 47.05; H, 5.11. Found: C, 47.09; H, 5.07.

1-Phenyl-1,2,3-triazole Hydrobromide.—Dry hydrogen bromide was bubbled through a solution of 0.5 g. (0.00345 mole) of 1-phenyl-1,2,3-triazole in 15 ml. of dry ether. There precipitated 0.76 g. (97%) of salt, m.p. 76–77° after two recrystallizations from methanol–ethyl acetate, neut. equiv. 225.5 (calcd. 226).

ANN ARBOR, MICHIGAN

(44) Although these analyses are not too satisfactory, repeated attempts to obtain purer material were unsuccessful. Particular difficulty was experienced with chlorine analyses, which varied markedly depending on the age of the sample.

(45) H. von Pechmann, *Ber.*, **31**, 2950 (1898).

(46) O. Dimroth, *ibid.*, **35**, 1305 (1902).