

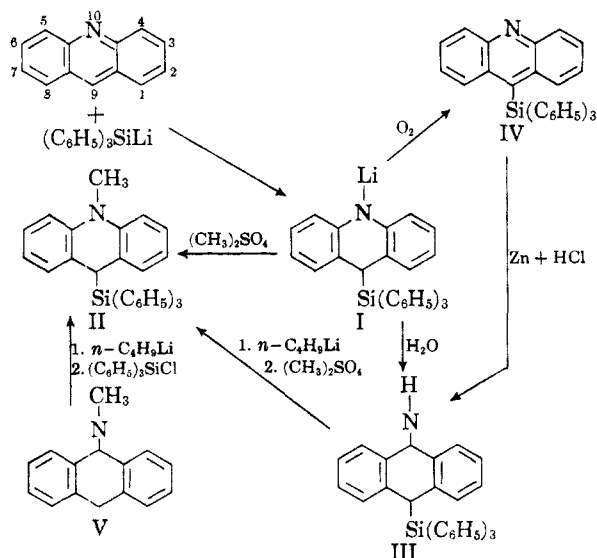
Addition of Triphenylsilyllithium to Acridine

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Recently it was reported¹ that triphenylsilyllithium acts as a selective nucleophile toward pyridine, undergoing attack exclusively at the 4-position. In contrast, it is known that alkyl- and aryllithium compounds undergo predominantly 1,2-addition to pyridine.^{2,3}

As an extension of the study of the addition of triphenylsilyllithium to aza-aromatic heterocycles, we have investigated the mode of addition of triphenylsilyllithium to acridine. 9,10-Addition takes place, as in the case of the analogous alkyl- and aryllithium compounds.^{4,5}



The resulting intermediate, 10-lithio-9-(triphenylsilyl)acridan⁶ (I) gives rise to 10-methyl-9-(triphenylsilyl)acridan (II) on treatment with methyl sulfate, and to 9-(triphenylsilyl)acridan (III) by hydrolysis. Oxygen⁷ converted the intermediate I to the totally aromatic compound, 9-(triphenylsilyl)acridine (IV). Compound IV was reduced to III by treatment with zinc and hydrogen chloride in benzene solution. Attempts to oxidize

(1) D. Wittenberg and H. Gilman, *Chem. & Ind. (London)*, 390 (1958).

(2) K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930).

(3) K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).

(4) E. Bergmann, O. Blum-Bergmann, and A. F. Cristiani, *Ann.*, **483**, 80 (1930).

(5) H. Gilman and D. A. Shirley, *J. Am. Chem. Soc.*, **72**, 2181 (1952). For a general reference see R. M. Acheson, *Acridines*, Interscience Publishers, Inc., New York, N. Y., 1956, p. 254.

(6) The nomenclature employed throughout this paper is that recommended by the editorial staff of *Chemical Abstracts*.

(7) For a discussion of this method see H. Gilman and J. T. Edward, *Can. J. Chem.*, **31**, 457 (1953).

III to IV by either nitrobenzene or ferric chloride failed.

The structure of II was established by the reaction of 10-methylacridan (V) with *n*-butyllithium to give 9-lithio-10-methylacridan, which coupled with chlorotriphenylsilane to give II in an excellent yield.

These derivatives of acridine are currently under investigation with regard to their possible use as high temperature antioxidants containing silicon.

EXPERIMENTAL⁸

Materials. Triphenylsilyllithium was prepared in tetrahydrofuran solution in accordance with published directions.⁹ Commercial acridine was recrystallized from petroleum ether (b.p. 60–70°) before use. 10-Methylacridan was prepared by reduction of 10-methylacridone with sodium in amyl alcohol.⁴

Addition of triphenylsilyllithium to acridine. To a solution of 6.9 g. (0.0386 mole) of acridine in 50 ml. of tetrahydrofuran was added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. The resulting dark solution gave a negative Color Test I¹⁰ indicating the triphenylsilyllithium had been consumed. Solutions of I prepared in this manner were used in the following three experiments.

Reactions of 10-lithio-9-(triphenylsilyl)acridan (I). A. With water. A solution of I prepared in the manner described above was hydrolyzed with water. The organic layer was dried over sodium sulfate and the tetrahydrofuran distilled. Crystallization of the residue from petroleum ether (b.p. 77–115°) gave a yellow powder, m.p. 177–190°. Recrystallization from the same solvent gave 4.63 g. (27%) of III, m.p. 179–181°. Since the product discolored on exposure to air, it was dried under reduced pressure at 0.01 mm. The infrared spectrum showed a strong N—H band at 2.9 μ .

Anal. Calcd. for $C_{21}H_{22}NSi$: Si, 6.39. Found: Si, 6.33, 6.58.

B. With methyl sulfate. To a solution of I, prepared in the same manner, was added excess methyl sulfate. After the reaction had subsided, water was added. The organic layer was dried over sodium sulfate and evaporated. Recrystallization from ethanol gave 10.6 g. (60%) of II, m.p. 173–177°. Recrystallization from the same solvent raised the melting point to 179–181°. The infrared spectrum showed no N—H band at 2.9 μ . A mixed melting point with I gave a large depression.

Anal. Calcd. for $C_{22}H_{27}NSi$: Si, 6.20. Found: Si, 6.42, 6.45.

C. With oxygen. Oxygen was passed through a solution of I prepared in the manner described, due care being exercised. Formation of a yellow precipitate accompanied the evolution of heat. After about 30 min. the reaction had subsided, and the suspension was filtered to give 5.3 g. (31%) of IV, m.p. 287–290°. Recrystallization from a benzene-petroleum ether (b.p. 60–70°) mixture gave bright yellow crystals, m.p. 287–289°. An unsuccessful attempt was made to obtain additional product from the original filtrate.

Anal. Calcd. for $C_{21}H_{22}NSi$: Si, 6.42. Found: Si, 6.40, 6.12.

Reduction of 9-(triphenylsilyl)acridine (IV) to 9-(triphenylsilyl)acridan (III). Dry hydrogen chloride was passed for several hours over the surface of a benzene solution of 1.0 g.

(8) Organometallic reactions were carried out under an atmosphere of dry nitrogen using oven-dried glassware. Melting points are uncorrected.

(9) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(10) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(0.00229 mole) of IV in contact with 10.0 g. (0.153 g.-atom) of powdered zinc. The suspension was filtered. The filtrate was neutralized with aqueous sodium carbonate and dried over solid sodium carbonate. A black tar left by evaporation of the benzene was dissolved in petroleum ether (b.p. 77–115°) and cooled. A black oil formed which was removed by filtration and discarded. The clear filtrate was seeded with III and set aside in the cold. The slow-forming crystals weighed 0.1 g. (10%), m.p. 179–182°. A mixed melting point with III was not depressed, and the infrared spectra were practically indistinguishable.

Alternate synthesis of 10-methyl-9-(triphenylsilyl)acridan (II). To a solution of 0.4 g. (0.00205 mole) of 10-methylacridan in 20 ml. of ether was added 2.5 ml. of an ethereal solution containing 0.0025 mole of *n*-butyllithium.¹¹ The solution became bright red in color. To this solution was added, all at once, 0.71 g. (0.0025 mole) of chlorotriphenylsilane. The red color was discharged. Ether was added to increase the volume of the reaction mixture, and hydrolysis was effected with water. The ether layer was dried over sodium sulfate and evaporated. The solid was recrystallized from ethanol to give 0.75 g. (81%) of II, m.p. 179–181°. A mixed melting point with a sample of II prepared by the first procedure was not depressed. The infrared spectra were identical.

10-Methyl-9-(triphenylsilyl)acridan(II) from 9-(triphenylsilyl)acridan(III). Five ml. of an ethereal solution containing 0.005 mole of *n*-butyllithium¹¹ was added to a solution of 1.5 g. (0.00342 mole) of III in 20 ml. of ether, followed by an excess of methyl sulfate. Ether was added to increase the volume of the reaction mixture, which was then hydrolyzed with water. The organic layer was dried over sodium sulfate and evaporated. Recrystallization of the solid from ethanol gave 0.92 g. (59%) of II, m.p. 179–181°. A mixed melting point with a sample of II prepared by the first method described was not depressed. The infrared spectra were identical.

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(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

Base Strengths of Some Alkylhydrazines¹

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In connection with studies on the acylation³ and alkylation of hydrazine and some of its deriva-

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tives the base strengths of a number of alkylhydrazines were needed. A survey of the literature revealed that aside from that of hydrazine itself,⁴ only the values of trimethyl- and tetramethylhydrazine have been reported.⁵ Accordingly, the apparent dissociation constants of the remaining members of the methylhydrazine series and of a number of ethylhydrazines were determined by potentiometric titration in water at 30°.

EXPERIMENTAL

Methylhydrazine and 1,1-dimethylhydrazine were purchased. The other alkylhydrazines were prepared by known methods (see Table I for references). Each hydrazine was carefully purified before use by drying over calcium sulfate and then over freshly cut sodium. The sample was finally distilled through a short Vigreux column in an atmosphere of nitrogen. A middle fraction with a boiling range of not more than one degree was collected for use in the determinations of base strengths.

Since hydrazines of low molecular weight are volatile, hygroscopic, easily oxidized compounds, the freshly distilled materials were sealed in weighed glass ampoules. The neutralization equivalent was used as a check on the purity of the sample, and in general agreed to within 2% of the calculated value. Ethylhydrazine, 1,2-dimethylhydrazine, and 1,2-diethylhydrazine were obtained as the dihydrochlorides and were titrated in this form. In these cases the neutralization equivalents were 5–6% low, which may be accounted for by the fact that hydrazine dihydrochlorides tend to lose hydrogen chloride on standing or during recrystallization.⁶

The base strength of each hydrazine, measured and recorded in Table I as pK_a' , was taken as the half-neutralization point of the titration curve of the hydrazine (pH vs. volume of standard hydrochloric acid added). The ampoules of hydrazines, containing samples weighing from 0.1 g. to 0.4 g., were crushed below the surface of the water just before beginning the titration. Sufficient water was used to give an initial concentration of from 0.02M to 0.05M. The surface of the solution was bathed in nitrogen throughout the titration. The temperature of the reaction mixture was maintained at $30 \pm 0.1^\circ$. The titration was followed with a Beckman pH Meter, Model F, equipped with glass and calomel electrodes, and standardized before use with a buffer solution of pH 7.00. The pK_a' 's in Table I are the averages of the several titrations in each case. The average deviation of the pK_a' was no larger than ± 0.05 in any case.

In some cases the hydrochlorides of the hydrazines were used for the determination of the pK_a' . With dihydrochlorides, like those of the 1,2-dialkylhydrazines, two breaks were observed in the curve, of which the second break was not sharp. In the latter case calculation of the second derivative in the region of the curve's steepest slope (*i.e.*, near the end point) gave reproducible results.⁷ As a check on this method the pK_a' values of methylhydrazine and of 1,1-dimethylhydrazine were determined by titration of their hydrochlorides with base. The results agreed within 0.1 pK unit of those obtained by titration of the free hydrazine with acid.

(3) R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

(4) N. Yui, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **20**, 256 (1941); *Chem. Abstr.*, **35**, 4660 (1941).

(5) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953).

(6) H. Hatt, *Org. Syntheses, Coll. Vol. II*, 208 (1943).

(7) J. J. Lingane, *Electroanalytical Chemistry*, Interscience Publishers, New York, N. Y., 1953, p. 70.