ing to the procedure of Shirley and Cameron.[7] The resulting magnetically stirred solution of 2-lithiobenzothiophene was cooled in a Dry Ice–acetone bath and treated with 64.5 g (0.280 mol) of tributylborate giving a gelatinous precipitate. Hydrochloric acid (1 *N*, 200 ml) was added to the stirred mixture at 0°. After stirring 1 hr at 0–25°, the layers were separated and the aqueous phase extracted with ether. The combined ether layers were extracted with 200 ml of 1 *N* NaOH and the basic aqueous layer was backwashed with ether. Acidification of the aqueous layer with ice cold 3 *N* hydrochloric acid gave a pink-yellow odiferous precipitate of crude boronic acid which was collected and washed with water by suction. The crude boronic acid was dissolved in a small volume of ether and the stirred solution treated with 96 ml of 10% hydrogen peroxide containing 2 ml of saturated aqueous sodium carbonate. The resulting mixture was refluxed and stirred for 1 hr and then stirred overnight at room temperature. The layers were separated; the aqueous layer was extracted with ether. The combined ether extracts were washed with water until free of H_2O_2 by the ferrous ion test. The ether layer was then washed with saturated NaCl solution, dried over $MgSO_4$, filtered, and evaporated *in vacuo* giving 21.7 g (72%) of crystalline thianaphthen-2-one, mp 32–34°. Recrystallization from hot aqueous methanol by cooling to −20° gave pale yellow needles: mp 34–35° (lit. mp 33–34°, 44–45°[3,8]); $\nu_{max}^{CCl_4}$ No–OH absorption, 1723, 1595, 1460 (doublet), 1390, 1130, 1088, 1010 cm^{-1}; nmr ($CDCl_3$) 7.24 (4 H, m), 3.92 (2 H, s).

(7) D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, **72**, 2788 (1950).

Registry No.—**1**, 1194-57-6; **2**, 25606-96-6; **3**, 25606-97-7; **3** oxime, 25606-98-8; **4**, 25606-99-9; **8**, 496-31-1; **10**, 25607-01-6; vinyllithium, 917-57-7.

Acknowledgment.—This work was generously supported by the Department of Chemistry, St. Louis University. Support from the National Science Foundation Grant No. GP-8510 for the 100-MHz nmr spectrometer is gratefully acknowledged.

(8) Two crystalline forms "stout prisms," mp 44–45°, and "fine needles," mp 33–34°, of **8** have been isolated.[3] The lower melting form is reported to be the more stable. In our laboratory sublimation of the low melting form at 0.005 mm gave nearly colorless, stout prisms, mp 46–48°. Recrystallization from aqueous methanol gave either form, with the high melting form being the more frequent. Infrared spectra of both materials in CCl_4 were identical and consistent *only* with the ketotautomer **8**.

N,N-Dialkylamino-1,2,3-triazole-α-diazoamidine Tautomers from Substituted Benzenesulfonyl Azides and Ynamines

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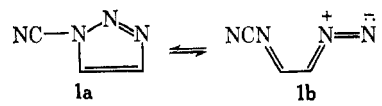
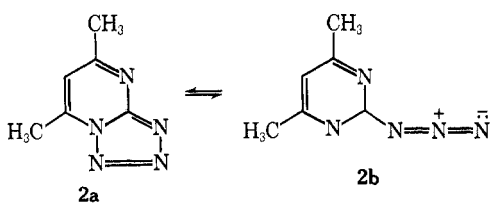
Received May 7, 1970

The 1,3 dipolar additions of a number of substituted benzenesulfonyl azides to *N,N*-diethylaminoprop-1-yne yielded 1,2,3-triazoles and α-diazoamidines which, in solution, were shown by nmr and ir spectroscopy to exist in a tautomeric equilibrium. The structure and stereochemistry of one of the products were proved by chemical degradation. The 1,3 dipolar additions of all the substituted benzenesulfonyl azides to *N,N*-dimethylaminophenylacetylene afforded only α-diazoamidines.

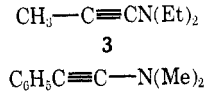
During the last few years, several interesting examples of ring–chain tautomerism involving a variety of functional groups have been reported.[1-3] For instance, in 1967, Hermes and Marsh[4] reported the existence of ring–chain equilibrium between 1-cyano-1,2,3-triazole (**1a**) and α-diazo-*N*-cyanoethylidenimine (**1b**). A similar type of equilibrium between 5,7-dimethyltetrazole[1,5-*a*]pyrimidine (**2a**) and 2-azido-4,6-dimethylpyramidine (**2b**) was also recently reported by Huisgen, *et al.*[5] From the reaction of substituted benzenesulfonyl azides and *N,N*-diethylaminoprop-1-yne (**3**), we have obtained strong evidence for the existence of a ring–chain equilibrium between *N,N*-diethylamino-1,2,3-triazole and α-diazoamidine functions. A number of 1,3 dipolar additions to ynamines have been reported to produce a series of five-membered heterocycles.[6-8] For example, the additions of both aryl and aroyl azides to *N,N*-dimethylaminophenylacetylene (**4**) gave only the corresponding 1,2,3-triazoles **5a** and **5b**, respectively. As an extension of this reaction, we studied the 1,3 dipolar additions of a number of substituted benzenesulfonyl azides (**6**) to ynamines **3** and **4**. The reactions were conducted by adding equimolar



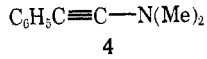
1a **1b**



2a **2b**



3



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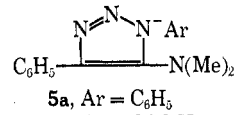

5a, Ar = C_6H_5
b, Ar = COC_6H_5

solutions of **6** to either **3** or **4** in tetrahydrofuran at 0 to −78°. Removal of the solvent by evaporation under reduced pressure afforded the corresponding crystalline *N,N*-dialkylamino-1,2,3-triazoles **7a–d**, and the diazoamidines **8e–f** and **9a–e**. The infrared (ir) spectra of compounds **8e–f** and **9a–e** in chloroform solutions or as KBr pellets showed strong peaks around 2060 cm^{-1},

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(1) R. E. Harmon, J. L. Parsons, and S. K. Gupta, *J. Org. Chem.*, **34**, 2760 (1969), and other references mentioned in this paper.

(2) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *ibid.*, **32**, 2241 (1967).

(3) M. Regitz and H. Schwall, *Justus Liebigs Ann. Chem.*, **728**, 99 (1969).

(4) M. E. Hermes and F. D. Marsh, *J. Amer. Chem. Soc.*, **89**, 4760 (1967).

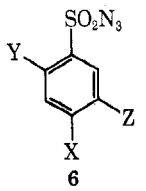
(5) R. Huisgen, K. V. Fraunberg, and H. J. Sturm, *Tetrahedron Lett.*, 2589 (1969).

(6) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

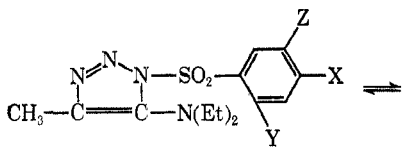
(7) R. Fuks., R. Buijle, and H. G. Viehe, *Angew. Chem.*, **78**, 594 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 585 (1966).

(8) H. G. Viehe, "Chemistry of Acetylenes," Marcel Dekker, New York, N. Y., 1969, p 901.

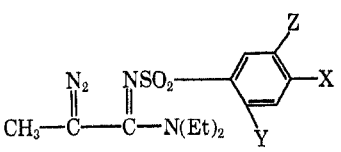
characteristic of the diazo group.[9] This suggested that compounds **8e–f** and **9a–e** existed mainly in one form as represented by the given structures. The ir spectra of compounds **7a–d** as KBr pellets showed the absence of diazoamidine form (no peaks around 2060 cm^{-1}). On the other hand, the ir spectra of chloroform solutions of the same compounds showed absorptions characteristic of the diazoamidine forms **8a–d**. Thus, the ir spectroscopy revealed the possibility of an equilibrium between **7a–d** and **8a–d**. However, this method was not very convenient to determine the equilibrium ratios of these



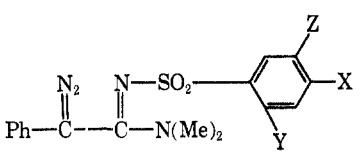
6



7a, X = Y = Z = H
b, X = OCH_3
c, X = CH_3
d, X = $NHCOCH_3$



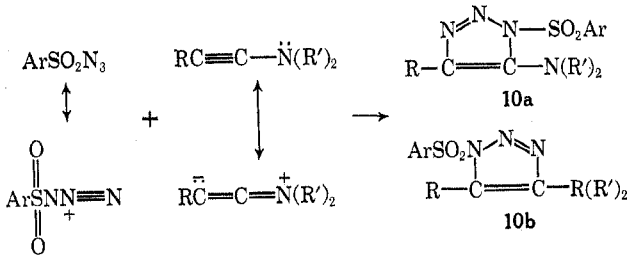
8a, X = Y = Z = H
b, X = OCH_3
c, X = CH_3
d, X = $NHCOCH_3$
e, X = NO_2
f, X = Y = Cl



9a, X = OCH_3
b, X = NO_2
c, X = Br
d, Z = NO_2
e, Y = Z = Cl

two forms. The nuclear magnetic resonance (nmr) spectra of compounds **9a–e** were consistent with the proposed structures and they did not indicate the possibility of ring–chain equilibrium. The nmr spectra of the products obtained by the addition of sulfonyl azides **6** to the ynamine **3** were quite interesting. They revealed the existence of a definite equilibrium between structures **7a–d** and **8a–d**. The nmr data of **7a–d** are given in Table I, **8e–f** and **9a–e** in Table II. The *N*-methylene protons in structures **7a–d** and **8a–d** showed sharp quartets with different chemical shifts. The quartets at δ 3.04–3.09 were attributed to the $N(CH_2CH_3)_2$ protons in structures **7a–d**, whereas the quartets at δ 3.34–3.37 were assigned to the $N(CH_2CH_3)_2$ protons in structures **8a–d**. In each nmr spectrum, the combined integration for these two quartets was, as expected, for four protons. The relative ratios of these two quartets were correlated to the equilibrium ratios of structure **7a–d** and **8a–d** in solution. The results (given in Table III) indicate that in the equilibrium solutions of these compounds, the cyclic form (**7a–d**) predominates. This was also consistent with the ir data for these compounds mentioned earlier.

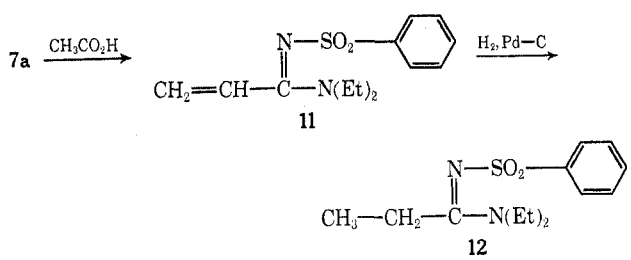
Structure Proof.—Theoretically, the addition of benzenesulfonyl azides to ynamines can occur in two ways, giving compounds of the type of **10a** and **10b**.



10a

10b

However, considering the most important resonance reference structures of the sulfonyl azides[10] and the ynamines,[8] the structure **10a** should be preferred over **10b**. This preferred mode of addition is also consistent with the known 1,3 cycloadditions to vinyl ethers and enamines.[11–13] In order to further substantiate the above theoretical considerations, a chemical structure proof of one of the reaction products was undertaken. Thus, 1-benzenesulfonyl-4-methyl-5-*N,N*-diethylamino-1,2,3-triazole (**7a**) was treated with glacial acetic acid to yield *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**11**) in 70% yield. The structure of the amidine **11** was proved by elemental (C, H, N) analysis and spectroscopic (nmr and ir) data. Catalytic hydrogenation of **11** afforded *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**12**) in almost quantitative yield. The structure of compound **12** was proved by elemental analysis, spectroscopic (nmr and ir) data and



11

12

an independent synthesis which was accomplished by the method of Pinner.[14] This involved treating propionitrile with equivalent amounts of absolute ethanol and hydrogen chloride gas at 0°. The resulting ethyl propionimidate hydrochloride **13** was treated with an excess of diethylamine to yield *N,N*-diethylaminopropionamidine hydrochloride (**14**). Treatment of **14**, as free base, with benzenesulfonyl chloride in the presence of sodium hydroxide afforded *N,N*-diethylamino-*N*-

(9) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y. 1963, p 269.

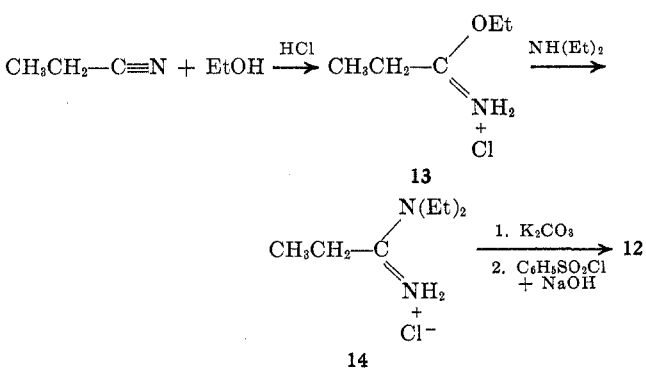
(10) G. L'Abbé, *Chem. Rev.*, **69**, 347 (1969).
(11) D. L. Rector and R. E. Harmon, *J. Org. Chem.*, **31**, 2837 (1966).
(12) G. Caronna and S. Palazzo, *Gazz. Chim. Ital.*, **82**, 292 (1952).
(13) J. E. Franz, M. W. Dietrich, A. Henshall, and C. Osuch, *J. Org. Chem.*, **31**, 2847 (1966).
(14) E. G. Pinner, *Chem. Ber.*, **16**, 1654 (1883).

TABLE I

ANALYTICAL AND NMR DATA OF COMPOUNDS 7a–d

Compd	Mp, °C	Yield, %	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Nmr data (δ)
7a	84–85	62	$C_{13}H_{16}N_4O_2S$	54.41	6.55	18.17	54.74	6.63	18.07	0.8 and 1.12 [two triplets, 6, J = 7 cps, $N(CH_2CH_3)_2$], 2.18 and 2.24 (two singlets, 3, J = 7 cps, CH_3), 3.09 (quartet, 2.7, J = 7 cps, NCH_2 structure **7a**), 3.39 (quartet, 1.3, J = 7 cps, NCH_2 structure **8a**), 7.79 (multiplet, 5, ArH)
7b	54–56	58	$C_{14}H_{20}N_4O_3S$	51.85	6.17	17.60	51.91	6.13	17.45	0.87 and 1.17 [two triplets, 6, J = 7 cps, $N(CH_2CH_3)_2$], 2.24 and 2.3 (two singlets, 3, CH_3), 3.05 (quartet, 3.42, J = 7 cps, NCH_2 structure **7b**), 3.39 (quartet, 0.58, J = 7 cps, NCH_2 structure **8b**), 4.1 (singlet, 3, OCH_3), 8.8 (multiplet 4, ArH)
7c	49–52	65	$C_{14}H_{20}N_4O_2S$	54.51	6.55	18.17	54.74	6.63	18.07	0.83 and 1.13 [two triplets, 6, J = 7 cps, $N(CH_2CH_3)_2$], 2.17 and 2.25 (two singlets, 3, J = 7 cps, CH_3), 3.04 (quartet, 3.2, J = 7 cps, NCH_2 structure **7c**), 3.37 (quartet, 0.8, J = 7 cps, NCH_2 structure **8c**), 4.06 (singlet, 3, OCH_3), 7.5 (multiplet, 4, ArH)
7d	131–132	78	$C_{15}H_{21}N_5O_3S$	51.26	6.03	19.93	51.32	6.11	19.63	1.0 [mulitplet, 6, $N(CH_2CH_3)_2$], 2.25 (multiplet, 3, CH_3), 3.05 (quartet, 2.72, J = 7 cps, NCH_2 structure **7d**), 3.36 (quartet, 1.28, J = 7 cps, NCH_2 structure **8d**), 7.91 (multiplet, 4, ArH), 8.86–9.34 (multiplet, 1, NH)

benzenesulfonylpropionamidine (**12**) which was identical in all respects with the degradation product of the triazole **7a**.



Summary and Conclusion

The existence of ring–chain type of equilibrium between *N*,*N*-diethylamino-1,2,3-triazole and α-diazoamidines has been demonstrated. The mode of addition of benzenesulfonyl azides to ynamines has been proved by degradation methods.

Experimental Section

Melting points were taken on a Thomas–Hoover Unimelt apparatus and are uncorrected. A Beckman IR-8 spectrophotometer was used to determine the ir spectra. The nmr spectra were run using a Varian A-60 spectrometer using tetramethylsilane as internal standard. The elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. The substituted benzenesulfonyl azides **6** were prepared by treating the appropriately substituted benzenesulfonyl chlorides with

TABLE II

ANALYTICAL AND NMR DATA OF COMPOUNDS 8e–f AND 9a–e

Compd	Mp, °C	Yield, %	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Nmr data (δ)
8e	97–98	81	$C_{13}H_{17}N_5O_4S$	46.06	5.01	20.65	46.01	5.11	20.39	1.15 [multiplet, 6, $N(CH_2CH_3)_2$], 2.24 (singlet, 3, CH_3), 3.47 (quartet, 4, J = 7 cps, NCH_2–), 8.5 (multiplet, 4, ArH)
8f	87–88	62	$C_{13}H_{16}Cl_2N_4O_2S$	42.98	4.45	15.4	43.09	4.46	15.16	1.18 [multiplet, 6, $N(CH_2CH_3)_2$], 2.20 (singlet, 3, CH_3), 3.47 (quartet, 4, J = 7 cps, NCH_2–), 7.90 (multiplet, 3, ArH)
9a	95–96	79	$C_{17}H_{18}N_4O_3S$	56.96	5.06	8.95	56.89	5.01	8.63	3.0 [singlet, 6, $N(CH_3)_2$], 3.75 (singlet, 3, OCH_3), 6.6–7.8 (multiplet, 9, ArH)
9b	106–107	70	$C_{16}H_{15}N_5O_4S$	56.48	4.02	18.76	56.20	4.10	18.48	3.1 [singlet, 3, $N(CH_3)_2$], 6.7–8.1 (multiplet, 9 ArH)
9c	102–103	65	$C_{16}H_{15}BrN_4O_2S$	47.19	3.68	13.75	46.93	3.82	13.35	3.0 [singlet, 6, $N(CH_3)_2$], 6.7–7.8 (multiplet, 9, ArH)
9d	104–105	78	$C_{16}H_{15}N_5O_4S$	51.48	4.02	18.76	51.44	4.06	18.51	3.1 [singlet, 6, $N(CH_3)_2$], 6.7–8.2 (multiplet, 9, ArH)
9e	112–113	83	$C_{16}H_{14}Cl_2N_4O_2S$	48.38	3.52	14.10	48.09	3.83	13.98	3.1 [singlet, 6, $N(CH_3)_2$], 6.7–8.1 (multiplet, 8, ArH)

TABLE III

EQUILIBRIUM RATIOS OF COMPOUNDS 7a–d AND 8a–d IN $CDCl_3$ SOLUTION AS CALCULATED FROM THEIR NMR SPECTRA DETERMINED AT 40°[a]

Compd (%)	Compd (%)
7a (67)	**8a** (33)
7b (85)	**8b** (15)
7c (80)	**8c** (20)
7d (68)	**8d** (32)

[a] In crystalline form all these compounds exist only in the 1,2,3-triazole form **7a–d**. These equilibrium ratios were found to be independent of temperature.

sodium azide according to the method of Leffler and Tusno.[15] *N,N*-Diethylaminoprop-1-yne (**3**) was obtained from Fluka AG Chemische Fabrik, Switzerland, whereas *N,N*-dimethylaminophenylacetylene (**4**) was prepared by treating 1-chloro-2-phenylacetylene with trimethylamine according to the procedure of Fuks and Viehe.[16]

General Procedure for the Reaction of Benzenesulfonyl Azides 6 with the Ynamine 3.—A solution of the sulfonyl azide **6** (0.01 mole), in THF (10 ml) was added to a solution of the ynamine **3** (0.01 mol) in THF (5 ml) at −78° (cooled in Dry Ice–acetone bath) over a period of 1 hr. The solution was then allowed to warm to room temperature and filtered through anhydrous alumina, and the solvent was removed by evaporation under reduced pressure. The resulting solid (or oil) was crystallized from ether–petroleum ether (bp 30–60°) to afford the appropriate triazole (**7a–d**) or α-diazoamidine (**8e–f**).

General Procedure for the Reaction of Benzenesulfonyl Azides 6 with the Ynamine 4.—A solution of the azide **6** (1.4 mmol) in THF (10 ml) was added dropwise to a constantly stirred solution of the ynamine **4** (1.4 mmol) in THF (10 ml) at 0°. The reaction mixture was stirred at room temperature for about 1 hr and the solvent was removed under vacuum. The resulting brown-orange oil was crystallized from anhydrous ether to give the α-diazoamidines **9a–e**.

The melting points, yields, and elemental analyses of compounds **7a–d**, **8e–f**, and **9a–e** are recorded in Tables I and II.

Reaction of 7a with Acetic Acid.—When 1.5 g (0.00564 mol) of 1-benzenesulfonyl-4-methyl-5-*N,N*-diethylamino-1,2,3-triazole (**7a**) was treated with 5 ml of glacial acetic acid, the solution turned yellow, and it soon started to effervesce. After the yellow color had disappeared, the excess acetic acid was removed under pressure. The clear oil that remained was treated with an excess of saturated $NaHCO_3$ solution and extracted with two 10-ml portions of $CHCl_3$. The organic layer was dried (Na_2SO_4) and filtered, and the solvent was removed under reduced pressure to yield 1.09 g (73.5%) of a white solid which was recrystallized three times from ether to give an analytical sample of *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**11**): mp 85.5–86.5; nmr ($CHCl_3$-*d*) δ 1.13 (t, 6, J = 7 cps, CH_3), 3.47 q, 4, J = 7 cps, CH_2), 5.30–6.89 (m, 3, vinyl hydrogens), 7.68 (m, 5, ArH).

Anal. Calcd for $C_{13}H_{18}N_2SO_2$: C, 58.61; H, 6.82; N, 10.52. Found: C, 58.39; H, 6.84; N, 10.47.

Hydrogenation of 11.—To a solution of 0.201 g (0.0075 mol) of **11** in 10 ml of ethyl acetate was added 0.2 g of 10% palladium on carbon. The solution was hydrogenated at atmospheric pressure and room temperature. The hydrogen uptake was 0.0076 mol and appeared to be complete at the end of 10 min. The solution was filtered and the solvent removed under reduced pressure to give a quantitative yield (0.203 g) of *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**12**), mp 94–95°.

The analytical sample was obtained by three recrystallizations from ether: mp 95.5–96.5°; nmr ($CHCl_3$-*d*) δ 1.18 (m, 9, CH_3), 3.18 (m, 6, CH_2), 7.66 (m, 5, ArH).

Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.23; H, 7.53; N, 10.45. Found: C, 58.22; N, 7.46; N, 10.22.

The Synthesis of *N,N*-Diethylamino-*N*-benzenesulfonylpropionamidine (12).—This compound was prepared according to the method of Pinner.[14] Equivalent amounts (0.1 mol) of absolute ethanol, propionitrile, and dry hydrogen chloride gas were allowed to react at 0°. After standing overnight, ethyl propionamidate hydrochloride (**13**) crystallized out from the solution. This was treated with an excess of diethylamine to give the *N,N*-diethylaminopropionamidine hydrochloride (**14**) which was then converted to the free amidine by treatment with 33%

(15) J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, **28**, 902 (1963).

(16) R. Fuks and H. G. Viehe (private communication), *Chem. Ber.*, in press.

K_2CO_3 (aqueous). The amidine was then distilled, collecting the fraction between 179 and 181° (lit.[14] bp 181°).

To 1 g (0.0078 mol) of *N,N*-diethylaminopropionamidine was added 2.74 g (0.0156 mol) of benzenesulfonyl chloride and 10 ml of sodium hydroxide. The reaction mixture was heated on a steam bath for 5 min and extracted with chloroform. The chloroform layer was dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The resulting white solid was recrystallized from ether three times to give the analytical sample of *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**12**): mp 95.5–96.5°; nmr ($CHCl_3$-*d*) δ 1.18 (m, 9, CH_3), 3.18 (m, 6, CH_2), 7.66 (m, 5, ArH).

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.

Registry No.—**7a**, 25866-46-0; **7b**, 25866-47-1; **7c**, 25866-48-2; **7d**, 25907-88-4; **8e**, 25866-49-3; **8f**, 25907-89-5; **9a**, 25907-90-8; **9b**, 25907-91-9; **9c**, 25866-50-6; **9d**, 25957-51-1; **9e**, 25866-51-7; **11**, 25866-52-8; **12**, 25866-53-9.

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1,2,4-Triazoles. XXIV. Isomerization of *s*-Triazolo[4,3-*c*]quinazoline Derivatives[1]

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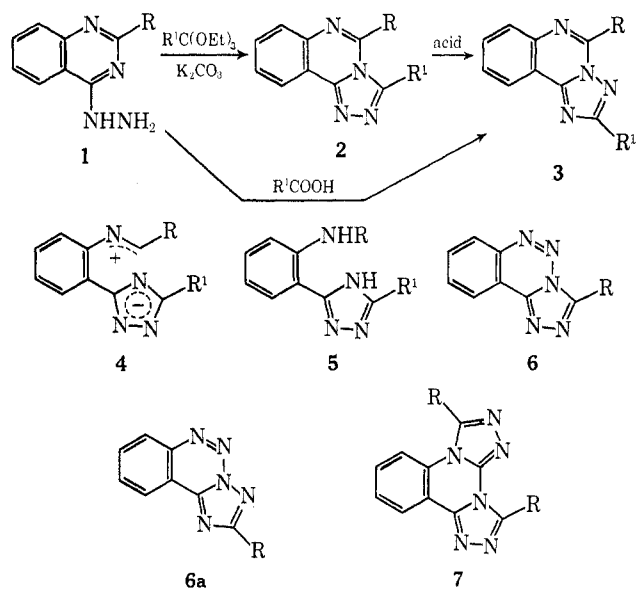
s-Triazolo[4,3-*c*]quinazolines, under the influence of acid or heat, underwent an extremely facile isomerization to *s*-triazolo[1,5-*c*]quinazolines. With alkali, ring opening occurred to 3-(2-aminophenyl)-*s*-triazoles which, with nitrous acid, gave the *s*-triazolo[4,3-*c*][1,2,3]benzotriazine system. Reduction of *s*-triazolo[1,5-*c*]quinazolines with sodium borohydride occurred at the 5,6 bond. Cyclization of 2,4-dihydrazinoquinazoline with ortho esters yielded bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazolines.

Isomerization in ring-fused *s*-triazoles induced by acid, base, or heat has been reported for several of these ring systems.[2] A particularly facile isomerization was observed with derivatives of the *s*-triazolo[4,3-*a*]-pyrimidine[3a] and *s*-triazolo[4,3-*c*]pyrimidine[3b] systems, and we now report an even more facile isomerization of the *s*-triazolo[4,3-*c*]quinazoline system to the *s*-triazolo[1,5-*c*]quinazoline system.

The synthesis of a fused *s*-triazole in which the 3,4 side of the *s*-triazole moiety is involved in the fusion is possible from a suitable 2-heterylhydrazine and carboxylic acids or ortho esters.[4] Thus, reaction of 4-quinazolylhydrazine (**1**, R = H) with aliphatic acids or ortho esters should give 3-substituted *s*-triazolo[4,3-*c*]quinazolines (**2**). We have now found that reaction of the hydrazine (**1**) with aliphatic acids always yielded the *s*-triazolo[1,5-*c*]quinazolines (**3**) by an extremely facile *in situ* rearrangement of the [4,3-*c*] system (**2**). This rearrangement could also be effected by gentle warming of the isomer **2** with carboxylic acids or by heating above the melting point.

It was possible to obtain the *s*-triazolo[4,3-*c*]quinazoline system (**2**) from the hydrazine and ortho esters as long as the reaction was carried out in the presence of potassium carbonate (Table I). Omission of the potassium carbonate always resulted in a mixture of the two isomers being formed, no doubt owing to traces of the appropriate acid (detected by glc) in the redistilled ortho esters. With triethyl orthopropionate, however, isomerization of the expected [4,3-*c*] system did not occur over a 16-hr reaction period, but the isomerization was essentially complete over a 48-hr period in the absence of potassium carbonate.



Substituents in the 2 position of the quinazoline nucleus exerted a predictable effect on the isomerization. 2-Methylquinazolin-4-ylhydrazine (**1**, R = CH_3) and ortho esters–potassium carbonate should yield 5-methyl-*s*-triazolo[4,3-*c*]quinazolines (**2**, R = CH_3), but in all cases isomerization occurred with such ease that only mixtures of the two isomers could be isolated. On the other hand, 2-phenylquinazolin-4-ylhydrazine (**1**, R = Ph) underwent ring closure with ortho esters–potassium carbonate to 5-phenyl-*s*-triazolo[4,3-*c*]quinazolines (**2**,

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