3-Substituted 6-Amino-*s*-triazolo[3,4-*b*][1,3,4]thiadiazoles.—The following general procedure was used. Cyanogen bromide (5.0 g, 0.05 mole) and the 3-substituted 4-amino-*s*-triazole-5-thiols (0.04 mole) were refluxed in 75% aqueous alcohol for 2–3 hr. The initial red solution gradually turned yellow in color. The reaction mixture was evaporated to one-fourth volume and diluted with a saturated solution of sodium acetate. The precipitated amine was collected and purified by crystallization from the solvent listed in Table I.

3-Substituted *s*-Triazolo[3,4-*b*][1,3,4]thiadiazole-6-thiols.—The following general procedure was used. The 3-substituted 4-amino-*s*-triazole-5-thiols (0.09 mole) and potassium hydroxide (5.0 g, 0.09 mole) were dissolved in methanol (100 ml) and, after the addition of carbon disulfide (20 ml), the solution was refluxed for 24 hr. During this time, the odor of hydrogen sulfide was noticeable. The solution was then evaporated to dryness and aqueous hydrochloric acid (50 ml) was added. The crude 3-substituted *s*-triazolo[3,4-*b*][1,3,4]thiadiazole-6-thiols were collected and recrystallized from pyridine–ethyl acetate and these products are described in Table I.

3-Amino-6-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole.—5-Phenyl-1,3,4-thiadiazol-2-ylhydrazine (2.0 g, 0.01 mole) and cyanogen bromide (1.0 g, 0.01 mole) were refluxed for 3 hr in aqueous methanol (100 ml, 75%) and the solution was then poured into ether (*ca.* 300 ml). The solid that precipitated was collected and dissolved in boiling water and, after filtering, sodium acetate was added. The precipitated amine crystallized from methanol–ethyl acetate as yellow prisms: 1.0 g (47%); mp 260°; infrared spectrum (Nujol) 3125, 2994, 2841, 1634, 1582, 1529, 1508, 1484, 1451, 1381, 1319, 1304, 1232, 1160, 1127, 1065, 946, and 916 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 267 mμ (log ε 4.29) and 240 mμ (sh) (log ε 4.26).

Anal. Calcd for $C_9H_7N_5S$: C, 49.8; H, 3.25; N, 32.25. Found: C, 49.6; H, 3.2; N, 32.4.

6-Phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole-3-thiol.—5-Phenyl-1,3,4-thiadiazol-2-ylhydrazine (1.9 g, 0.01 mole) and potassium hydroxide (0.55 g, 0.01 mole) were dissolved in methanol (100 ml) and, after adding carbon disulfide (5 ml), the reaction mixture was refluxed for 24 hr. The methanol was then removed under reduced pressure and the product was precipitated by the addition of aqueous hydrochloric acid (50 ml, 1 *N*). The thiol was recrystallized from benzene–methanol and separated as stout, colorless needles: 1.2 g (60%); mp 262°; infrared spectrum (Nujol) 2882, 1534, 1508, 1462, 1379, 1330, 1314, 1255, 1092, 1019, 952, and 920 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 258 mμ (log ε 4.19).

Anal. Calcd for $C_9H_6N_4S_2$: C, 46.1; H, 2.6; N, 23.9. Found: C, 46.3; H, 2.8; N, 23.7.

3-Methylthio-6-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole.—The thiol (0.2 g, 0.0001 mole) and a few drops of sodium hydroxide solution (50%) were mixed in water and shaken with methyl iodide (5 ml). The excess methyl iodide was removed by heating and the crude methylthio ether was separated. It crystallized as colorless plates: 0.21 g (97%); mp 146°; infrared spectrum ($CHCl_3$) 2950, 2907, 1603, 1471, 1453, 1441, 1377, 1311, 1229, 1036, and 1026 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 271 mμ (log ε 4.51); nmr spectrum ($CDCl_3$), τ 7.20 (SCH_3), 2.14, and 2.46 (aromatic).

Anal. Calcd for $C_{10}H_8N_4S_2$: C, 48.4; H, 3.25; N, 22.6. Found: C, 48.6; H, 3.6; N, 22.8.

4-Formamido-3-methyl-*s*-triazole-5-thiol.—4-Amino-3-methyl-*s*-triazole-5-thiol (4.8 g, 0.04 mole) was refluxed in formic acid (100 ml, 100%) for 24 hr. The excess acid was evaporated, and the residue crystallized from methanol as stout, colorless needles: 2.0 g (34%); mp 233°; infrared spectrum (Nujol) 2967, 1650, 1585, 1575, 1486, 1441, 1368, 1351, 1332, 1189, 1112, 1074, 1021, 981, 886, 817, and 761 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 257 mμ (log ε 4.23).

Anal. Calcd for $C_4H_6N_4OS$: C, 30.4; H, 3.8; N, 35.4. Found: C, 30.4; H, 3.8; N, 35.2.

Ethyl N-(3-Methyl-5-mercapto-*s*-triazol-2-yl)formimidate.—Triethyl orthoformate (100 ml) and 3-methyl-4-amino-*s*-triazole-5-thiol (5.0 g, 0.039 mole) were refluxed for 24 hr and the excess ortho ester was then removed under reduced pressure. The gummy residue was mixed with petroleum ether (500 ml) and the precipitate that formed crystallized from benzene–petroleum ether as colorless needles, 1.2 g (17%), mp 145°.

Anal. Calcd for $C_6H_{10}N_4OS$: C, 38.8; H, 5.4; N, 30.8. Found: C, 39.3; H, 5.5; N, 30.6.

N-(5-Phenyl-1,3,4-thiadiazol-2-yl)benzamidine.—2-Amino-5-phenyl-1,3,4-thiadiazole (36.0 g, 0.20 mole) was mixed with benzonitrile (21.0 g, 0.25 mole) and aluminum chloride (26.6 g, 0.25 mole). Solution occurred with evolution of heat and the reaction mixture was then heated in an oil bath at 180–190° for 15 min. After cooling, ice water was added, followed by a 10% sodium hydroxide solution and the precipitated product was collected and dried. Recrystallization from benzene afforded colorless needles: 36.0 g (63%); mp 183°; infrared spectrum ($CHCl_3$) 2801, 1621, 1449, 1379, 1071, 1002, and 989 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 mμ (log ε 4.64).

Anal. Calcd for $C_{15}H_{12}N_4S$: C, 64.3; H, 4.3; N, 20.0. Found: C, 63.8; H, 4.6; N, 19.6.

N-(5-Methyl-1,3,4-thiadiazol-2-yl)benzamidine was prepared in a similar manner from 2-amino-5-methyl-1,3,4-thiadiazole, and was obtained as colorless needles: 8.3 g (29%); mp 177°; infrared spectrum (Nujol) 3155, 3012, 3817, 1637, 1527, 1497, 1460, 1377, 1326, 1195, 1149, 1070, and 975 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 302 mμ (log ε 4.26) and 235 mμ (log ε 3.99).

Anal. Calcd for $C_8H_{10}N_4S$: C, 55.0; H, 4.6; N, 25.7. Found: C, 55.0; H, 4.4; N, 25.5.

Sulfostyril (2,1-Benzothiazine 2,2-Dioxide). II.[1] Synthesis

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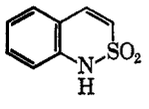
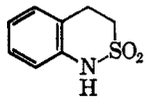
Received May 9, 1966

The synthesis of sulfostyril (**1**), the parent member of the 2,1-benzothiazine dioxide ring system, is described. The critical step in the successful synthesis, reduction of an intermediate ketone (**8**), could not be carried out by the usual chemical or catalytic means. It was finally transformed to the olefin by the Bamford–Stevens reaction. No carbon skeleton rearrangements were observed in this tosylhydrazone decomposition.

In a previous paper[1] we described the synthesis of 3,4-dihydrosulfostyril (dihydro-2,1-benzothiazine 2,2-dioxide) (**2**), which was prepared as a potential intermediate to the hitherto unknown aromatic sultam sulfostyril[2] (**1**). All attempts to convert **2** to **1** by thermal, oxidative, or other chemical methods failed; consequently, it became necessary to devise an alternate route.



1



2

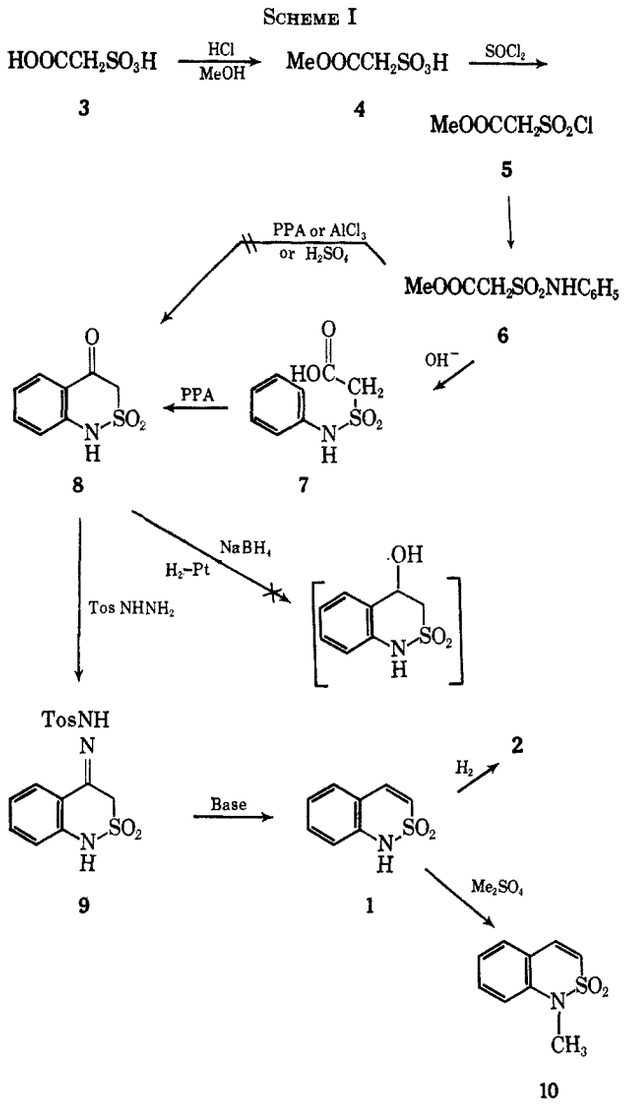
In this paper, we describe the successful synthesis of sulfostyril (Scheme I). Sulfoacetic acid (**3**) was converted to the half-ester **4** and then to the sulfonyl chloride[3] (**5**). Attempts to prepare **5** or chlorosul-

(1) Part I of this series: B. Loev and M. F. Kormendy, *J. Org. Chem.*, **30**, 3163 (1965).

(2) Compound **1** can be systematically named as 2,1-benzothiazine 2,2-dioxide or, less satisfactorily, as *o*-aminostyrene-β-sulfonic acid sultam; for convenience, we prefer the name "sulfostyril," by analogy with the name "carbostyril" used for the carbonyl analog.

(3) R. Viellefosse, *Bull. Soc. Chim. France*, 351 (1947).

SCHEME I



3 4 5 6 7 8 9 1 2 10

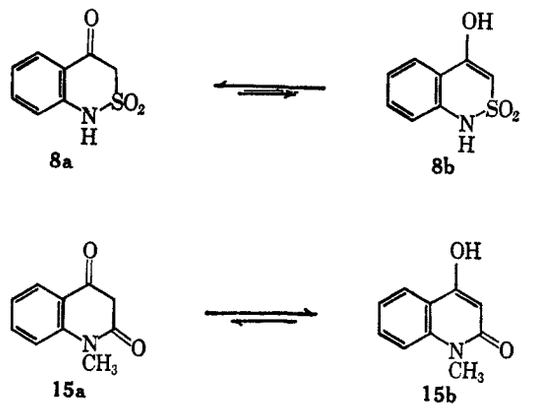
fonylacetic acid by controlled alcoholysis or hydrolysis of the diacid chloride (**11**) failed. Compound **11** was extraordinarily reactive and readily hydrolyzed to sulfoacetic acid within a few moments just on exposure to the humidity in the air.

The ester **5** reacted readily with aniline to give the sulfonanilide, **6**. This ester–amide could not be cyclized directly, but after hydrolysis to the acid **7** cyclization to the ketone **8** readily proceeded using polyphosphoric acid.

The ketone showed the expected carbonyl absorption for **8a** at 5.95 μ in the infrared, a methylene absorption at 4.65 ppm in the nmr, and it readily formed a 2,4-dinitrophenylhydrazone.

By contrast, the *carbonyl* analog (**15**) is almost solely in the enol form (**15b**) as shown by the lack of any ketone absorption in the infrared, a single olefinic hydrogen at 6.00 ppm in the nmr, a positive $FeCl_3$ test, and its failure to form any carbonyl derivatives.

In view of the ketonic properties of **8** as described above, it was surprising to find that **8** could not be reduced to the alcohol either by catalytic reduction (hydrogenation in various solvents using platinum or nickel catalysts at various temperatures and pressures) or chemical means (borohydride, lithium aluminum hydride, or sodium and alcohol).



Since the ketone **8** readily formed hydrazones, the applicability of the Bamford–Stevens reaction[4] was investigated. This technique, which involves the decomposition of a tosylhydrazone, may yield either olefins, *via* hydrogen migration, or cyclopropanes, *via* intramolecular insertion.[5a] The effect of homocyclic ring size on product composition has been studied[5b,6] and it has been found that the five- and six-membered ring tosylhydrazones yield cyclopentene and cyclohexene, respectively, but that the tosylhydrazones of cycloheptanone and higher cycloalkanones produced extensive intramolecular insertion products, in addition to the cycloalkenes. Since introduction of heterocyclic atoms into the ring affects the conformation and ring size, it might be expected to influence the product composition resulting from tosylhydrazone decomposition. Thus, it could not be predicted, *a priori*, which way the reaction would go.

When the tosylhydrazone **9** was decomposed using sodium methoxide in ethanol containing a small amount of water, the sole isolable product in good yield was the desired unrearranged compound sulfostyril (**1**). Anhydrous systems or *t*-butyl alcohol as solvent gave very low yields of **1** but no other identifiable products.

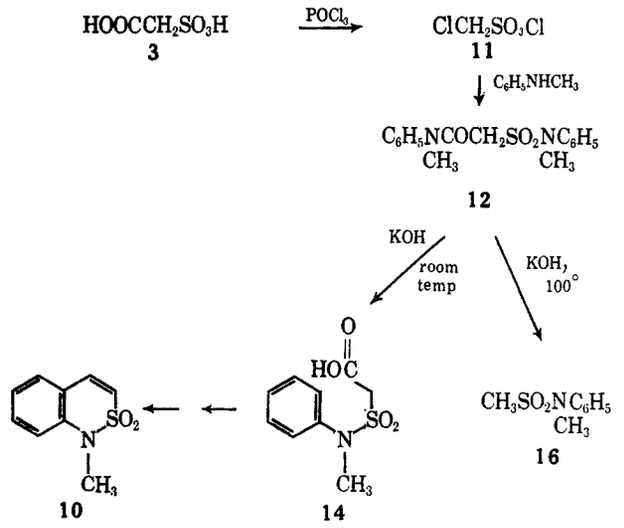
The structure **1** was confirmed both by nmr and by reduction to dihydrosulfostyril (**2**) identical with that previously prepared by an alternate route.[1]

A variation of the above is shown in Scheme II. The highly reactive bisacid chloride **11**, prepared from sulfoacetic acid, was treated with N-methylaniline to give the bisanilide **12**. This compound proved to be quite stable; it could not be cyclized using aluminum chloride and was recovered unchanged from refluxing hydrochloric acid. Vigorous refluxing with alkali resulted in hydrolysis and decarboxylation, and N-methyl methanesulfonanilide (**23**) was the only product isolated. On standing with alcoholic base at room temperature, hydrolysis of the carboxanilide occurred and the acid (**14**) was obtained. This was cyclized and then reduced to N-methylsulfostyril (**10**) *via* the Bamford–Stevens reaction, in the same manner as described above. The structure of the compound was confirmed by comparison with material prepared by direct methylation of sulfostyril.

Another synthesis of sulfostyril that was explored, involved a route similar to that which had been successfully used for the synthesis of dihydrosulfostyril.[1]

(4) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
(5) (a) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (b) *ibid.*, **83**, 3159 (1961).
(6) J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 168, 278 (1961).

SCHEME II



Styrene was sulfonated, then converted to styrenesulfonyl chloride[7] which, on nitration,[8] gave a mixture from which *o*-nitrostyrenesulfonyl chloride could be isolated. This was then hydrolyzed to the sodium sulfonate. Reduction, either chemically (ferrous sulfate and ammonia), or catalytically (hydrogenation in the presence of 5% palladium on carbon until the theoretical amount of hydrogen was absorbed), gave sodium *o*-aminostyrenesulfonate. Reaction with phosphorous pentachloride and/or acetyl chloride, conditions that were successful for the cyclization of sodium *o*-aminophenethylsulfonate to **2**,[1] failed when applied to the styrenesulfonate.

Another route to sulfostyrils that was investigated involved attempts to dehydrogenate "pulegone sultams."[9] This route did not appear promising and, in view of the very low yield of the sultam obtained in our hands, was abandoned.

Experimental Section[10]

Methyl N-Phenylsulfamoylacetate (6).—A concentrated ethereal solution of 40.0 g (0.232 mole) of methyl chlorosulfonylacetate,[3] bp 128–131 (9 mm), $n^{27}D$ 1.4613, was added to a solution of 45.3 g of aniline in 500 ml of ether, while maintaining the temperature at 10°. The mixture was stirred for 1 hr at room temperature and then filtered. The filtrate was concentrated and the residual solid was recrystallized from isopropyl ether, giving the product as a white solid, mp 76–78°, 33.2 g, 63% yield. A small sample recrystallized again melted at 79.5–80°.

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84; N, 6.11. Found: C, 47.36; H, 4.91; N, 6.17.

N-Phenylsulfamoylacetic Acid (7).—A solution of 20 g of the ester **6** in 77 ml of 10% sodium hydroxide was heated for 3 hr at reflux. The solution was cooled and acidified with dilute hydrochloric acid. The resulting solid was extracted with chloroform and the organic solution was dried and concentrated, giving a solid, mp 113–115° (91% yield), which was recrystallized from benzene, mp 118.5–119°.

Anal. Calcd for $C_8H_9NO_4S$: C, 44.64; H, 4.21. Found: C, 44.92; H, 4.16.

On repetition of this reaction, the melting point of the product was sometimes found to be 166–167°. This material gave the same cyclized product that the low-melting solid did and is evidently a polymorphic form.

4-Keto-3,4-dihydrosulfostyril (8).—A mixture of N-phenylsulfamoylacetic acid and 200 g of polyphosphoric acid was heated to 125° and maintained at this temperature for 5 min with stirring. The resulting mixture was cooled and poured into 1 l. of ice water. A tan solid precipitated, 4.8 g, mp 190–192°. A sample was recrystallized from ether for analysis, mp 192–193°.

Anal. Calcd for $C_8H_7NO_3S$: C, 48.72; H, 3.58; N, 7.10. Found: C, 49.05; H, 3.76; N, 6.88.

The compound is soluble in sodium bicarbonate solution. It forms a 2,4-dinitrophenylhydrazone, mp 276–277° dec, and a phenylhydrazone, mp 241–244° dec.

4-Keto-3,4-dihydrosulfostyril, *p*-Toluenesulfonylhydrazone (9).—A mixture of 4-ketodihydrosulfostyril (50 g, 0.254 mole), 52 g of *p*-toluenesulfonylhydrazine, 500 ml of alcohol, and 0.5 ml of concentrated hydrochloric acid was heated at reflux for 3 hr. The mixture was concentrated to approximately 200 ml and then poured into 2 l. of ice water. The gum which first separated slowly crystallized. The solid was filtered, 85.5 g, mp 203–205° dec, and recrystallized from alcohol–water, mp 213–214° dec.

Anal. Calcd for $C_{15}H_{16}N_2O_4S_2$: C, 49.30; H, 4.14; N, 11.50. Found: C, 49.13; H, 4.23; N, 11.49.

Sulfostyril (1).—The hydrazone, **9**, (85 g) was dissolved in 1.7 l. of hot alcohol, then 39.4 g (0.703 mole) of sodium methoxide was added. Heat was evolved and a precipitate formed. Sufficient water was added to dissolve the solid, and the resulting brown solution was refluxed for 18 hr. The solution was concentrated to a small volume then diluted with water. On acidification with concentrated hydrochloric acid a precipitate separated and was filtered. The solid was extracted twice with boiling water; on cooling, a white solid precipitated, 53.5 g. This was recrystallized from chloroform, 28.2 g, mp 153–155°.

Anal. Calcd for $C_8H_7NO_2S$: C, 53.02; H, 3.89; N, 7.73. Found: C, 53.02; H, 3.99; N, 7.68.

Compound **1** (5 g) was hydrogenated at 50 psig using a 5% palladium-on-carbon catalyst and ethanol solvent. The theoretical amount of hydrogen was absorbed in 20 min. The catalyst was filtered and the solvent was removed *in vacuo* giving 5 g of dihydrosulfostyril (**2**), mp 155–156°. Mixture melting point with sulfostyril was 137–145°.

N-Methylsulfostyril (10).—To a solution of sulfostyril (10 g, 0.053 mole) dissolved in dilute sodium hydroxide was added 25 ml of dimethyl sulfate. The mixture was heated; at about 40° the reaction became slightly exothermic and an oil started to separate. Sodium hydroxide (10% solution) was added as required to keep the solution on the alkaline side. The solution was heated on the steam bath until it no longer became acidic after addition of base, then it was cooled. The oil crystallized and was filtered, 8.3 g, mp 67–70°. The dark solid was recrystallized from isopropyl ether, giving a white solid, mp 70–71°, 7.3 g (68% yield).

Anal. Calcd for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.73; H, 4.59; N, 7.08.

The same compound was obtained when the carboxymethylsulfonanilide (**14**) was cyclized with polyphosphoric acid, by a procedure identical with that described above for the cyclization of **7**. The ketone was converted to **10**, mp 70–71°, *via* the Bamford–Stevens reaction, as described for sulfostyril itself.

N-Methylsulfostyril shows the following ultraviolet absorption spectrum: λ_{max}^{MeOH} 222 mμ (ε 27,300), 268 (8840), and 322 (3030). For comparison, N-methylcarbostyril shows the following: λ_{max}^{MeOH} 228 mμ (ε 36,650), 260 (ε 7290), and 330 (6150).

N,N'-Dimethyl-N,N'-diphenylsulfamoylacetamide (12).—A solution of 59 g (0.33 mole) of chlorosulfonylacetyl chloride[11] (**11**) in dry benzene was added, with cooling and stirring, to a solution of 143 g (1.33 moles) of N-methylaniline in benzene. After 18 hr the suspension was filtered, and the filtrate was concentrated *in vacuo* to give 112 g of a viscous oil, $n^{24}D$ 1.5726. On standing, the oil crystallized, and the product was recrystallized from alcohol–water, mp 79–81°.

Anal. Calcd for $C_{16}H_{18}N_2O_3S$: C, 60.36; H, 5.70; N, 8.80. Found: C, 60.15; H, 5.75; N, 8.53.

N-Methylmethanesulfonanilide (13).—A solution of 42 g of crude **12** in excess alcoholic potassium hydroxide was heated at reflux for 3 days. Some product which had separated was filtered off, mp 71–76°. The filtrate was heated *in vacuo* to

(7) F. G. Bordwell, *et al.*, *J. Am. Chem. Soc.*, **68**, 139 (1946).

(8) F. G. Bordwell, A. B. Colbert, and B. Alan, *ibid.*, **68**, 1778 (1946).

(9) B. Helferich, R. Dhein, K. Geist, H. Junger, and D. Wiehle, *Ann.*, **646**, 32 (1961).

(10) All melting points are corrected. Analyses were performed by the Analytical Department of these laboratories.

(11) L. Hinman and L. Locatell, *J. Am. Chem. Soc.*, **81**, 5655 (1959).

remove most of the alcohol, then water and dilute hydrochloric acid were added. An upper layer separated and crystallized on cooling, mp 71–75°. The combined solids were recrystallized from ethanol, giving 8.0 g, mp 73–75°.

Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.9; H, 6.0; N, 7.6. Found: C, 52.5; H, 6.1; N, 7.3.

N-Methyl-N-phenylsulfamoylacetic Acid (14).—A solution of crude **12** in excess alcoholic potassium hydroxide was kept at room temperature for 3 days. Some inorganic solid which had separated was filtered, and the filtrate was concentrated *in vacuo*. On addition of dilute hydrochloric acid to the residue, an oil separated which was extracted with methylene chloride. The solution was dried and the solvent was removed, leaving a semisolid. This was rinsed with ether and ethyl acetate, after which an ivory solid remained, mp 120–122°.

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84; N, 6.11. Found: C, 47.01; H, 4.83; N, 6.11.

Acknowledgment.—We wish to thank Dr. James W. Wilson for his encouragement and many helpful discussions.

Studies on the Preparation and Rearrangements of Allylic Azides[1]

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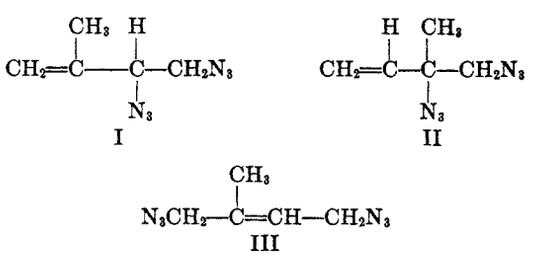
Received April 4, 1966

A study of the preparations and rearrangements of the following diazides is reported: 3,4-diazido-1-butene (IV), *trans*-1,4-diazido-2-butene (V), *cis*-1,4-diazido-2-butene (VI), 3,4-diazido-2,3-dimethyl-1-butene (VII), and *trans*-1,4-diazido-2,3-dimethyl-2-butene (VIII). *trans*-1,4-Diazido-2-butene (V) rearranges more slowly than crotyl azide although the former has two potentially mobile groups. 3,4-Diazido-1-butene (IV) rearranges faster than *trans*-1,4-diazido-2-butene (V), and slower than α-methylallyl azide. The decreased rates of rearrangement of IV and V may result from the electron-withdrawing effect of the azide group on the transition state. *cis*-1,4-Diazido-2-butene (VI) rearranges slower than the *trans* isomer. This may result from greater steric hindrance in the transition state of the *cis* isomer. The rate of rearrangement of 3,4-diazido-2,3-dimethyl-1-butene (VII), a tertiary azide, is slower than that of *trans*-1,4-diazido-2,3-dimethyl-2-butene (VIII), a primary azide; in all allylic azide systems that have been studied, the secondary and tertiary azides rearrange more rapidly than the primary ones. Steric interactions between the methyl groups in VII may hinder approach to coplanarity of the double bond and the rearranging azide group in the transition state, and a decreased rate of rearrangement results. The stabilities of the diazides are discussed. The equilibrium mixture of IV and V exploded violently during the course of the investigation. These two compounds are considered to be *extremely* dangerous.

Winstein and co-workers[3] were the first to undertake a study of the rearrangement of allylic azides. They showed that crotyl azide rearranges reversibly to give α-methylallyl azide and that γ,γ-dimethylallyl azide rearranges reversibly to give α,α-dimethylallyl azide. They also demonstrated that the rates of rearrangement increase only slightly with an increase in polarity of the solvent and that the rearrangements exhibit negative entropies of activation. The effect of pressure on the equilibration of α- and γ-methylallyl azide was reported by le Noble.[4] He assumed that the rearrangement occurred through a cyclic transition state.

We became interested in the rearrangements of azides when it was discovered that 1,4-dibromo-2-methyl-2-butene reacts with sodium azide to give 3,4-diazido-2-methyl-1-butene (I) and another diazide suspected of being 3,4-diazido-3-methyl-1-butene (II), in addition to the expected 1,4-diazido-2-methyl-2-butene (III).[5] In an effort to expand the knowledge of azide rearrangements and to study the preparation and the properties of allylic diazides,[6] an investigation of

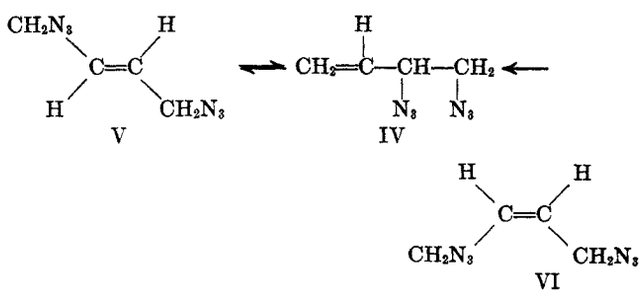


I II III

the following azides was undertaken: 3,4-diazido-1-butene (IV), *trans*-1,4-diazido-2-butene (V), *cis*-1,4-diazido-2-butene (VI), 3,4-diazido-2,3-dimethyl-1-butene (VIII), and *trans*-1,4-diazido-2,3-dimethyl-2-butene (VIII).

Results and Discussion

The kinetics of the reversible rearrangement of 3,4-diazido-1-butene (IV) to *trans*-1,4-diazido-2-butene (V) were determined by infrared analysis. The rates of



V IV VI

(1) (a) From the Ph.D. Dissertation of V. L. Heasley; (b) presented in part at the 144th National Meeting of the American Chemical Society, Los Angles, Calif., April 1963; (c) this project was performed as a part of American Petroleum Institute Research Project 52. This work was also supported in part by a research grant from the Petroleum Research Fund of the American Chemical Society (Type C) to C. A. V.

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(3) S. Winstein, A. Gagneux, and W. G. Young, *J. Am. Chem. Soc.*, **82**, 5956 (1960).

(4) W. le Noble, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 10M.

(5) Studies were not continued on the diazides from 1,4-dibromo-2-methyl-2-butene because of the extreme difficulty involved in an accurate analysis of the product, and because it is still uncertain whether 1,4-dibromo-2-methyl-2-butene has the *cis* or *trans* configuration.

(6) As far as we can determine, this is the first report on the preparation of allylic diazides. By the term "allylic diazides" we refer to those diazides (V, VI, and VIII) in which both azide groups are located on carbon atoms adjacent to a double bond.