steps, which were identical with those described above, yielded acridine-9-d_1 N-oxide (14%), m.p. 168.4–169.0°. The product contained 10.25 (corresponding to 92.3/9) atom % deuterium.

Acetic anhydride and the solvent system of acidified methanol were the same as those used previously.[2]

Rate Measurement.—The procedure followed was identical with that described earlier.[2] Aliquots (2 ml.) of the reaction solution (0.1 *M* acridine N-oxide in acetic anhydride) were quenched by delivery into 50-ml. portions of the methanol–perchloric acid solvent. The spectrophotometric method of analysis was used. All runs were followed to 60–70% completion.

An attempt was made to follow the rate of rearrangement conductometrically.[11] The apparatus was less sophisticated than that used previously[2] and, although k_H/k_D was 1.07 by these data, the absolute rate constants did not correspond well to those determined spectrophotometrically.

Acknowledgment.—We are grateful to the Research Corporation for a Frederick Gardner Cottrell grant which supported this work.

---

[11] We are indebted to Dr. R. C. Petersen of the Sprague Electric Co. for assistance with these measurements.

Reaction of Benzyne with Nitrosobenzene. A New Route to the Carbazole Ring System

GÜNTER W. STEINHOFF AND MALCOLM C. HENRY

U. S. Army Natick Laboratories, Natick, Massachusetts

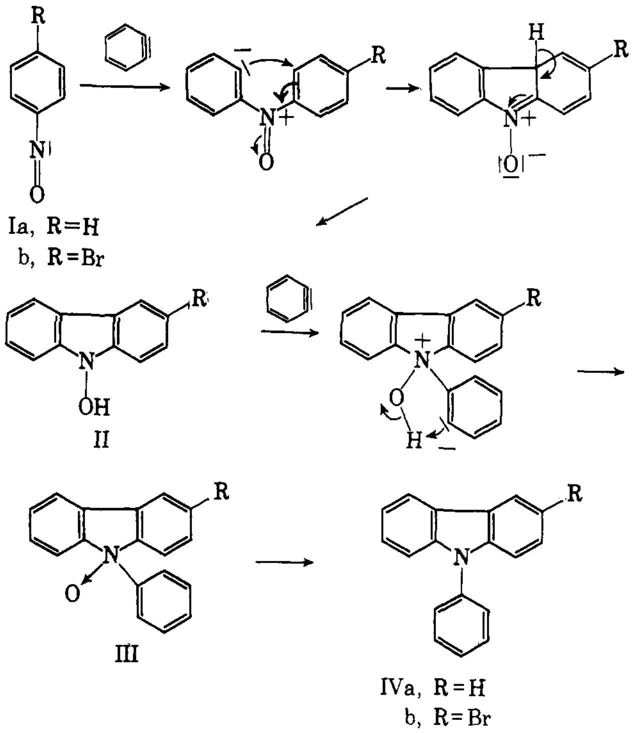
Received May 8, 1964

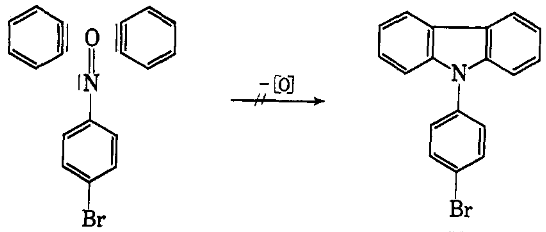
Nitrosobenzene has been reported to react as a dienophile.[1] It has also been noted to react with diphenylketene,[2] substituted ethylenes,[3] and azomethines[4] to form four-membered rings. We wish to report that the reaction of nitrosobenzene (Ia) with benzyne results in the formation of the carbazole ring system. Generation of benzyne by the decomposition of 4,5-benzothiadiazol 1,1-dioxide[5,6] in tetrahydrofuran in the presence of nitrosobenzene gave a 45% yield of N-phenylcarbazole (IVa).

It appears likely that, because of the electrophilic nature of benzyne,[7] the reaction path involves initial coordination of the nitrogen lone pair of electrons with benzyne. The second step is the formation of the hydroxylamine derivative II, which itself reacts with a second molecule of benzyne to yield the N-oxide III. The unstable N-oxide then loses oxygen to give IV (Chart I).

An alternative but less likely route to the carbazole ring system would involve the direct reaction of the nitroso compound with two molecules of benzyne. This mechanism could be excluded when it was found that the product of the analogous reaction of benzyne with *p*-bromonitrosobenzene[8] (Ib) was 3-bromo-N-phenylcarbazole (IVb, 40% yield) instead of the N-(*p*-bromophenyl)carbazole[9] (V) which should have been formed from the direct reaction. As expected, N-phenylcarbazole and its 3-bromo derivative had very similar ultraviolet spectra.

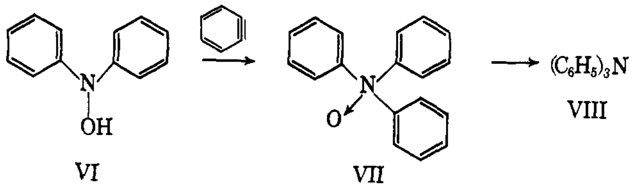
CHART I





V

Evidence that the postulated hydroxyamine derivative II is an intermediate in the reaction was provided by reacting the structurally similar diphenylhydroxyamine[10] (VI) with benzyne under the same experimental conditions. Triphenylamine (VIII) was formed in 40% yield, identical in all respects with an authentic sample.



VI VII VIII

---

[1] S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, **62**, 407 (1962).

[2] H. Staudinger and J. Jelagin, *Ber.*, **44**, 365 (1911).

[3] C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, 1456 (1924).

[4] C. K. Ingold, *ibid.*, 87 (1924).

[5] G. Wittig and R. W. Hoffman, *Angew. Chem.*, **73**, 435 (1961); *Chem. Ber.*, **95**, 2718 (1962).

[6] Other techniques for generating benzyne in nonalkaline media have been presented by (a) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963); (b) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); *Ann.*, **650**, 20 (1961); (c) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962); F. M. Behringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964); (d) L. Friedmann and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

[7] R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

[8] C. K. Ingold, *J. Chem. Soc.*, 94 (1924).

[9] C. Buchanan and S. H. Tucker, *ibid.*, 2750 (1958).

[10] H. Wieland and K. Roth, *Ber.*, **53**, 216 (1920).

The amine oxides, III and VII, could not be isolated, probably because of the facile elimination of oxygen displayed by N-oxides of weakly basic amines.[11]

Experimental

N-Phenylcarbazole.—A cold solution (−5°) of 815 mg. (4.85 mmoles) of 4,5-benzothiadiazol 1,1-dioxide[5] and 857 mg. (8.0 mmoles) of nitrosobenzene in 15 ml. of dry tetrahydrofuran was allowed to warm to room temperature. After removal of solvent, the dark residue was chromatographed on basic alumina. The column was eluted with CCl_4, and the eluate was evaporated to yield N-phenylcarbazole which crystallized as colorless crystals from ethanol–ethyl acetate (267 mg., 45.5%), m.p. 89–90°; picrate, m.p. 129–130° (lit.[12] m.p. 126–129°). The N-phenylcarbazole was identified by means of its mixture melting point with an authentic sample,[13] infrared spectrum, and thin layer chromatography.

3-Bromo-N-phenylcarbazole was prepared from 788 mg. (4.7 mmoles) of 4,5-benzothiazdiazol 1,1-dioxide and 1.49 g. (8.0 mmoles) of *p*-bromonitrosobenzene in 20 ml. of dry tetrahydrofuran by the procedure described above. Elution with CCl_4 yielded 306 mg. (40.5%) of 3-bromo-N-phenylcarbazole which crystallized as colorless crystals from ethanol–ethyl acetate, m.p. 79–80°.

Anal. Calcd. for $C_{18}H_{12}BrN$: C, 67.10; H, 3.75; Br, 24.80; N, 4.35. Found: C, 67.06; H, 3.70; Br, 24.36; N, 4.45.

Further elution with CCl_4–benzene (1:1) gave 420 mg. of 4,4′-dibromoazoxybenzene, which crystallized as yellow needles from ethanol–ethyl acetate, m.p. 169–170° (lit.[14] m.p. 168.5–169.5).[15]

Anal. Calcd. for $C_{12}H_8Br_2N_2O$: C, 40.49; H, 2.27; Br, 44.89; N, 7.87. Found: C, 40.70; H, 2.40; Br, 44.28; N, 7.94.

Reaction of Benzyne and Diphenylhydroxyamine.—A cold solution (−5°) of 737 mg. (4.4 mmoles) of 4,5-benzothiadiazol 1,1-dioxide and 1.48 g. (8.0 mmoles) of freshly prepared diphenylhydroxyamine[10] in 10 ml. of dry tetrahydrofuran was allowed to warm to room temperature. After removal of solvent, chromatography of the dark residue on basic alumina provided 424 mg. (39%) of triphenylamine, which was crystallized from ethanol, m.p. 126–126.5°, identical in all respects with an authentic sample.

Acknowledgment.—G. S. is indebted to the National Academy of Sciences for a postdoctoral research fellowship at the U. S. Army Natick Laboratories. The authors wish to thank Dr. R. W. Hoffmann for helpful suggestions.

---

[11] (a) G. Wittig and G. Steinhoff, *Ber.*, **95**, 205 (1962). (b) E. Bamberger and P. Leyden, *ibid.*, **34**, 12 (1901). (c) An unsuccessful attempt to convert triphenylamine to the corresponding N-oxide has been reported by V. N. Belov and U. K. Savich [*Zh. Obshch. Khim.*, **17**, 257 (1947); *Chem. Abstr.*, **42**, 530*h* (1948)].

[12] H. G. Dunlop and S. H. Tucker, *J. Chem. Soc.*, 1950 (1939).

[13] F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 547.

[14] E. Bamberger, H. Büsdorf, and B. Szolayski, *Ber.*, **32**, 221 (1899).

[15] The 4,4′-dibromoazoxybenzene probably was formed by the decomposition of the *p*-bromonitrosobenzene, possibly when it was chromatographed on the basic alumina.

1,3-Diphenyldisiloxanetetrol

John F. Brown, Jr., and George M. J. Slusarczuk

General Electric Research Laboratory, Schenectady, New York

Received May 19, 1964

The crystalline polyol, m.p. 114°, obtained by the hydrolysis of phenyltriacetoxysilane in ether,[1] is of interest as one of the very few partial condensation products of a trifunctional silane hydrolysate to have been isolated as an individual compound. Andrianov and Zhdanov formulated this substance as a trisiloxanepentol,[1] *i.e.*, as the trimeric condensation product of phenylsilanetriol.

We have repeated the preparation of this polyol, and obtained analytical and spectroscopic data which agree more closely with its formulation as a disiloxanetetrol. This was confirmed by the preparation and analysis of two trimethylsilylated derivatives: treatment with an equivalent quantity of trimethylchlorosilane–pyridine gave a pentasiloxanol; with excess trimethylchlorosilane–pyridine a hexasiloxane, the known[2] tetrakis(trimethylsiloxy)diphenyldisiloxane, was obtained.

$$PhSi(OH)_2OSi(OH)_2Ph \xrightarrow[C_5H_5N]{Me_3SiCl} PhSi(OSiMe_3)_2OSi(OH)(OSiMe_3)Ph \xrightarrow[C_5H_5N]{Me_3SiCl} PhSi(OSiMe_3)_2OSi(OSiMe_3)_2Ph$$

The diphenyldisiloxanetetrol resembles the one other known disiloxanetetrol, namely the 1,3-dicyclohexyl derivative,[3] in being a rather reactive intermediate isolatable by conducting the hydrolysis of a trifunctional silane under very mild conditions. Presumably, the silanetriol[4] is formed first and then undergoes partial condensation to the disiloxanetetrol.

$$PhSi(OAc)_3 \xrightarrow{H_2O} PhSi(OH)_3 \xrightarrow{-H_2O} Ph(HO)_2SiO(OH)_2Ph$$

Experimental

1,3-Diphenyldisiloxanetetrol.—A solution of 70 g. (0.25 moles) of phenyltriacetoxysilane in 70 ml. of ether was added slowly with stirring to 250 ml. of an ice–water slurry.[1] After 3 hr., the ethereal layer was separated, washed with ten 25-ml. portions of water, dried over sodium sulfate, and evaporated in a nitrogen stream. The partially crystalline residue was triturated with benzene and the insoluble solid washed and dried *in vacuo*, yielding 3.2 g. (9%), m.p. 114–114.5°. Reprecipitation from ethereal solution with hexane gave the raised m.p. 114.5–115°. The infrared spectrum (in *t*-butyl alcohol *vs.* *t*-butyl alcohol) showed a single ν_aSiOSi band at 1095 cm.$^{-1}$ (in contrast to the doublet seen in trisiloxanes[5]), very strong SiOH absorption around the 915-cm.$^{-1}$ solvent peak, and a weaker SiOH band at 850 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_5Si_2$: C, 49.0; H, 4.8; mol. wt., 294. Calcd. for $C_{18}H_{20}O_7Si_3$: C, 50.0; H, 4.6; mol. wt., 432. Reported[1]: C, 49.3; H, 4.9; mol. wt., 433 (dioxane, 11°). Found: C, 49.4; H, 4.9; mol. wt., 301 ± 5% (1.060 g./l. in acetone, 25°).

3,5-Diphenyl-1,1,1,7,7,7-hexamethyl-5-trimethylsiloxytetrasiloxane-3-ol.—To a solution of 0.430 g. (1.46 mmole) of the tetrol in 50 ml. of ether was added 1.0 ml. (7.9 mmole) of trimethylchlorosilane and 1.0 ml. of pyridine. After stirring 1.5 hr., water was added to extract the hydrochloride; the ether layer was then washed with 1% HCl, then with water until neutral, dried over sodium sulfate, and evaporated. Distillation of the residue at 100° (0.02 mm.) yielded 0.400 g. (54%) of a thick liquid. Vapor phase chromatography on a 2-ft. SE-30 column showed 95% of this to be a single compound. An analytical sample of the major constituent was isolated by v.p.c. The infrared spectrum (in CS_2) showed a very strong ν_aSiOSi at 1059 cm.$^{-1}$ (possibly a doublet) with a weak shoulder near 1100 cm.$^{-1}$; the SiOH group gave bands at 3680 and 909 cm.$^{-1}$.

---

[1] K. A. Andrianov and A. A. Zhdanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1033 (1954).

[2] W. Simmler, *Angew. Chem.*, **72**, 580 (1960); German Patent 1,046,049 (Dec. 11, 1958); British Patent 848,719 (Sept. 21, 1960).

[3] J. F. Brown, Jr., U. S. Patent 2,992,263 (July 11, 1961).

[4] L. J. Tyler, *J. Am. Chem. Soc.*, **77**, 770 (1955); T. Takiguchi, *ibid.*; **81**, 2359 (1959).

[5] N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).