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The Reaction of Substituted Benzenesulfonyl Azides with N,N-Diethylaminoprop-1-yne

Frederick Warren Stanley Jr.
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THE REACTION OF SUBSTITUTED
BENZENESULFONYL AZIDES
WITH N,N-DIETHYLAMINOPROP-1-YNE

by

Frederick Warren Stanley Jr.

A Thesis
Submitted to the
Faculty of The Graduate
College in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
December 1970

THE REACTION OF SUBSTITUTED BENZENESULFONYL AZIDES
WITH N,N-DIETHYLAMINOPROP-1-YNE

Frederick Warren Stanley Jr., M.A.

Western Michigan University, 1970

When aryl sulfonyl azides substituted with electron releasing groups reacted with N,N-diethylaminoprop-1-yne, the products were found to be 1-substituted-4-methyl-5-diethylamino-1,2,3-triazoles. However, when the aryl substituents were electron withdrawing, the products were α -diazo amidines.

In solution, the triazoles were found to exist in equilibrium with an α -diazo tautomer. NMR provided a quantitative method of measuring the percentage of triazole and α -diazo amidine tautomer. The equilibrium was measured in various solvents.

The structures of the compounds were proven by chemical degradation to a N,N-diethyl-N'-arylsulfonyl-propion-amidine.

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INTRODUCTION

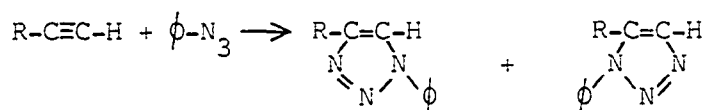
The reactions of substituted benzenesulfonyl azides with N,N-diethylaminoprop-1-yne give products which show an interesting and unusual tautomerization between an α -diazo-N,N-diethyl-N - substituted-propionamidine and a 1-substituted-4-methyl-5-diethyl-amino-1,2,3-triazole. The purpose of this research has been to study the nature of these reactions and to establish the structure of the adducts.

HISTORICAL REVIEW

Vicinal or 1,2,3-triazoles were first prepared by Zinin¹ in 1860, from the nitration of azoxybenzene. The structure of v-triazoles was not known until H. V. Pechmann² first proposed a five membered ring containing three adjacent nitrogen atoms.

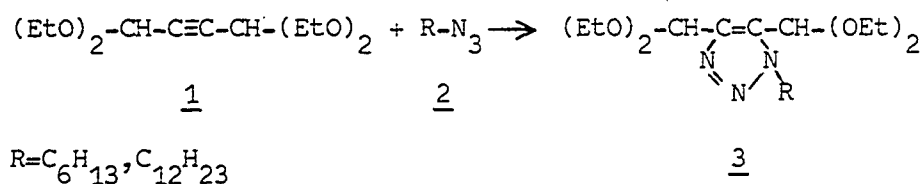
Triazoles have since been studied extensively and many synthetic methods for their preparation have been found.^{3, 4} Perhaps the easiest and most often used method of entry into the triazole system has been the 1,3 dipolar additions of azides to acetylenic compounds.

Phenyl azides react with monosubstituted acetylenes to give two isomeric v-triazoles.⁵ The orientation of phenyl azide is determined



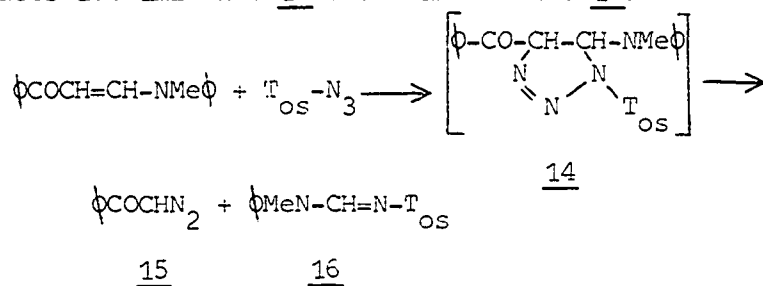
by both steric and electronic effects.^{5, 6}

Aliphatic azides have also been used in the preparation of 1,2,3-triazoles. When bis(di Et acetal)-acetylenedicarboxaldehyde (1) reacts with hexyl or dodecal azides (2) the 1-substituted-4,5-diethylacetal-1,2,3-triazole (3) is formed.⁷



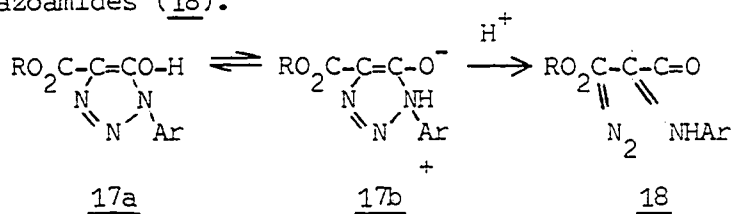
It was found that this equilibrium was influenced by temperature and solvent. The equilibrium was shifted in favor of the diazo compound when the temperature was increased or the polarity of the solvent was increased.

Analogous reactions occur with the addition of benzenesulfonyl azides to enamines 13. Instead of the expected triazolene, the products are amidines 15 and diazoketones 16.¹⁴



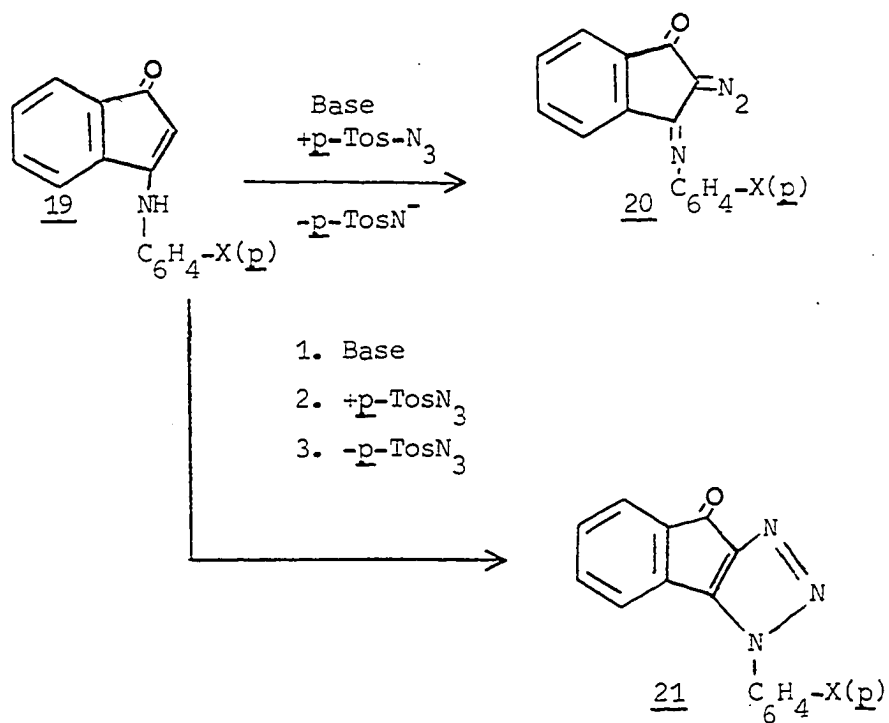
The products are easily explained if a triazolene intermediate 14 is postulated.¹⁴

In the Dimroth rearrangement 1-aryl-4-carbethoxy-5-hydroxy-1,2,3-triazole (17) isomerize in the presence of acid to form -diazouamides (18).¹⁵



The rearrangement is favored by electron withdrawing groups in the para position of the aryl group. The reaction is reversible and in the presence of a base the α -diazouamides are converted to the salt of the triazoles.

It has been recently reported¹⁶ that 1-anilino-3-oxo-indenes (19) are converted to 1-oxo-3-arylimino-2-diazo-indanes (20) or 1-oxo-3-aryl-3H,8H-indeno(1,2-d) triazoles (21).



20, X=H, Cl, NO₂

21, X-CH₃, OCH₃

Upon heating 21 could be converted to 20.

EXPERIMENTAL

Analytical Procedure. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. A Beckmann IR-8 spectrophotometer was used to determine the ir spectra. Varian models A-60 and A-100 were used to determine the nmr spectra using tetramethylsilane as an internal reference. All elemental analyses were performed by Midwest Microlabs, Inc., Indianapolis, Indiana.

Chemicals. The substituted benzenesulfonyl azides used in this study were prepared by the method of Leffler and Tsuno,¹⁸ in which the substituted benzene sulfonyl chloride is treated with sodium azide in aqueous acetone. The mp or bp of compounds 22-27 were in agreement with the literature values as shown in Table I. The N,N-diethylaminoprop-1-yne was purchased as reagent grade and used without further purification.

TABLE I

Compound Number	Compound	mp.	Lit. mp	Ref.
<u>22</u>	<u>p</u> -methoxybenzenesulfonyl azide	51-52 ^o	52.5 ^o	20
<u>23</u>	<u>p</u> -toluenesulfonyl azide	18-20 ^o	19-20 ^o	20
<u>24</u>	<u>p</u> -acetamidobenzenesulfonyl azide	113-114 ^o	114 ^o	19
<u>25</u>	benzenesulfonyl azide	12-14 ^o	14 ^o	18
<u>26</u>	<u>p</u> -nitrobenzenesulfonyl azide	101-102 ^o	102 ^o	20
<u>27</u>	2,5-dichlorobenzenesulfonyl azide	50-52 ^o	52.5 ^o	20

The Addition of Substituted Benzenesulfonyl Azides to N,N-Diethylaminoprop-1-yne

Preparation of 1-p-methoxybenzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole (28a). To a mixture of 2.13g (0.010 mole) of p-methoxybenzenesulfonyl azide and 20 ml THF at 0^oC was added 1.30g (0.011 mole) of N,N-diethylaminoprop-1-yne in 20 ml of THF over a period of one hour. The solution was filtered over alumina and the solvent was removed under reduced pressure. A yellow oil remained which was dissolved in 10 ml of ether and pet. ether (60-110^o) was added until the solution just turned cloudy. Upon standing, clear colorless crystals formed. The yield was 2.0g (58%). Three recrystallizations afforded an analytical sample of 1-p-methoxy-4-methyl-5-diethylamino-1,2,3-triazole, mp 54-56^o; nmr (CHCl₂-d) δ 0.88 and 1.17 (two triplets, 6, J=7, CH₃), 2.24

and 2.30 (two singlets, 3, CH₃), 3.19 (quartet, 4, J=7, CH₂), 4.10 (singlet, 3, -OCH₃), 8.80 (multiplet, 4, aromatics).

Anal. Calcd. for C₁₄H₂₀N₄O₃S: C, 51.85; H, 6.17; N, 17.60.
Found: C, 51.91; H, 6.13; N, 17.45.

Preparation of 1-p-toluenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole (28b). A solution of 1.5g (0.013 mole) of N,N-diethylaminoprop-1-yne in 10 ml of THF was added to 2.26g (0.013 mole) of p-toluenesulfonyl azide in 20 ml of THF. The reaction was maintained at 0° and the addition time was 1 hour. The reaction mixture was then allowed to warm to room temperature and filtered through alumina. The solvent was removed under reduced pressure leaving a yellow oil, which upon scratching turned to a crystalline solid, mp 45-46°. The yield was 4.0g (65%). Three recrystallizations from ether, pet. ether (60-110°) gave clear colorless crystals of 1-p-toluenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole, mp. 49-52°; nmr (CHCl₃-d) δ 0.83 and 1.13 (two triplets, 6, J=7, CH₃), 2.17 and 2.25 (two singlets, 3, J=7, CH₃), 3.09 (quartet, 4, J=7, CH₂), 4.06 (singlet, 3, J=7, -CH₃), 7.50 (multiplet, 4, aromatics).

Anal. Calcd. for C₁₄H₂₀N₄O₃S: C, 51.85; H, 6.17; N, 17.60.
Found: C, 51.91; H, 6.13; N, 17.45.

Preparation of 1-p-acetamidobenzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole (28c). A mixture of 7.80g (0.320 mole) of p-acetamidobenzenesulfonyl azide in 30 ml of THF was cooled to 0°C and to it was added 3.60g (0.320 mole) of N,N-diethylaminoprop-1-yne in 10 ml of THF over a period of 45 minutes. The solution was

allowed to warm to room temperature, filtered through alumina, and the solvent was removed under reduced pressure. The resulting solid was recrystallized three times from acetone, pet. ether (60-110°) to yield an analytical sample of 8.91g (78%) of brown crystalline solid, mp. 131.5-132.5°; nmr (CHCl₃-d) δ 0.71 and 1.09 (two triplets, 6, J=7, CH₃), 2.03 (singlet, 3, $\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$), 2.14 and 2.19 (two singlets, 3, CH₃), 3.07 and 3.44 (two quartets, 4, J=7, CH₂), 7.78 (multiplet, 4, aromatics), 8.88 and 9.33 (two singlets, 1, N-H).

Anal. Calcd. for C₁₅H₂₁N₅O₃S: C, 51.26; H, 6.03; N, 19.93.
Found: C, 51.32; H, 6.11; N, 19.63.

Preparation of 1-benzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole (28d). To a solution of 2.60g (0.0144 mole) of benzenesulfonyl azide and 20 ml of tetrahydrofuran (THF) was added 1.60g (0.0144 mole) of N,N-diethylaminoprop-1-yne in 20 ml of THF over a period of one hour. The reaction was maintained at 0°C. After addition the yellow solution was allowed to warm to room temperature and was filtered over alumina (to remove any peroxide formation in the THF). The solvent was removed under reduced pressure to give a yellow solid which was recrystallized from ether, pet. ether (60-110°) to yield 2.2g (52%), mp 83-84°, of white crystalline 1-benzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole. Three recrystallizations afforded an analytical sample, mp 84-85°; nmr (CHCl₃-d), 0.18 and 1.12 (two triplets, 6, J=7, CH₃), 2.18 and 2.24 (two singlets, 3, J=7, CH₃), 3.09 and 3.39 (two quartets, 4, J=7, CH₂), 7.79 (multiplet, 5, aromatics).

Anal. Calcd. for C₁₃H₁₈N₄O₂S: C, 54.51; H, 6.55; N, 18.17.
Found: C, 54.74; H, 6.63; N, 18.07.

Preparation of α -diazo-N,N-diethyl-N'-2,5-dichlorobenzenesulfonyl-propionamide (29a). A solution of 2.58g (0.010 mole) of 2,5-dichlorobenzenesulfonyl azide in 20 ml of THF was cooled to -78° . To this solution was added 1.33g (0.012 mole) of N,N-diethylaminoprop-1-yne in 5 ml of THF over a period of one hour. The solution was allowed to warm to room temperature. It was then filtered through alumina and the solvent removed under reduced pressure. The yellow solid was recrystallized from ether, pet. ether ($60-110^{\circ}$) to give 2.25g (61.9%) of yellow platelet crystals. Three recrystallizations gave an analytical sample of α -diazo-N,N-diethyl-N'-2,5-dichlorobenzenesulfonyl-propionamide, mp $87-88^{\circ}$; nmr (CHCl_3 -d) δ 1.18 (triplet, 6, $J=7$, CH_3), 2.20 (singlet, 3, CH_3), 3.47 (quartet, 4, $J=7$, CH_2), 7.90 (multiplet, 3, aromatic).

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{Cl}_2\text{N}_4\text{O}_2\text{S}$: C, 42.98; H, 4.45; N, 15.43. Found: C, 43.09; H, 4.46; N, 15.16.

Preparation of α -diazo-N,N-diethyl-N'-p-nitrobenzenesulfonyl-propionamide (29b). To a mixture of 5.70g (0.025 mole) of p-nitrobenzenesulfonyl azide in 30 ml THF, at -78° was added 3.06g (0.027 mole) of N,N-diethylaminoprop-1-yne in 5 ml of THF. The addition time was 1.5 hours. The solution was allowed to warm to room temperature and filtered through alumina. The solvent was removed under reduced pressure and the solid that remained was recrystallized from ethanol to give orange platelet crystals. During the heating of the compound in ethanol it was observed that a gas was given off, presumably N_2 . Afterwards all recrystallizations were done in ether, pet. ether ($60-110^{\circ}$) to prevent this

thermal decomposition. The yield was 7.05g (81%) of -diazo-N,N-diethyl-N'-p-nitrobenzenesulfonyl-propionamidine, mp 95-96°. Three recrystallizations from ether, pet. ether (60-110°) gave an analytical sample, mp 97-98°; nmr (CHCl₃-d) δ 1.15 (triplet, 6, J=7, CH₃), 2.24 (singlet, 3, CH₃), 3.47 (quartet, 4, J=7, CH₂), 8.50 (multiplet, 3, aromatics).

Anal. Calcd. for C₁₃H₁₇N₅O₄S: C, 46.06; H, 5.01; N, 20.65. Found: C, 46.01; H, 5.11; N, 20.39.

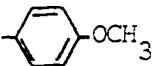
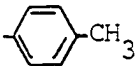
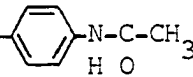

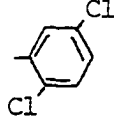
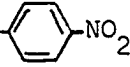
Determination of ir spectra. The ir spectra were determined for compounds 28a-d and 29a, b as solutions (CHCl₃) and in the solid state. The main absorptions and their intensity are shown in Table II.

Degradation of 1-Benzenesulfonyl-4-Methyl-
5-Diethylamino-1,2,3-Triazole

Preparation of N,N-diethyl-N'-benzenesulfonyl-acryloamidine (35). When 1.5g (0.0056 mole) of 1-benzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole was treated with 5 ml of glacial acetic acid, the solution turned yellow and started to effervesce. The yellow color disappeared and when the bubbling stopped, the excess acetic acid was removed under reduced pressure. The remaining clear oil was treated with bicarbonate solution. This solution was extracted with two 10 ml portions of chloroform. The organic layer was dried over sodium sulfate, filtered and the solvent removed under reduced pressure. There remained 1.09g (73%) of white solid, mp 83-84°, which was recrystallized three times from ether to give

TABLE II

Summary of Infrared Spectra^{a, b} and
the Structural Interpretation²³

Compound Number	R	(SO ₂)-N=C	C=N ₂	R-SO ₂ -N	-N=N-N
<u>28a</u> (KBr)		-----	-----	1380(s) 1170(s) 1150(m)	1280(s)
<u>28a</u> (CHCl ₃)		1510(s)	2060(s)	1380(s) 1170(s) 1155(w)	1290(s)
<u>28b</u> (KBr)		-----	-----	1385(s) 1175(s) 1145(m)	1280(m)
<u>28b</u> (CHCl ₃)		1520(s)	2060(s)	1385(s) 1175(s) 1145(w)	1280(m)
<u>28c</u> (KBr)		-----	-----	1380(s) 1170(m) 1150(w)	1280(m)
<u>28c</u> (CHCl ₃)		1525(s)	2060(s)	1380(s) 1165(w) 1145(w)	1280(m)
<u>28d</u> (KBr)		-----	-----	1380(s) 1190(s) 1150(m)	1285(s)
<u>28d</u> (CHCl ₃)		1510(s)	2060(s)	1385(m) 1190(s) 1145(m)	1285(s)
<u>29a</u> (KBr)		1520(s)	2060(s)	-----	-----
<u>29a</u> (CHCl ₃)		1520(s)	2060(s)	-----	-----
<u>29b</u> (KBr)		1525(s)	2060(s)	-----	-----
<u>29b</u> (CHCl ₃)		1520(s)	2060(s)	-----	-----

(a) absorption maxima are expressed in cm.⁻¹.

(b) s = strong, m = medium, w = weak.

an analytical sample of N,N-diethyl-N'-benzenesulfonyl-acryloamide, mp 85.5-86.5°; nmr (CHCl₃-d) δ 1.13 (triplet, 6, J=7, CH₃), 3.47 (quartet, 4, J=7, CH₂), 5.30 (multiplet, 3, vinyl protons), 7.68 (multiplet, 5, aromatics).

Anal. Calcd. for C₁₃H₁₈N₂SO₂: C, 58.61; H, 6.82; N, 10.52.
Found: C, 58.39; H, 6.84; N, 10.47.

Hydrogenation of N,N-diethyl-N'-benzenesulfonyl-acryloamide

(35). To a solution of .201g (0.0076 mole) of N,N-diethyl-N'-benzenesulfonyl-acryloamide in 10 ml of ethyl acetate was added .5g of palladium on carbon (10%). The material was hydrogenated at atmospheric pressure and room temperature. The hydrogen uptake was measured and was 0.0074 mole. The reaction was complete after 10 minutes. The solution was filtered, and the solvent was removed under reduced pressure to give a quantitative yield (0.20g) of N,N-diethyl-N'-benzenesulfonyl-propionamide (36). The analytical sample was obtained by three recrystallizations of the sample from ether to give needle like crystals, mp 95.5-96.5°; nmr (CHCl₃-d) δ 1.18 (multiplet, 9, CH₃), 3.18 (multiplet, 6, CH₂), 7.66 (multiplet, 5, aromatics).

Anal. Calcd. for C₁₃H₂₀N₂O₂S: C, 58.23; H, 7.53; N, 10.45.
Found: C, 58.22; H, 7.46; N, 10.22.

The Synthesis of N,N-Diethyl-N'-
Benzenesulfonyl-Propionamide

The preparation of N,N-diethyl-propionamide (38). The title compound was prepared by the method of Pinner,²⁷ in which equimolar

amounts of absolute ethanol, propionitrile and HCl (gas) were allowed to react to give N,N-diethyl-propionimide hydrochloride (37). This imide was then reacted with an excess of diethylamine to produce N,N-diethyl-propionamide hydrochloride. The amidine hydrochloride was converted to the free amidine by treatment with an excess of 33% aqueous K_2CO_3 , extraction of the solution with $CHCl_3$, and drying the $CHCl_3$ layer over Na_2SO_4 . The solution was distilled at atmospheric pressure, collecting the fraction between $179-181^\circ$ (Lit bp. 182°).²¹

Preparation of N,N-diethyl-N'-benzenesulfonyl-propionamide

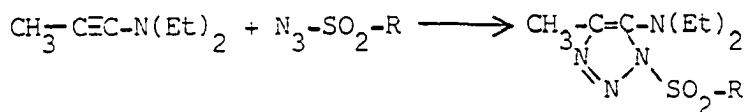
(36). To 1.0g (0.0078 mole) of N,N-diethyl-propionamide was added 2.74g (0.0156 mole) of benzenesulfonyl chloride and 10 ml of 10% aqueous sodium hydroxide. The solution was stirred for 10 minutes and then extracted with chloroform. The organic layer was dried over Na_2SO_4 . The excess solvent was removed under reduced pressure. There remained 1.01g (50%) of white crystalline material, mp $95-96^\circ$. Three recrystallizations from ether gave an analytical sample of N,N-diethyl-N'-benzenesulfonyl-propionamide, mp $95.5-96.5^\circ$; nmr ($CHCl_3$ -d) δ 1.18 (multiplet, 9, CH_3), 3.18 (multiplet, 6, CH_2), 7.66 (multiplet, 5, aromatics).

Anal. Calcd. for $C_{13}H_{20}N_2O_2S$: C, 58.23; H, 7.53; N, 10.45.
Found: C, 58.00; H, 7.51; N, 10.37.

DISCUSSION

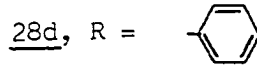
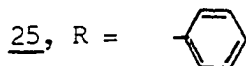
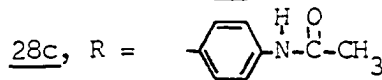
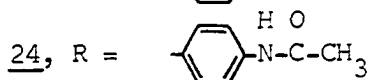
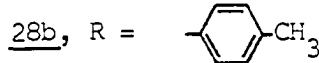
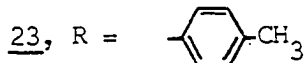
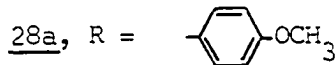
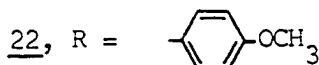
The Reactions of Substituted Benzenesulfonyl Azides with N,N-Diethylaminoprop-1-yne

Benzenesulfonyl azide or benzenesulfonyl azides substituted with electron donating groups reacted with N,N-diethylaminoprop-1-yne at 0°C to give colorless, crystalline, 1:1 adducts whose ir (KBr) and elemental analysis were consistent with a triazole structure 28.



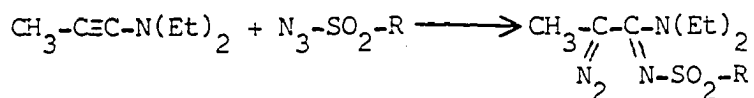
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28a-d



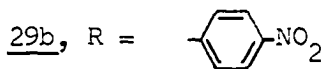
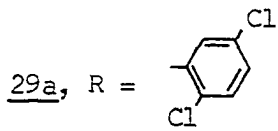
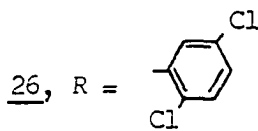
However, when substituted benzenesulfonyl azides containing electron withdrawing groups were reacted with N,N-diethylaminoprop-1-yne at 0°C no products were isolated. When these reactions were performed at -78°C, highly colored (yellow to orange) crystalline compounds were obtained in high yield. The ir (KBr) spectra of these compounds showed an absorption at 2060 cm.⁻¹, characteristic of the diazo functional group. The spectral data (Table II) and

the elemental analyses were consistent with the formation of an α -diazo amidine 29.

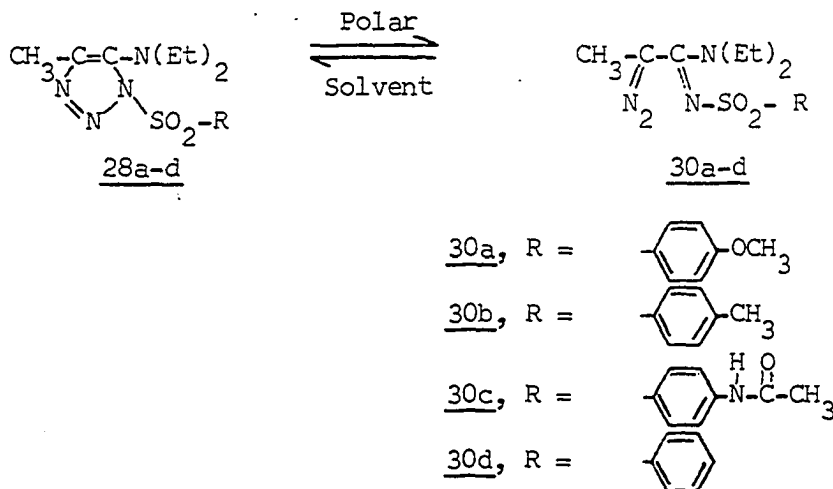


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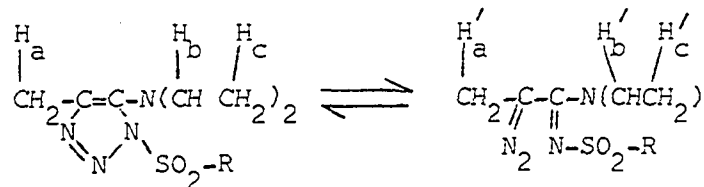
29a, b



Further, when any one of the triazole compounds (28a-d) was dissolved in a polar solvent such as CHCl_3 , a yellow solution resulted, whose color was roughly dependent upon the polarity of the solvent (i.e., the more polar the solvent, the more intensely colored was the solution). The ir of the solution showed the diazo absorption at 2060 cm^{-1} . If the solvent was then allowed to slowly evaporate, a solid triazole was obtained whose ir (KBr) again showed the absence of the diazo group. These experiments show that compounds 28a-d as solids are completely in the triazole form but in solution these triazoles exist in equilibrium with acrylic α -diazo-amidines 30a-d.



The nmr spectra provided a method of quantitatively measuring the equilibrium mixtures of 28a-d and 30a-d. Protons H_a and H'_a appeared as two separate singlets, H_b and H'_b as two closely appearing quartets, and H_c and H'_c are seen as two triplets in the



nmr spectra. By comparing the integration ratios of H_a and H'_a , H_b and H'_b or H_c and H'_c , the percentage of triazole, α -diazo-amidines adducts was measured (Table III). In addition, the nmr spectra of a day old solution ($CHCl_3$) of *p*-toluenesulfonyl adduct (28b, 30b) was taken. The ratio of the triazole, α -diazo-amidines tautomers remained unchanged, showing that the equilibrium was established quickly after the sample was dissolved and did not change with time.

TABLE III

Compound Number	% α -diazo amidine ($CHCl_3$)	Hammett Sigma value ²²
<u>28a</u>	15	-0.268
<u>28b</u>	18	-0.170
<u>28c</u>	32	0.00
<u>28d</u>	33	0.00
<u>29a</u>	100	> 0
<u>29b</u>	100	+0.778

The percent of triazole is dependent upon the electron releasing or withdrawing ability of the substituted benzenesulfonyl group. When the Hammett sigma values of the substituents were compared with the percent triazole (Table III) it was found that

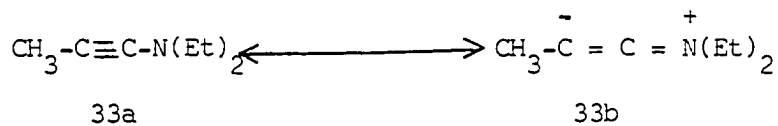
the more negative the sigma value (more electron releasing the substituent) the greater the percent triazole found. However, when the benzenesulfonyl group was substituted with electron withdrawing groups the equilibrium was shifted entirely in favor of the α -diazo-amidine adduct.

The effect of solvents on the equilibrium of 28d and 30d was measured and the results are shown in Table IV. In general, the greater the polarity of the solvent, as measured by its dipole moment, the greater the percent of 30d. This is in agreement with the experiments of Hermes and Marsh¹³ with tautomeric mixtures of 1-cyano-1,2,3-triazole and α -diazo-n-cyanoethylidenimine. The exception to this trend was chloroform, here the percent of 30d was greater than would be expected on the bases of dipole moment alone. However, chloroform would be able to hydrogen bond with the more polar 30d, shifting the equilibrium towards 30d.

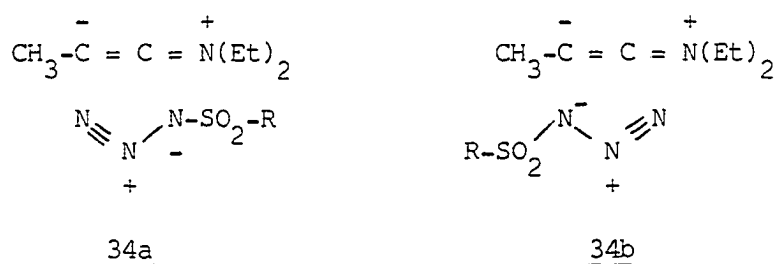
TABLE IV

Solvent	<u>28d</u> (%)	<u>30d</u> (%)	Dipole Moment (DEBYE) ²⁸
Benzene	81	19	0
Chloroform	64	36	1.10
Pyridine	76	24	2.20
Acetonitrile	67	33	3.39

Also, from all experiments on ynamines it appears that the resonance reference structure 33b is of predominance.²⁶



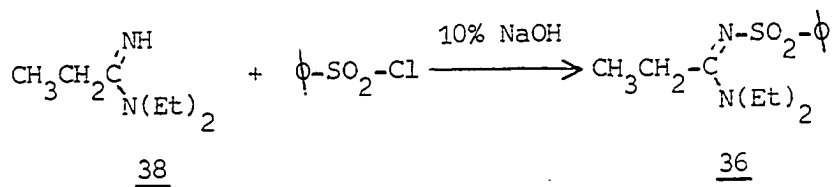
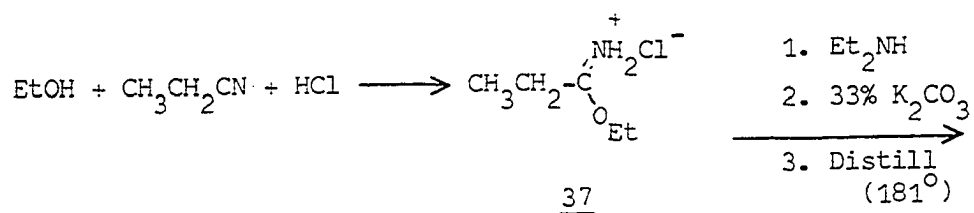
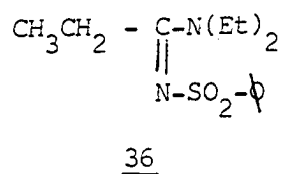
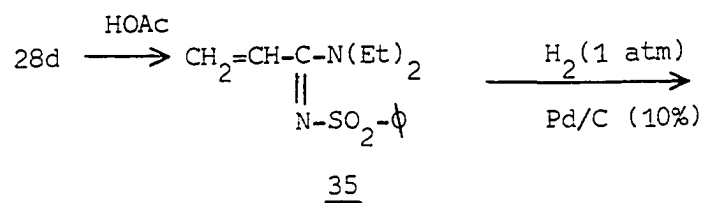
Therefore, for the present reactions 34a would be the expected mode of addition because of the greater separation of negative charges than in 34b.



The actual structure of the triazole (or -diazomidine) was determined by chemical degradation. When 1-benzenesulfonyl-4-methyl-5-diethylamino-1,2,3-triazole was dissolved in glacial acetic acid a yellow solution was formed. This solution began to effervesce, heat was evolved, and the yellow color disappeared. A white crystalline solid was isolated from this reaction in high yield (70%). Analysis of this compound indicated that a molecule of nitrogen had been lost and the nmr showed the characteristic ABC pattern of vinyl protons. The compound that best explained this data was the acryloamidine, 35. This compound was then hydrogenated using palladium on charcoal (10%) to give N,N-diethyl-N'-benzenesulfonyl-propionamidine (36). Although, amidines are a well known class of compounds, this particular one has not been reported in the literature. This compound was synthesized by reacting

N,N-diethylpropionamide (38), prepared by the method of Pinner,²⁷ with benzenesulfonyl chloride in the presence of aqueous sodium hydroxide (10%). The *N,N*-diethyl-*N'*-benzenesulfonyl-propionamide (36) prepared by this method had identical ir and nmr to amidine prepared by the degradation of the triazole. Further the elemental analyses, melting points and mixed melting points were identical proving compounds to be identical.

The formation of the propionamide (36) and its precursor (35) can only be explained if the mode of addition is as indicated in structure 28d. This also means that the addition of substituted benzenesulfonyl azides, studied in this work, to *N,N*-diethylamino-prop-1-yne is determined largely by electronic effects. It would also seem reasonable to assume that the α -diazoamides are formed through triazole intermediates, as in the case of the addition of benzenesulfonyl azides to ethoxyacetylene or enamines, and therefore have the structure 29. In fact, when *N,N*-diethyl-*N'*-*p*-nitrobenzenesulfonyl-propionamide (29b) was reacted with glacial acetic acid, similar to 28d, it gave a compound whose nmr spectra was identical with that of the acrylamide, 35, except of course for the aromatic protons. This again can only be explained if the *p*-nitrobenzenesulfonyl adduct has the structure 29a.



BIBLIOGRAPHY

1. N. Zinin, Ann., 114, 217 (1860).
2. H. V. Pechmann, Ber., 21, 2756 (1888).
3. F. R. Benson and W. L. Savell, Chem. Rev., 46, 1 (1950).
4. J. H. Boyer, "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, 1961, p. 387.
5. J. C. Sheehan and R. C. Robinson, J. Amer. Chem. Soc., 73, 1207 (1951).
6. W. Kirmse and L. Horner, Ann. Chem., 614, 1 (1958).
7. K. Henkel and F. Weygand, Ber., 43, 76, 812 (1943).
8. R. Fuks, R. Buijle, and H. G. Viehe, Angew. Chem., 78, 594 (1966).
9. P. Grünanger, P. Vita Finzi, and E. Fabbri, Gazz. Chem. Ital., 90, 413 (1960).
10. P. Vita Finzi and C. Scotti, Sci. Fis., Mat. Nat., 41, 204 (1966); Chem. Abstr., 67, 54080c (1967).
11. P. Grünanger and P. Vita Finzi, Tetrahedron Lett., 1839 (1963).
12. P. Grünanger, P. Vita Finzi, and C. Scotti, Chem. Ber., 98, 623 (1965).
13. M. E. Humes and F. D. Marsh, J. Am. Chem. Soc., 89, 4760 (1967).
14. R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, Chem. Ber., 96, 802 (1963).
15. Brown and Hammick, J. Chem. Soc., 1384 (1947).
16. M. Regitz and N. Schwall, Liebigs Ann. Chem., 728, 99 (1969).
17. F. H. Adams, U. S. 2,830,029, Apr. 8, 1958. Chem. Abstr., 52, 13303 (1958).
18. J. E. Leffler and Y. Tsuno, J. Org. Chem., 28, 902 (1963).
19. J. N. Ashley, G. L. Berchanan, and A. P. T. Easson, J. Chem. Soc., 60 (1947).

20. D. Rector and R. E. Harmon, J. Org. Chem., 31, 2837 (1966).
21. A. Penner, "Berlstein's Handbuch der Organischen Chemie," Vol. 4, Edwards Brothers, Inc., Ann Arbor, 1944, p. 111.
22. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 87.
23. C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963.
24. G. L'Abbé, Chem. Rev., 69, 345 (1969).
25. R. Huisgen, G. Szeimies, and L. Mobius, Chem. Ber., 100, 2494 (1967).
26. H. G. Viehe, "Chemistry of Acetylenes," Marcel Dekker, New York, 1969, p. 889.
27. H. Gilman, "Organic Synthesis, Collective Volume I," John Wiley and Sons, Inc., New York, 1932, p. 5.
28. A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, 1963.
29. A. G. Williamson, "An Introduction to Non-Electrolyte Solutions," John Wiley and Sons, Inc., New York, 1967, p. 132.

SUMMARY

The reaction of substituted benzenesulfonyl azide with N,N-diethylaminoprop-1-yne has been studied. As solids, the products were found to be dependent upon the electron donating or withdrawing ability of the aryl group. For electron withdrawing substituents on the aryl group the products are α -diazo amidine adducts. When the substituents on the aryl group are electron donating, the crystalline products are v-triazoles. Further it was observed that in solution the v-triazole existed in equilibrium its α -diazo-tautomer. This equilibrium was found to be influenced by the electron donating ability of the aryl substituent and the polarity of the solvent.

VITA

Frederick Warren Stanley Jr. was born April 26, 1943 in Cleveland, Texas. He was married to the former Caroline Hughes on July 26, 1969.

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