

sition to that obtained at the end of the pyrolysis. Considerable amounts of tar-like substances remained in the reaction flask after the pyrolysis of the *p*-toluenesulfonate, but no attempt was made to identify the residue.

Acetolysis of cyclohexanemethyl *p*-toluenesulfonate was re-investigated with some modifications (in an open system at 115° for 50 hr., instead of in a sealed ampoule at 110° for 60 hr.). In a 500-ml., round-bottomed flask equipped with a reflux condenser, the top of which was connected to a trap immersed in Dry Ice-methanol bath, there were placed the *p*-toluenesulfonate (26.8 g., 0.1 mole), anhydrous sodium acetate (9 g., 0.11 mole), and glacial acetic acid (250 ml.). The flask was heated for 50 hr. in an oil bath at 115°, then was cooled to 0–5°. The contents was neutralized with dilute sodium hydroxide solution and extracted with ether. The trap and condenser were rinsed with ether. The combined ether extracts were dried over magnesium sulfate, and distilled, giving 1.5 g. of a low-boiling fraction (b.p. 90–112°), and 8.8 g. of a high-boiling fraction [55° (20 mm.) to 85° (15 mm.)]. No attempt was made to identify the residue.

Product Analysis.—Gas chromatographic analysis was carried out using 500 × 0.35 cm. columns packed with 80–100-mesh Celite which was coated with the appropriate stationary phase. The stationary phases employed were (A) 30% (w./w.) of a 40% solution of silver nitrate in tetraethylene glycol; (B) 25% (w./w.) of octyl phthalate; and (C) 30% (w./w.) of Apiezon grease L. Columns A and B were used to analyze hydrocarbons at 60 and 100°, respectively. Alcohols and their acetates were analyzed using column C at 150°. Helium outlet flow rates were 45 (A), 55 (B), and 60 (C) cc./min. The relative retention time is the ratio of a retention time of a substance to the retention time of benzene as measured from an air peak. Quantitative analysis was done following the procedure of Messner, *et al.*,²⁵ using benzene as an internal standard.

The n.m.r. spectra were determined at 25° in carbon tetrachloride on a Varian Associates Model V-4311 high-resolution spectrometer operating at 60 Mc. with tetramethylsilane (τ 10.00) as an internal standard. The resonance lines used for structural assignment follow: 1-methylcyclohexene (an incompletely resolved multiplet, τ 4.71, an olefinic proton; an incompletely resolved doublet, 8.40, methyl protons), 3-methylcyclohexene (a complex multiplet, three main lines, τ 4.44, 4.47, and 4.53, olefinic protons; an asymmetrical doublet, 9.00 and 9.11, apparent coupling constant $J = 6.6$ c.p.s., methyl protons), methylenecyclohexane (an incompletely resolved quintet, τ 5.47, terminal methylene protons), cycloheptene (a triplet, τ 4.30, $J = 3.7$ c.p.s., olefinic protons), cyclohexene (a triplet, τ 4.43, $J = 1.5$ c.p.s., olefinic protons), methylcyclohexane (an asymmetrical doublet, τ 9.07 and 9.15, $J = 4.8$ c.p.s., methyl protons), and toluene (a singlet, τ 2.90, ring protons; a singlet, 7.66, methyl protons).

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(25) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

The Reaction of Benzyne with Phenyl Isocyanate

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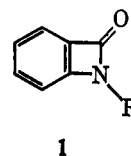
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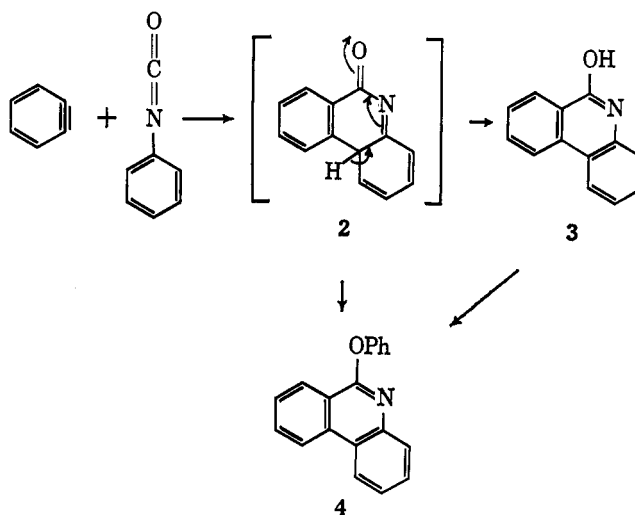
Consideration of the chemistry of benzyne² and especially reactions in which benzyne has undergone

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cyclic addition with an olefin³ suggested that benzazetidiones⁴ (1) might be produced by the reaction of benzyne with isocyanates.⁵



However, when diazotized anthranilic acid⁶ was decomposed thermally in benzene in the presence of excess phenyl isocyanate, no product with properties attributable to 1 ($R = Ph$) was isolated. Chromatography of the complex reaction mixture on Florisil resulted in the isolation of phenanthridinone⁷ (3) and 9-phenoxyphenanthridine⁸ (4) in low yields. The formation of 3 and 4 is most simply formulated as involving an initially formed Diels–Alder adduct (2).⁹ A proton shift restores aromaticity to the system to produce phenanthridinone (3). Reaction of 3 with a second molecule of benzyne accounts for the formation of 9-phenoxyphenanthridine (4). Alternately, reaction of benzyne with the Diels–Alder adduct 2 would produce 4 directly.



Phenyl isocyanate dimer,¹⁰ 1,3,5-triphenylbiuret,¹¹ and several fractions containing highly colored, heterogeneous, polar material were isolated. Structure elucidation of this material was not undertaken.

(2) See H. Heaney, *Chem. Rev.*, **62**, 81 (1962); J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

(3) See, for example, H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961); M. E. Kuehne, *ibid.*, **84**, 837 (1962).

(4) A number of benzazetidione structures have been assigned in the early literature; however, modern reviewers have either ignored these reports altogether or viewed them with skepticism: A. H. Cook, *Quart. Rev. (London)*, **2**, 243 (1948); H. T. Clark, J. R. Johnson, and R. Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, pp. 983–984.

(5) Recently isocyanates have been shown to undergo similar ring closures with enamines to form azetidiones: M. Perelman and S. A. Mizsak, *J. Am. Chem. Soc.*, **84**, 4988 (1962); G. Opitz and J. Koch, *Angew. Chem.*, **75**, 167 (1963).

(6) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(7) P. A. S. Smith, *ibid.*, **76**, 431 (1954).

(8) D. H. Hey and T. M. Moynehan, *J. Chem. Soc.*, 1563 (1959).

(9) J. Nieuwenhuis and J. F. Arens [*Rec. trav. chim.*, **76**, 999 (1957)] formulated the reaction of phenyl isocyanate with ethoxyacetylene similarly.

(10) I. C. Kogon, *J. Am. Chem. Soc.*, **76**, 4911 (1956).

(11) I. C. Kogon, *ibid.*, **79**, 2253 (1957).

Experimental^{12,13}

Reaction of Benzene with Phenyl Isocyanate in Benzene.—The combined product resulting from the diazotization of two portions of 2.74 g. (0.04 M total) of anthranilic acid according to the procedure of Stiles, Miller, and Burekhardt⁶ was added to 25 ml. of benzene and 10 ml. (~0.08 M) of phenyl isocyanate. The resulting mixture was stirred mechanically and heated under gentle reflux for 12 hr. The solvent and excess phenyl isocyanate were removed by lyophilization. The residue in approximately 5 ml. of benzene was introduced onto a column (50 cm.) containing 85 g. of Florisil prepared with hexane. Hexane, benzene, ethyl acetate, and methanol were used as elution solvents. The products were eluted from the column in the order mentioned; yields reported are of isolated crystalline material: (A) phenyl isocyanate dimer, 0.029 g., m.p. 168–172° (lit.¹⁰ m.p. 176°); (B) 9-phenoxyphenanthridine (4), 0.424 g., m.p. 110–119° (Recrystallization from ethanol gave needles, m.p. 118–119°. Positive identification was made by comparison of an infrared spectrum with that of an authentic sample.¹⁴ A mixture melting point was undepressed.); (C) 1,3,5-triphenylbiuret, 0.337 g., m.p. 150–151° (lit.¹¹ m.p. 150–151°); (D) phenanthridinone, 0.110 g., m.p. 285–290° with sublimation (An authentic sample¹⁵ exhibited identical infrared spectral and melting point behavior.); (E) A total of 0.249 g. of highly colored, heterogeneous material was eluted with the more polar solvents. This material was not further investigated.

(12) Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 237 recording spectrophotometer. Mass spectra were recorded with a Consolidated Electrodynamics Corp., Type 21-103C mass spectrophotometer. Microanalytical data were supplied by Dr. S. M. Nagy and his associates.

(13) We are indebted to Mr. Heinrich K. Schnoes for the measurement and interpretation of mass spectra of the products. These data greatly simplified the problem of structure elucidation.

(14) We are indebted to Professor D. H. Hey, King's College, London, for a generous sample of authentic 9-phenoxyphenanthridine.

(15) Purchased from Aldrich Chemical Co.

A New Synthesis of 5,10-Dihydrophenazasilines

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The phenazasilines have been shown to have excellent high-temperature stability coupled with antioxidant activity. Their main use has been in the stabilization of polyester lubricants used in high-speed jet engines. An improved synthesis for these compounds was needed.

Previous work in this field was pioneered by Gilman and co-workers. They prepared 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline by the high-temperature reaction between diphenylsilane and N-ethylphenothiazine.^{1,2} Yields of only 6–7% were thus obtained.

A better method for preparing the phenazasilines was reported soon after by Gilman and Zuech.³ However, the key intermediate, 2,2'-dibromodiphenylamine was obtained by a sophisticated but lengthy synthesis using the Chapman rearrangement.⁴

The new synthesis developed in our laboratory is shown in Scheme I which represents a simpler scheme

- (1) H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957).
- (2) D. Wittenberg, H. A. McNinch, and H. Gilman, *ibid.*, **80**, 5418 (1958).
- (3) H. Gilman and E. A. Zuech, *Chem. Ind.* (London), 1227 (1958).
- (4) E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 786 (1956).

of obtaining these compounds. The key intermediate was the 2,2'-dilithio derivative of N-ethyl-4,4'-dibromodiphenylamine (III) necessary for cyclization with diphenyldichlorosilane to the phenazasiline (IV). This entailed using N-ethyl-2,2',4,4'-tetrabromodiphenylamine (II). The reaction of the latter compound (II) with 2 equiv. of *n*-butyllithium at 0° resulted in halogen-metal interconversion of the 2,2'-bromine atoms without appreciable reaction of the 4,4'-bromine atoms, yielding compound III. Reaction with dichlorodiphenylsilane produced the 2,8-dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV) in yields as high as 85%. The latter compound is converted to 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (V) either by direct catalytic hydrogenation with palladium on carbon in the presence of sodium or potassium acetate or by an interconversion reaction with *n*-butyllithium at 25° (IX) followed by water hydrolysis. If the 2,8-dilithio intermediate is treated with methyl iodide, the 2,8-dimethyl-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (X) is produced.

The use of dimethyldichlorosilane instead of diphenyldichlorosilane yielded 2,8-dibromo-5-ethyl-10,10-dimethyl-5,10-dihydrophenazasiline (XI). Substitution of silicon tetrachloride for diphenyldichlorosilane yielded the 2,2',8,8'-tetrabromo-5,5'-diethyl-10,10-spiro(5,10-dihydrophenazasiline) (VI) which was converted to the debrominated compound (VII) by hydrogenation.

Derivatives based on tin may also be used instead of silicon. Thus, using diphenyltin dichloride instead of diphenyldichlorosilane, we obtain the corresponding tin compound VIII.

This new route to phenazasilines, starting with diphenylamine and involving four relatively easy steps, is accomplished in 40–43% over-all yield. Readily obtained intermediates such as the 2,8-dibromo-5-alkyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV) can be converted to substituted alkyl- and aryl-substituted phenazasilines through the 2,8-dilithio derivative IX. The dibromo compound is obtained pure without the side reactions that occur on bromination of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline as shown by Gilman and Zuech.⁵

A comprehensive account of other recent work in the field of organometallics as high-temperature additives for lubricants was given by Tamborski.⁶ Preparation of the phosphorus analog of these compounds was recently described by the same laboratory.⁷

Experimental⁸

2,2',4,4'-Tetrabromo-N-ethyldiphenylamine (II).—A suspension of 2,2',4,4'-tetrabromodiphenylamine⁹ (48.5 g., 0.1 mole) in dry tetrahydrofuran (250 g.) was treated with 0.104 moles of methylolithium in ether¹⁰ at 20–24°. After distillation of the ether a tetrahydrofuran solution of diethyl sulfate (15.4 g., 0.1

(5) H. Gilman and E. A. Zuech, *J. Org. Chem.*, **26**, 3481 (1961).

(6) C. Tamborski, New York Academy of Sciences, International Symposium on Organometallic Chemistry, June 1964.

(7) G. Baum, H. A. Lloyd, and C. Tamborski, *J. Org. Chem.*, **29**, 3410 (1964).

(8) Melting points and boiling points are uncorrected. Organometallic reactions were run under a blanket of oxygen-free, dry nitrogen. Color Test I for aryllithium, and Color Test II for alkylolithium were applied throughout to determine reaction completion.

(9) A. W. Hoffmann, *Ann.*, **182**, 166 (1872).

(10) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).