

Anal. Calcd. for $C_{13}H_8O_4S$: C, 58.06; H, 3.22; S, 12.91. Found: C, 58.02; H, 3.30; S, 12.97.

Reduction of juglone-2-thioglycolic acid and lactonization of the product. The reduction of juglone-2-thioglycolic acid was carried out in the same manner as reduction of the 3-isomer, using 87 mg. of catalyst and a solution of 355 mg. of the quinone, in ca. 125 ml. of dioxane. Lactonization was effected by adding a solution of 288 mg. of *N,N'*-dicyclohexylcarbodiimide in 15 ml. of dioxane to the hydrogenated product under nitrogen. The reaction mixture was worked up in the same way as the 3-isomer, yielding 0.35 g. of a brown powder as the crude product. No crystalline material was obtained on attempted crystallizations from various solvents or chromatography on silicic acid. On sublimation at 160° (ca. 0.1 mm.) for a week, about 15% of the crude material was obtained as a very light tan amorphous solid, λ_{\max}^{KBr} 5.80, 6.22, 6.35, 6.93, 7.21, 7.30, 7.58, 8.08, 8.20, 8.75, 8.92, 9.07, 9.50, 10.16, 11.06, 11.24, 12.10, 12.20, 12.35, 13.20 μ . A second sublimation did not change the infrared spectrum.

Determination of the effect of compounds on the acidity of boric acid. One part (volume) of a 0.05*M* solution of the compound to be tested in tetrahydrofuran was added to one part of 0.5*M* aqueous boric acid solution, and the pH was measured on a Beckman pH meter, Model G. The pH of a blank consisting of one part tetrahydrofuran and one part 0.5*M* boric acid was 4.8–5.2 depending on the sample of tetrahydrofuran used.

A solution of 12.5 mg. (0.05 mmoles) of analytically pure compound D in 1 ml. of tetrahydrofuran was added to 1 ml. of 0.5*M* boric acid. The pH decreased from 4.8 to 3.5 in an hour. After the mixture had stood in an open cup for 2.5 hr., bronze crystals, m.p. 190–193° (dec.), λ_{\max} 235 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 71), 252 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 36), 322 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 14), 334 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 15), 350 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 14), 410 $m\mu$ ($E_{1\text{cm}}^{1\%}$ 3.6) had separated.

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Reactions of Sodium Phenylacetylide and Sodium Alkoxide with Tosyl and Mesyl Azides¹

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Six examples of nitrogen singly bound to *sp* carbon have been described in the literature.²

(1) This research was supported by the Office of Ordnance Research, U. S. Army, under Contract No. DA-01-009-ORD-428, a National Institutes of Health Grant No. H-2295, and by a grant from Eli Lilly & Co. Presented at the 131st National Meeting of the American Chemical Society, Miami, April 7–12, 1957.

(2) The observation that 1-aminoacetylenes are probable intermediates in the transformation of substituted propionic acid amides into fatty acid nitriles by the action of alkaline hypohalite [I. J. Rinkes, *Rec. trav. Chim.*, **46**, 268 (1927)] renders unlikely the claim that a 1-aminoacetylene was isolated upon reduction of a 1-nitroacetylene [F. Krafft and G.

Current interest in the azidoacetylene unit recognized the possibility for further demonstration of this single bond and for making observations on the properties of this unknown unit.

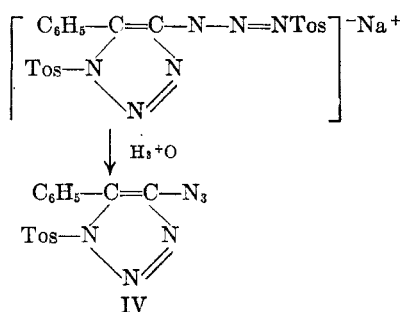
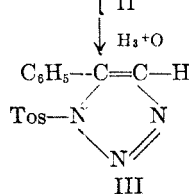
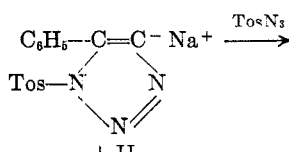
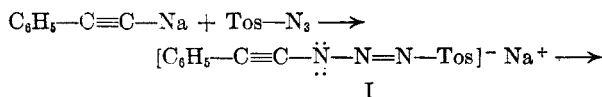
Initial attempts to prepare phenylazidoacetylene from either phenyliodo- or phenylbromo acetylene and sodium azide were unsuccessful. Attention was then directed to adducts obtained from sulfonyl azides and sodium phenylacetylide since aryl azides had resulted from hydrolysis of triazene salts obtained from aromatic organometallic reagents and tosyl azide.³ The adduct (I) from sodium phenylacetylide and tosyl azide apparently underwent ring-closure isomerization with the formation of a sodium salt (II) of 1-tosyl-5-phenyltriazole (no triple bond absorption near 4.6 to 4.8 μ). Upon hydrolysis linear compounds were not isolated. With equimolar amounts of sodium phenylacetylide and tosyl azide or with an excess of sodium phenylacetylide, a product was obtained to which the structure of 1-tosyl-5-phenyltriazole (III) was assigned,⁴ whereas an excess of tosyl

Heizmann, *Ber.*, **33**, 3586 (1900)]. Trimethylethynylammonium hydroxide [(J. Bode, *Ann.*, **267**, 268 (1890)] and cyanogen azide [A. Angeli, *Atti accad. Lincei*, [6], **5**, 732 (1927); *Chem. Abstr.*, **21**, 3603 (1927)] have been reported and nitroynitrile oxide has been considered as an intermediate [R. A. Barnes, "Isoxazoles" in R. C. Elderfield, *Heterocyclic Compounds*, John Wiley, New York, 1957, Vol. **5**, p. 459]. An adduct, $[Ar=N=N=N=C=C=N=N=N=Ar]^{-(MgX)_2^{++}}$, obtained from the acetylenic Grignard reagent and aryl azide [H. Kleinfeller and G. Bonig, *J. prakt. Chem.*, **132**, 175 (1932)] contained an eight atom system in conjugation with two aromatic rings over which the π electron density of the doubly charged anion could be spread. Ring closure isomerization also occurred and upon hydrolysis a substituted triazole was obtained along with a bis-acetylenic triazene or its tautomer, $Ar-N=N-N=CH-CH=N-N=N-Ar$.

(3) P. A. S. Smith, private communication. See J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 40 (1954). In contrast hydrolysis of the triazene salt obtained from a sulfonyl azide and the lithium salt of cyclopentadiene led to the formation of diazocyclopentadiene and a sulfonamide [W. von E. Doering and C. H. Depuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953)], a reversal of earlier observations that diazonium salts and sulfonamides reacted with the formation of the expected triazene salt [P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921); P. K. Dutt, *J. Chem. Soc.*, **125**, 1463 (1924); A. Key and P. K. Dutt, *J. Chem. Soc.*, 2035 (1928)].

(4) In 1937 it was claimed [S. G. Fridman and N. N. Lisovskaja, *Zapiski Inst. Khim., Akad. Nauk Ukr. R.S.R., Inst. Khim.*, **6**, 353 (1940); *Chem. Abstr.*, **35**, 2470 (1941)] that sodium phenylacetylide reacted with β -chloroethyl azide with the formation of 4-vinyl-5-phenyltriazole. This required initial attack by the acetylide anion upon carbon, elimination of hydrazoic acid and then recombination presumably by a Diels-Alder reaction to form the disubstituted triazole. The structure proof consisted in oxidation with facile decarboxylation to the known 4-phenyltriazole. Since triazole-4-carboxylic acid did not decarboxylate at temperatures under 210° [O. Baltzer and H. v. Pechmann, *Ann.*, **262**, 317 (1891); O. Dimroth, *Ber.*, **35**, 1044 (1902)], the assignment of the above product as 1-vinyl-5-phenyltriazole is now suggested. Its formation would require initial attack by acetylide ion upon the terminal azido nitrogen, ring-closure isomerization, and hydrolysis. Now, oxidation

azide apparently led to the formation of 1-tosyl-4-azido-5-phenyltriazole (IV) (azide absorption at 4.68μ). Attempts to prepare either III or its isomer, 1-tosyl-4-phenyltriazole, by a Diels-Alder reaction between tosyl azide and phenylacetylene were unsuccessful and it was not possible to obtain 4-phenyltriazole from III since conditions required for hydrolysis were sufficient for rupturing the triazole ring.

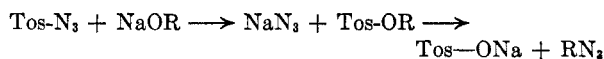


Phenylmethanesulfonyl⁵ and now methanesulfonyl (mesyl) azides are the known examples of alkanesulfonyl azides. Combination of mesyl azide and sodium phenylacetylide led to intractable tars. Formation of a sodium salt of mesyl azide using sodium metal in ether suggested that attack upon mesyl azide by sodium phenyl acetylide occurred at carbon as well as nitrogen. A strong odor of a volatile azide (presumably methyl azide) was detected during the reaction between sodium methoxide and either mesyl azide or tosyl azide in methanol. In the latter case sodium tosylate was isolated in good yield. Apparently an initial reaction afforded sodium azide and methyl tosylate which subsequently combined to give sodium tosylate and methyl azide. Isolation of *n*-butyl tosylate

would bring about the formation of 1-carboxy-5-phenyltriazole, a carbamic acid derivative which would be expected to undergo spontaneous decarboxylation with the formation of 4-phenyltriazole.

(5) T. Curtius and F. W. Haas, *J. prakt. Chem.*, **102**, 85 (1921).

and sodium azide from tosyl azide and sodium butoxide suspended in ether confirmed the intermediates. Alkylation of sodium azide by alkyl tosylates has been recorded;^{6,7} presumably it did not occur in this case because of the insolubility of sodium azide in ether.



EXPERIMENTAL^{8,9}

Addition of sodium phenylacetylide to an excess of *p*-toluenesulfonylazide. Sodium phenylacetylide was prepared from 5.1 g. (0.05 mole) of phenylacetylene in 25 ml. of dry ethyl ether to which 1.15 g. (0.05 mole) of sodium was added slowly. The solution was stirred for 24 hr. A white, ether insoluble solid was separated by filtration and added to 25 ml. of dry ether. This slurry of sodium phenylacetylide in ether was added slowly to a stirred solution of 19.7 g. (0.10 mole) of *p*-toluenesulfonylazide in 50 ml. of dry ether at a rate which maintained an ether reflux. As the reaction mixture was stirred for 24 hr. a brown solid adduct separated, weight 15.2 g. (58%). Infrared absorption (cm.^{-1}) from a potassium bromide disk was observed at 3425 (m), 3003 (w), 1597 (w), 1490 (w), 1466 (w), 1443 (w), 1393 (w), 1258 (m), 1198 (s), 1131 (s), 1082 (m), 1046 (s), 1013 (s), 995 (m), 975 (s), 813 (s), 766 (w), 706 (m), 692 (s).

From 5.0 g. of the adduct treated with 10 ml. of hot glacial acetic acid a light yellow solid was obtained upon cooling and was recrystallized twice from glacial acetic acid. The product was assigned the structure of 1-tosyl-4-azido-5-phenyltriazole (IV), 0.52 g. (16%), m.p. 170-171° (dec.). Infrared absorption (cm.^{-1}) from a potassium bromide disk was observed at 3425 (w), 3030 (w), 2137 (s) (azide), 1590 (m), 1553 (w), 1527 (w), 1502 (s), 1466 (s), 1445 (s), 1397 (s), 1333 (w), 1309 (m), 1295 (s), 1277 (m), 1190 (s), 1179 (s), 1163 (s), 1118 (w), 1087 (m), 1021 (w), 953 (m), 920 (w), 820 (s), 775 (m), 720 (m), 702 (m), 687 (s), 684 (s), 671 (s). An absorption maximum at $296\text{ m}\mu$ (ϵ 31.48) was attributed to the azido group.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_6\text{SO}_2$: C, 52.93; H, 3.55; N, 24.70. Found: C, 53.19; H, 3.63; N, 23.56.

Addition of *p*-toluenesulfonylazide to an excess sodium phenylacetylide. To 12.5 g. (0.1 mole) of sodium phenylacetylide in 50 ml. of ether, 9.85 g. (0.05 mole) of *p*-toluenesulfonylazide in 50 ml. of ether was added dropwise with stirring and external cooling as the color gradually turned dark brown. The solution was stirred for 12 hr. and saturated with dry hydrogen chloride. Removal of ether left a viscous oil which solidified upon standing for several days. It recrystallized from 95% ethanol as colorless needles of 1-tosyl-5-phenyltriazole monohydrate, 1.5 g. (9.5%), m.p. 171° (dec.).

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_3\text{SO}_3$: C, 56.78; H, 4.76; N, 13.24. Found: C, 57.00; H, 5.00; N, 14.04.

Mesyl azide. To a well stirred solution of 11.4 g. (0.10 mole) of methanesulfonylchloride in 40 ml. of absolute methanol was added over a period of one hour in half gram portions,

(6) L. Horner and A. Gross, *Ann.*, **591**, 117 (1955).

(7) R. H. Wiley and J. Moffat, *J. Org. Chem.*, **22**, 995 (1957).

(8) Microanalyses by Micro-Tech Laboratories, Skokie, Ill., and Alfred Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut, Mülheim (Ruhr), Germany.

(9) We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory for infrared and ultraviolet absorption data.

8.5 g. (0.13 mole) of solid sodium azide. The solution was stirred for 30 min., filtered, and methanol removed *in vacuo*. Mesityl azide distilled at 56° (0.5 mm.), 7.4 g. (61%). It was thermally unstable above 100° and was not attacked by cold concentrated sulfuric acid whereas rapid decomposition occurred in this solution above 100°. Elemental analysis was not attempted; nitrogen and sulfur were detected by sodium fusion analysis. Infrared absorption (cm.^{-1}) from a four per cent chloroform solution was observed at 4310 (w), 4149 (w), 3922 (w), 3546 (w), 3279 (w), 3021 (w), 2924 (w), 2500 (w), 2336 (m), 2137 (s) (azide), 1613 (w), 1449 (w), 1406 (m), 1361 (s), 1326 (s), 1156 (s), 1095 (w), 1003 (m), 966 (s).

For methanesulfonyl chloride, $d_{20} = 1.4805$; $n_D^{20} 1.4464$; M_R (obs.) 20.65. This allowed an assignment of 14.68 as the M_R contribution from the methanesulfonyl group. For methane-sulfonyl azide, $d_{20} = 1.4024$; $n_D^{20} 1.4532$; M_R (calcd.) 23.58, M_R (obs.) 23.35.

Reaction of *p*-toluenesulfonylazide with sodium alkoxide. To a solution of 2.3 g. (0.10 mole) of sodium in 160 ml. of absolute methanol, 19.7 g. (0.10 mole) of tosyl azide was slowly added with stirring. The mixture was heated at reflux temperature for 24 hr. as an azide odor was detected and colorless crystals of sodium tosylate, 19.0 g. (98%), separated. From 1.0 g. of this salt suspended in 5 ml. of absolute ether saturated with dry hydrogen chloride a colorless precipitate of *p*-toluenesulfonic acid was obtained, m.p. 104°¹⁰ after recrystallization from benzene. The m.p. of its *o*-toluidine salt was 190°.¹¹

The reaction was repeated with 14.4 g. (0.15 mole) of sodium butoxide in 200 ml. refluxing ether. A solution of 19.7 g. (0.10 mole) of tosyl azide in 50 ml. of ether was added dropwise with stirring. The mixture was held at reflux temperature for 12 hr., cooled, and filtered. The solid, 5.3 g. (81.5%), was identified as sodium azide by a positive azide test with ferric chloride solution. An oil residue, 10.4 g. (46%), from the ether layer was dried over anhydrous sodium sulfate and identified as *n*-butyl tosylate, b.p. 100° (0.2 mm.)¹² and $n_D^{25} 1.5042$.¹² After storage in the refrigerator in a stoppered bottle for four weeks redistillation of 8.0 g. was attempted at 0.2 mm. When the heating bath was at about 70° a violent explosion occurred. The ester apparently had become contaminated with the corresponding acid since a fine white precipitate was noted in the distillation flask just prior to the explosion.¹³ A portion of *n*-butyl tosylate was hydrolyzed to *p*-toluenesulfonic acid, m.p. and mixture m.p. 106–107°.¹⁰

Reaction of methyl tosylate with sodium azide in methanol. To a solution of 18.6 g. (0.1 mole) of methyl tosylate in 160 ml. of absolute methanol was added 6.5 g. (0.1 mole) of solid sodium azide. With efficient stirring the reaction mixture was refluxed for 24 hr. during which time an azide odor was detected. Solid sodium tosylate, 15.4 g. (80%), was separated from the cold mixture and identified by the m.p. and mixture m.p. 104° for the corresponding acid monohydrate and m.p. and mixture m.p. 190° for its *o*-toluidine salt.

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(10) K. H. Slotta and W. Franke, *Ber.*, **63**, 678 (1930).

(11) N. D. Cheronis and J. B. Entrikin, *Semi-micro Qualitative Organic Analysis*, T. Y. Crowell, New York, 1947, pp. 442–444.

(12) H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47**, 518 (1925) reported b.p. 163–165° (3.0 mm.) and $n_D^{20} 1.5050$. K. Slotta and W. Franke¹⁰ reported b.p. 146° (1.0 mm.) and 191–192° (17 mm.).

(13) H. Gilman and N. J. Beaber¹² reported that decomposition rapidly commenced after this precipitation became evident. They found that *sec*-butyltosylate decomposed without distilling.

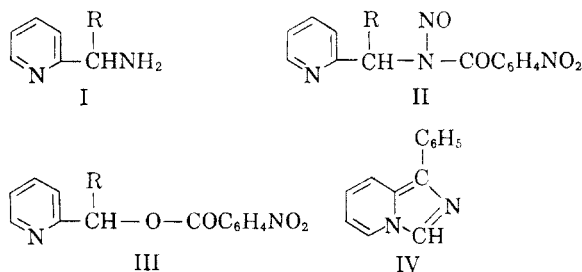
Diazotization of 2-Pyridylmethyl Amine¹

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Received December 6, 1957

An oxidation was observed upon attempted diazotization of 2-pyridylmethyl amine (I, R = H).^{3,4} The pyrolysis of *N*-*p*-nitrobenzoyl-*N*-nitroso-2-pyridylmethyl amine (II, R=H) into 2-pyridylmethyl *p*-nitrobenzoate (III, R=H) has now been realized and offers a more successful method for the transformation of this amine into the corresponding carbinol. An *N*-nitroso derivative of *N*-benzoyl phenyl(2-pyridyl)methyl amine could not be obtained.

Catalytic reduction of α -cyanopyridine and the oxime of 2-benzoylpyridine are efficient methods for the synthesis of 2-pyridylmethyl amine and phenyl(2-pyridyl)methyl amine, respectively. A Leuckhart reduction of 2-benzoylpyridine apparently occurs with cyclization and the formation of a product to which the structure of 1-phenyl-2:3a-diazaindene (IV) has been assigned.⁵ Attempted reduction of phenyl 2-pyridyl ketoxime with zinc and acetic acid is unsuccessful.⁶



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(2) Texas Eastman Fellow, 1955–1956.

(3) J. H. Boyer, R. Borgers, and L. T. Wolford, *J. Am. Chem. Soc.*, **79**, 678 (1957).

(4) C. Niemann, R. N. Lewis, and J. T. Hays, *J. Am. Chem. Soc.*, **64**, 1679 (1942) reported a successful diazotization of 2-pyridylmethyl amine in the presence of concentrated hydrochloric acid.

(5) Cyclization during Leuckart reductions of aromatic acylloins was found to be general and produced 4,5-diaryl-imidazoles [A. Novelli, *Anales Assoc. quim. Arg.*, **27**, 161 (1939); *Chem. Abstr.*, **34**, 1659 (1940)]. W. H. Davies and A. T. Rogers, *J. Chem. Soc.*, 126 (1944). Upon heating α -hydrazinopyridine with formic acid a similar ring closure brought about the formation of 1,2,4-pyridotriazole [R. G. Fargher and R. Furness, *J. Chem. Soc.*, **107**, 688 (1915); see reference 4]. In a similar reaction, 2:3a-diazaindene was prepared by cyclization with dehydration using phosphorus chloride of *N*-formyl 2-pyridylmethyl amine [J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 2834 (1955)].

(6) F. B. LaForge, *J. Am. Chem. Soc.*, **50**, 2484 (1928) successfully reduced phenyl 3-pyridyl ketoxime by this method.