*Some Reactions of Pentamethylenediaziridine**

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Increasing attention has been attracted to diaziridines, and it would be worth while to report some preliminary results on the reactions of pentamethylenediaziridine (I).

Schmitz and Ohme[1] reported that diaziridines are readily dehydrogenated with silver oxide to give diazirines. The present authors have attempted the preparation of diazirines by the action of bromine on diaziridines, and have found that when pentamethylenediaziridine (I) was treated with bromine in the presence of triethylamine, bromination-dehydrobromination took place to afford pentamethylenediazirine (II), which was identified by addition of cyclohexylmagnesium bromide and conversion to urea derivative III by treatment with phenylisocyanate.

As to the reaction with acyl chloride, Abendroth et al.[2] reported that when 3, 3-dimethyldiaziridine was treated with an excess of benzoyl chloride in an aqueous medium, acetone and *N, N'*-dibenzoylhydrazine were formed. The present authors have studied the reaction of I with an equivalent amount of benzoyl chloride in tetrahydrofuran in the presence of pyridine. In this case also, *N, N'*-dibenzoylhydrazine was obtained. When diaziridine I was treated with *p*-tosyl chloride in benzene in the presence of triethylamine, the reaction product was not a diaziridine derivative but an open ring isomer, *N*-cyclohexylidene-*N'*-*p*-tosylhydrazine (IV). The structure of IV was determined by comparison with a specimen of IV, prepared by the reaction between *p*-tosyl hydrazine and cyclohexanone.

Diaziridine I could neither be metalated with sodium amide, sodium hydride, or Grignard reagent, nor be alkylated directly with cyclohexyl bromide.

Experimental[3]

Pentamethylenediaziridine (I)[4]. — Finely powdered hydroxylamine-*O*-sulfonic acid (11.4 g.) was added portionwise under cooling, to a stirred mixture of concentrated ammonia (34 ml.), cyclohexanone (15 g.) and methanol (10 ml.). After two hours, the mixture was extracted with chloroform. The chloroform extracts were dried over potassium carbonate, concentrated and the residue was collected and washed with ether, to give white plates, m. p. 102°C (5.7 g.). Reported m. p.[6], 102~104°C.

Found: N, 25.20. Calcd. for $C_6H_{12}N_2$: N, 24.98%.

Reaction of Pentamethylenediaziridine with Bromine.—A solution of bromine (3.2 g.) in hexane (5 ml.) was added dropwise to a stirred suspension of pentamethylenediaziridine (2.24 g.) in a mixture of triethylamine (4.04 g.) and ether (20 ml.), while the mixture was maintained at 0~10°C. Stirring was continued for two hours after the addition of bromine was complete. The precipitate of triethylamine hydrobromide (6.6 g.) was filtered off;

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[1] E. Schmitz and R. Ohme, *Chem. Ber.*, **94**, 2166 (1961).

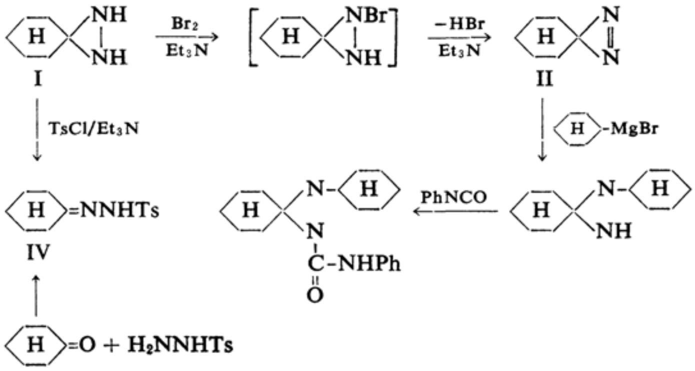
[2] H. J. Abendroth and G. Henrich, *Angew. Chem.*, **71**, 283 (1959).

[3] All the melting points reported are micro-melting points corrected.

[4] After the experiment had been performed, detailed descriptions of preparative method of I has appeared[1,5].

[5] E. Schmitz and D. Habisch, *Chem. Ber.*, **95**, 680 (1962).

[6] H. J. Abendroth, *Angew. Chem.*, **73**, 67 (1961).



the filtrate was washed with 1 N hydrochloric acid (5 ml.), and was dried over potassium carbonate. Distillation under reduced pressure gave colorless liquid (0.6 g.) which distilled at 28°C/35 mmHg[7].

To a solution of Grignard reagent prepared from cyclohexyl bromide (1.8 g.) and magnesium (0.27 g.) in ether, was added a solution of the above described distillate in ether (10 ml.) with stirring and cooling. After an hour, the mixture was decomposed with water and was extracted with ether (100 ml.). The ether layer was extracted with ice-cooled 2 N sulfuric acid (30 ml.); the acid extracts were neutralized with aqueous sodium hydroxide and again extracted with ether (50 ml.). The ether extracts were dried over potassium carbonate and was concentrated. Phenylisocyanate (0.3 ml.) was added to the residue and the crystals which separated out were collected. Recrystallization from *n*-hexane afforded white needles (0.4 g.), m. p. 146°C. Reported m. p.[1] for *N*-(1-cyclohexylaminocyclohexyl)-*N'*-phenylurea is 147~148°C.

Found: N, 13.24. Calcd. for $C_{19}H_{27}N_3O$: N, 13.42%.

Reaction of Pentamethylenediaziridine with Benzoyl Chloride. — Benzoyl chloride (0.7 g.) was added under cooling to a stirred solution of pentamethylenediaziridine (0.56 g.) and pyridine (0.4 ml.) in tetrahydrofuran (10 ml.). Stirring was continued for two hours; the precipitate of pyridine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure. The oily residue which slowly solidified on cooling was recrystallized from ethanol to give white silky needles, m. p. 241°C. Its melting point was undepressed on admixture with an authentic specimen of *N, N'*-dibenzoylhydrazine.

Found: N, 11.68. Calcd. for $C_{14}H_{12}N_2O_2$: N, 11.66%.

Reaction of Pentamethylenediaziridine with *p*-Tosyl Chloride.—To a stirred solution of pentamethylenediaziridine (2.24 g.) and triethylamine (4.04 g.) in benzene (20 ml.), was added *p*-tosyl chloride (3.82 g.) under cooling, and the mixture was allowed to stand overnight. The crystals of triethylamine hydrochloride (1.8 g.) were filtered off and the filtrate was concentrated under reduced pressure. The colorless prisms which separated out were collected (4.7 g., m. p. 155~156°C) and recrystallized from ethanol to afford colorless prisms, m. p. 160°C. Its melting point was undepressed on admixture with a sample of *N*-cyclohexylidene-*N'*-*p*-tosylhydrazine, prepared by the following method.

Found: C, 58.33; H, 6.60; N, 10.52. Calcd. for $C_{13}H_{18}N_2O_2S$: C, 58.63; H, 6.81; N, 10.52%.

***N*-Cyclohexylidene-*N'*-*p*-tosylhydrazine (IV).** — A solution of *p*-tosylhydrazine (1.86 g.) and cyclohexanone (0.98 g.) in ethanol (30 ml.) was refluxed for an hour. The colorless prisms which separated out on cooling were collected (1.35 g.), m. p. 160°C.

Found: N, 10.79. Calcd. for $C_{13}H_{18}N_2O_2S$: N, 10.52%.

Attempted Metalation and Alkylation of Pentamethylenediaziridine. — When pentamethylenediaziridine was treated with ethylmagnesium iodide in ether at room temperature, or with sodium amide or sodium hydride in benzene at reflux temperature in an atmosphere of nitrogen, and then with cyclohexyl bromide, unchanged starting material was recovered.

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[7] Uncorrected. Reported b. p.[1], 33°C/30mmHg.