BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1967—1972 (1967)

The Grignard Reaction of 1, 3-Diazaazulene[1]

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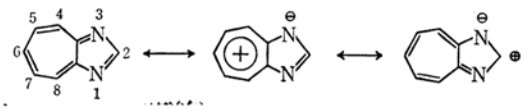
(Received March 11, 1967)

From the point of view of the nucleophilic substitution, the Grignard reaction of 1, 3-diazaazulene (I) was investigated using phenyl magnesium bromide and *t*-butyl magnesium chloride. Substitution occurred at 4- and/or 6-positions of I and 4-phenyl-4*H*- (II), 4-*t*-butyl-4*H*- (VIIIa) and 6-*t*-butyl-6*H*-cycloheptaimidazole (VIIIb) were isolated respectively. The NMR and UV spectra of these products were discussed. Of the products, II and VIIIb afforded 4-phenyl- (III) and 6-*t*-butyl-1, 3-diazaazulene (XI) by dehydrogenation.

1, 3-Diazaazulene (I), nitrogen analog of azulene, has been considered to be a resonance hybrid contributed from structures Ia, Ib and Ic, *etc.* The dipole moment of I (4.03D in benzene at 25°C)[2] supports much contribution of structure Ib, which is responsible for electron deficiency in the seven membered ring.



Ia Ib Ic

The calculation from the chemical shift of the ring protons of I indicates that electron density of the carbon atoms decreases in the order of 2—4(8)→6→5(7) positions and anticipates that the nucleophilic substitution would occur at the 2- or 4(8)-positions preferencially to at the 6- or 5(7)-positions.[3] Molecular orbital calculation clarified that electron density of 1- or 3-position is much higher than that of other positions, but it remained unknown which carbon atoms are most electron deficient.[4]

On the other hand, organic investigation disclosed that the nucleophilic replacement occurred easily at the 2-[5a] or 5-[5b] position of the corresponding monosubstituted 1, 3-diazaazulenes.

Furthermore, in the case of 2, 4-[6] and 2, 6-disubstituted 1, 3-diazaazulenes[7] the nucleophilic attack took place preferencially at the 4(8)- or 6-position to at the 2-position.

The Grignard reaction of 1, 3-diazaazulene (I), as a part of the series of the nucleophilic substitution reaction, was investigated to find relationships between the theoretical results described above and such nucleophilic substitution of I.

Another purpose is from the point of view of synthetical interest, namely, synthesis of aryl or alkyl derivatives of 1, 3-diazaazulene would be achieved by dehydrogenation of the expected products from the Grignard reaction of I.

When one equivalent of phenyl magnesium bromide was reacted with I at room temperature, a colorless crystalline product (II), mp 164—165°C, was obtained in 50% yield with recovery of 30% of I. Use of two equivalents of the Grignard reagent resulted in increase of the yield of II to more than 80%. The elemental analysis ($C_{14}H_{12}N_2$) indicated that II is the product arising from the addition of one hydrogen and one phenyl group.

In the ultraviolet spectrum of II (Fig. 1), the

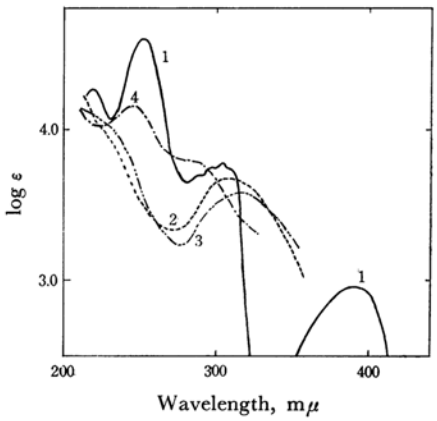
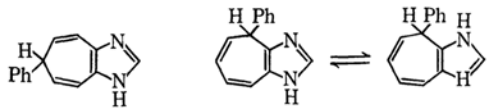


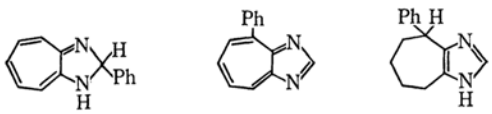
Fig. 1. Ultraviolet absorption spectra in MeOH of: 1, 1,3-diazaazulene (I); 2, 4-phenyl-4*H*-cycloheptaimidazole (II); 3, 4-phenyl-4*H*-*N*-methyl cycloheptaimidazole (V); 4, 4-phenyl-8*H*-*N*-methyl cycloheptaimidazole (VI).

1) Reaction of Seven-membered Aromatic Compounds with Organometallic Compounds. VII. The preceding paper, T. Nozoe, T. Mukai and T. Tezuka, This Bulletin, **34**, 619 (1961).
2) Y. Kurita and M. Kubo, *J. Am. Chem. Soc.*, **79**, 5460 (1957).
3) S. Ito and J. Tsunetsugu, to be published.
4) H. Kon, *Sci. Repts. Tohoku Univ., I*, **38**, 67 (1954).
5) a) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan. Acad.*, **30**, 482 (1954); b) I. Murata, This Bulletin, **34**, 580 (1961).
6) T. Mukai and K. Matsumoto, unpublished work.
7) T. Nozoe, T. Mukai and T. Asao, This Bulletin, **35**, 1188 (1962).

absorption maxima at 259 and 390 mμ characteristic of I disappeared, indicating lost of 1, 3-diazaazulenoid system. The infrared spectrum of II shows complex bands at 3000—2500 cm^{-1} which are characteristic of NH hydrogen bond of imidazole.[8] From these facts and analogy of the Grignard reaction of azulene,[9] as well as from the above theoretical consideration concerning the electron density, compound II was assumed to be the expected dihydrodiazaazulene derivative such as IIa, IIb or IIc.



IIa IIb, A IIb, B



IIc III IV

Of these three structures, IIb was chosen for the product on the basis of the NMR spectrum (Fig. 2).

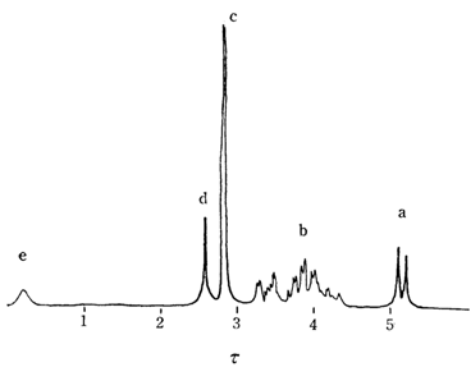
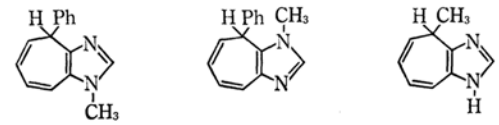


Fig. 2. NMR spectrum of 4-phenyl-4*H*-cycloheptaimidazole (II) (60 Mc in $CDCl_3$).

Compound II exhibits five groups of signals, *a* (methine proton, doublet with $J=7.1$ cps, 1H),[10] *b* (olefinic protons, complex, 4H), *c* (phenyl protons, singlet, 5H), *d* (imidazole ring proton, singlet, 1H) and *e* (NH, broad, 1H). The decisive structural proof of II as 4-phenyl-4H-cycloheptaimidazole (IIb) was provided by dehydrogenation of II. Treatment of II with tetrachloro-*o*-benzoquinone in benzene at room temperature afforded 4-phenyl-1, 3-diazaazulene (III),[11] mp 124°C, in 55% yield. This result established that the nucleophilic attack by phenyl magnesium bromide took place exclusively at the 4-position of I affording II. When II was hydrogenated over palladium carbon, it consumed two molar equivalents of hydrogen giving tetrahydro compound (IV), mp 203°C.

Although two tautomers A and B are possible for IIb, simplicity of the signals in the NMR spectrum of II may exclude the existence of such a tautomerism. However, methylation of II with methyl iodide afforded an oily mixture of two products in good yield, whose NMR spectrum exhibited two peaks for *N*-methyl protons at τ 6.49 and τ 6.59 with intensity ratio of about 1 : 1. Separation of the mixture was achieved by preparative thin layer chromatography and two components could be obtained, crystals, mp 147.5°C, with signal at τ 6.59 and an oil with signal at τ 6.49. These NMR spectra were not useful for assignment of their structure to V and VI, because the expected shielding effect for *N*-methyl protons by phenyl group at 4-position was too small to cause the separation of the signal. However, differences were observed in their ultraviolet spectra (Fig. 1). The crystalline product exhibits absorption in longer wavelength region compared with the oily product. Such a difference can not be explained by difference in degree of the extension of the conjugated system between V and VI,[12] but by the steric interferences between the phenyl and *N*-methyl group. For this reason the less hindered structure V would be proposed for the crystalline product and structure VI for the oily product.



V VI VII

Furthermore, the fact that the ultraviolet spectrum of II is more similar to that of V than VI indicates that compound II may exist as A form rather than B form.

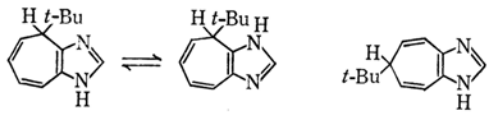
Recently so much attention has focused on the thermal isomerization of tropilidene derivatives,[13] that thermal stability of II was examined. When II was heated in boiling benzene or boiling toluene for 4 hr, no change was observed in its NMR spectrum. II was also considerably stable during

8) D. M. W. Anderson, J. L. Duncan and F. J. C. Rossotti, *J. Chem. Soc.*, **1961**, 2165.
9) K. Hafner and H. Weldes, *Ann.*, **606**, 90 (1957).
10) Doublet *a* appeared in lower field than a signal due to methine proton of 7-phenyl tropilidene, since hydrogen of 4-position of II would be affected by anisotropy of nitrogen and the ring current of imidazole ring.
11) K. Kikuchi and T. Muroi, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **77**, 1081 (1956).
12) There are no differences in the ultraviolet spectrum between 2-nitro- and 4-nitro-*N*-methylimidazoles. *Cf.* A. Grimison, J. H. Ridd and B. V. Smith, *J. Chem. Soc.*, **1960**, 1357.
13) a) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717, (1963); b) T. Nozoe and K. Takahashi, This Bulletin, **38**, 666 (1965).

heating with 2 N hydrochloric acid and 2 N potassium hydroxide solution.

For the synthesis of an alkyl derivative, the reaction of I with methyl magnesium iodide was carried out in the same manner as mentioned for the synthesis of II. The NMR spectrum of the product (see experimental part) seems to support the formation of the expected compound VII but it was unstable and changed to a tar during standing in air. Dehydrogenation of the freshly prepared product by tetrachloro-*o*-benzoquinone failed in the isolation of any methyl derivative of 1, 3-diazaazulene. The catalytic hydrogenation of the product, although after consumption of about two equivalents of hydrogen, did not furnish a simple hydrogenation product.

Under the expectation of obtaining more stable alkyl derivative of dihydrodiazaazulene, the reaction of I with *t*-butyl magnesium chloride was carried out. In this case, colorless crystals, mp 141—142°C, with formula $C_{12}H_{16}N_2$ could be obtained in about 80% yield. The product shows absorption bands characteristic of the NH group of the imidazole at 2500—3000 cm^{-1} and ultraviolet spectrum similar to that of II (Fig. 3). These facts support that the product is the expected dihydro-1, 3-diazaazulene having *t*-butyl group and the following structures VIIIa and VIIIb would be proposed for it on the basis of the nature of the nucleophilic reaction of I.



VIIIa, A VIIIa, B VIIIb

The NMR spectrum of the product (Fig. 4) exhibits five groups of signals, *i. e. a* (methine protons, doublet and triplet, 1H and 1H), *b* (olefinic protons, very complex bands, 8H), *c* (*t*-butyl protons, a couple of singlets, each 9H), *d* (imidazole ring proton, two singlets, each 1H) and *e* (NH protons, broad, 2H).

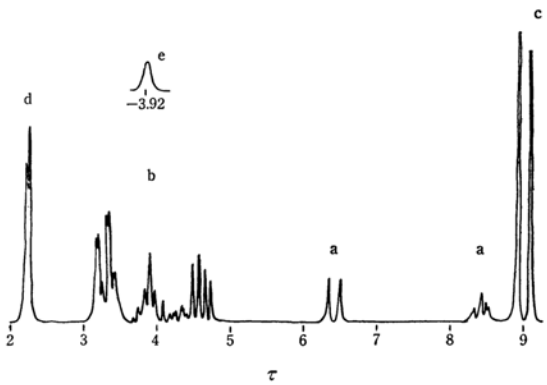
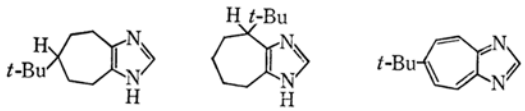


Fig. 4. NMR spectrum of the reaction product between I and *t*-butyl magnesium chloride. (60 Mc in $CDCl_3$)

Duality of the signal in *a*, *c* and *d* region can only be illustrated by the existence of two different compounds, although the product has a sharp melting point and shows one spot in its thin layer chromatogram. Appearance of a triplet and a doublet in the methine region *a* suggests that the product contains VIIIb in addition to VIIIa. When the product was hydrogenated over palladium carbon, two equivalents of hydrogen was consumed and two tetrahydro compounds IX, mp 211—212°C and X, mp 151—152°C were obtained in ratio of 1 : 1 in quantitative yield. Therefore the product is assumed to be a mixture of VIIIa and VIIIb.



IX X XI

Dehydrogenation of the product with tetrachloro-*o*-benzoquinone afforded two crystalline products, yellow crystals (XI) with formula $C_{12}H_{14}N_2$ and colorless crystals (VIIIa), mp 178°C with formula $C_{12}H_{16}N_2$ in 30 and 40% yields respectively. The compound XI is hygroscopic and basic enough to give a picrate and a styphnate, whereas the other VIIIa did not show such a basicity. The ultraviolet spectrum of XI is very similar to that of 1, 3-diazaazulene (Fig. 3) and its NMR spectrum (Fig. 5) shows a typical A_2B_2 pattern. From these facts compound XI was confirmed as 6-*t*-butyl-1, 3-diazaazulene. On the other hand, similarity of the ultraviolet spectrum to that of II rather than I suggests that compound VIIIa is not 1, 3-diazaazulene derivative, but dihydrodiazaazulene derivative. Except the signals ascribed to *t*-butyl and phenyl groups, the similarity of the NMR

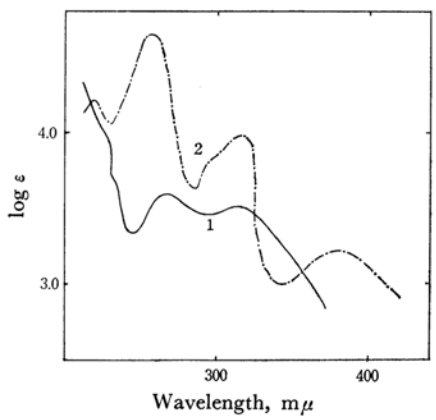


Fig. 3. Ultraviolet absorption spectra in MeOH of: 1, the reaction product of I with *t*-butylmagnesium chloride; 2, 6-*t*-butyl-1,3-diazaazulene (XI).

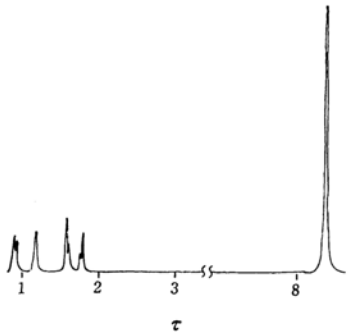


Fig. 5. NMR spectrum of *t*-butyl-1,3-diazaazulene (XI). (60 Mc in $CDCl_3$)

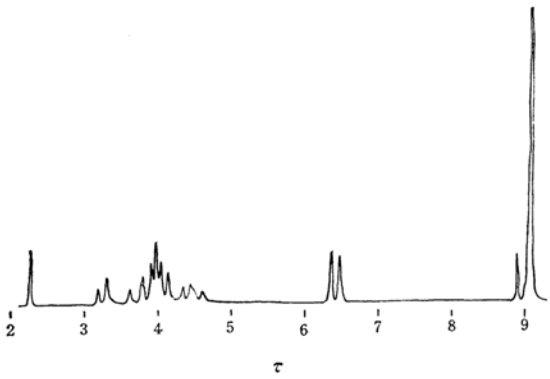


Fig. 6. NMR spectrum of 4-*t*-butyl-4*H*-cycloheptaimidazole (VIIIa) (60 Mc in $CDCl_3$).

spectrum (Fig. 6) to that of II should suggest that compound VIIIa is 4-*t*-butyl-4*H*-cycloheptaimidazole. As expected, hydrogenation of VIIIa over palladium carbon afforded compound (X) described above.

The dehydrogenation of the isolated VIIIa was attempted by treating with tetrachloro-*o*-benzoquinone in boiling benzene or in boiling chlorobenzene, but 4-*t*-butyl-1, 3-diazaazulene could not be obtained. This experiment clarified that the product of the reaction of I with *t*-butyl magnesium chloride was a mixture of VIIIa and VIIIb in a ratio of 1 : 1 (Fig. 4), and there is selectivity for the dehydrogenation between them. Unreactivity of VIIIa would be ascribed to the steric interference of the bulky *t*-butyl group and the imidazole ring.

Above series of the experiments established that, in the Grignard reaction of I, the introduction of aryl and alkyl groups occured exclusively at 4- and 6-positions of 1, 3-diazaazulene. However, it is not sure to correlate these results immediately with the fact that 4- or 6-positions is most electron-deficient at the carbon atoms of 1, 3-diazaazulene, because consideration should also be paid to other factors such as bulkieness of the Grignard reagent and the electronic state of the intermediate complex which may be different from the unreacted molecule.

Experimental

Preparation of 4-Phenyl-4*H*-cycloheptamidazole (II). A solution of I (1.5 g; 11.5 mm) dissolved in tetrahydrofuran (25 m*l*) was added dropwise to a solution of phenyl magnesium bromide (25.4 mm) in ether (21 m*l*) at room temperature for 20 min. The reaction mixture was stirred for 1 hr and decomposed by addition of 1 N hydrochloric acid. The organic layer from the resulted solution was extracted with dilute hydrochloric acid. The combined acidic portion was neutralized by addition of aqueous sodium bicarbonate solution and extracted with ether. Evaporation of the ether extract afforded II (1.9 g, 79%), mp 155—158°C, which was recrystallized from benzene to give a colorless powder, mp 164—165°C. ν_{max}^{KBr} 3086, 3021, 2809, 2646, 1900 (broad) cm^{-1}.

Found: C, 80.80; H, 5.73; N, 13.25%. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%.

Dehydrogenation of II. Preparation of 4-Phenyl-1, 3-diazaazulene (III). After a solution of II (200 mg; 0.9 mm) and tetrachloro-*o*-benzoquinone (284 mg; 1.1 mm) dissolved in benzene (25 m*l*) had been allowed to stand overnight, the solution was decomposed by addition of dilute hydrochloric acid. The acidic portion from the decomposed solution was neutralized with sodium bicarbonate and extracted with benzene. Evaporation of the benzene extracts furnished a brown oil (200 mg), which was decanted with cyclohexane-benzene (9 : 1) to dissolve an easily soluble portion. The solution obtained was passed through a short column containing alumina (Grade 0-1, 4 g) and eluted with chloroform. Evaporation of the chloroform-elute and recrystallization of residue from cyclohexane afforded III (105 mg), mp 122—124°C. III was found to be identical with an authentic sample of 4-phenyl-1, 3-diazaazulene[11] by mixed melting point method and comparison of their infrared spectra. It afforded also picrate, mp 215.5°C and styphnate, mp 196—197°C, both of which were also identical with an authentic sample.

Catalytic Hydrogenation of II affording 4-Phenylpentamethyleneimidazole (IV). When a solution of II (300 mg; 1.4 mm) dissolved in ethanol (10 m*l*) was hydrogenated in the presence of 10% Pd-C (30 mg) at room temperature, 75 m*l* of hydrogen (2.4 equivalent) was absorbed. After the catalyst had been removed, the solution was concentrated to give IV (288 mg) as an viscous oil, which, upon digestion with ether, crystallized giving crystals, mp 199—200°C. Recrystallization from benzene furnished colorless micro prisms, mp 202—203°C. λ_{max}^{MeOH} 256 mμ; log ε 3.38; ν_{max}^{KBr} 3096, 2933, 2915, 2035, 2635, 1880 cm^{-1}.

Found: C, 79.34; H, 7.80; N, 12.68%. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%.

Methylation of II and Preparation of V and VI. Methyl iodide (1.5 g; 10.5 mm) was added to a solution of II (400 mg; 1.9 mm) dissolved in ethanol (9 m*l*) and the resulted solution was stirred for 7 hr at room temperature. After the solution had been poured into water and neutralized by addition of sodium bicarbonate, the mixture was extracted with chloroform. Evaporation of the chloroform-extract afforded an brown oil (400 mg), which was a mixture of two methylated products with a ratio of 1 : 1. Preparative thin layer

chromatography (developed with chloroform-methanol 20 : 1 on silica gel) had the mixture separated to V (R_f= 0.58) (140 mg, 32.8%) as crystals which was recrystallized from benzene affording colorless prisms, mp 146.5—147.5°C and VI (R_f=0.69) (95 mg; 22.3%) as an oil, bp 185—195°C/0.9 mmHg. No NH band was observed in their infrared spectra.

Found for V; C, 81.09; H, 6.71; N, 12.37 and for VI: C, 80.06; H, 6.40; N, 12.17%. Calcd for $C_{15}H_{14}N_2$: C, 81.05 H, 6.35; N, 12.60%.

VI gave picrate, mp 161—163°C, bright yellow prisms.

Found: C, 55.76; H, 3.80; N, 15.29%. Calcd for $C_{21}H_{17}O_7N_5$: C, 55.87; H, 3.80; N, 15.52%.

Reaction of I with Methyl Magnesium Iodide. Compound I (870 mg; 6.7 mm) dissolved in tetrahydrofuran (18 m*l*) was reacted with methyl magnesium iodide (17.7 mm) in ether (13 m*l*) in the same manner as described above for the preparation of II, affording a yellow oil (1.06 g). NMR spectrum in $CDCl_3$: τ 8.75 (doublet with J=6.0 cps 3H), 6.47 (multiplet, 1H), 3.1—5.0 (complex multiplet, 4H), 2.39 (singlet, 1H), and 0.11 (NH, 1H). This oil turned into a black tar during standing at room temperature.

When the freshly prepared compound (595 mg) was dissolved in ethanol (25 m*l*) and hydrogenated over 5% Pd-C (100 mg), it consumed 1.8 equivalents of hydrogen (150 m*l*). After the catalyst had been removed, evaporation of ethanol afforded a brown oil (610 mg), which could not be purified by distillation or chromatography on silica gel. $\nu_{max}^{CHCl_3}$ 3460, 3236, 2833—2326, 1961 cm^{-1}.

When dehydrogenation of the product was attempted using tetrachloro-*o*-benzoquinone in methylene chloride under ice-salt cooling, a brown tar was immediately deposited. The reaction mixture containing tar was decomposed with dilute hydrochloric acid and treated in the same way as described above for dehydrogenation of II, but any 1, 3-diazaazulene derivative could not be obtained.

Reaction of I with *t*-Butyl Magnesium Chloride. To a solution of *t*-butyl magnesium chloride (24.8 mm) in ether (35 m*l*), a solution of I (1.05 g; 8.00 mm) in tetrahydrofuran (25 m*l*) was added drop by drop at room temperature. After-treatment was carried out as same as in the reaction of I with phenyl magnesium bromide, and a mixture of VIIIa and VIIIb (1.16 g; 76.5%) with a ratio of 1 : 1, mp 138.5—139.5°C was obtained as colorless crystals. Recrystallization from petroleum ether afforded colorless micro crystals, mp 141—142°C. ν_{max}^{KBr} 3106, 3021, 2941, 2859 cm^{-1}.

Found: C, 76.49; H, 8.87; N, 14.41%. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88%.

Hydrogenation of the Mixture of VIIIa and VIIIb. When a solution of the mixture of VIIIa and VIIIb (300 mg; 1.6 mm) dissolved in ethanol (15 m*l*) was hydrogenated at room temperature using 10% Pd-C (90 mg) as catalyst, it absorbed two equivalents of hydrogen (73 m*l*). Filtration of the catalyst followed by evaporation of ethanol afforded an oily compound (310 mg; 100%) whose NMR spectrum showed two *t*-butyl groups at τ 9.00 and τ 9.04 with intensity of 1 : 1. It partly crystallized on standing overnight. Digestion with petroleum ether followed by filtration gave colorless crystals (80 mg), mp 198—205°C, as a first crop. Recrystallization from water-ethanol afforded colorless scales, mp 211—212°C (IX), with a singlet at τ 9.04 (*t*-butyl group). λ_{max}^{MeOH} 217 mμ; log ε 3.98 (sh).

Found: C, 75.16; H, 10.37; N, 14.41%. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57%.

Another crop of colorless crystals (35 mg), mp 124—126°C was obtained, but NMR spectrum showed that it was a mixture of IX and X in a ratio of *ca.* 11 : 7, being IX predominant. The filtrate was separated by thin layer chromatography, using chloroform-ethanol (5 : 1) as developing solvent. From the part with R_f=0.76 were obtained colorless crystals (35 mg) which were recrystallized from water-ethanol to give micro needles, mp 151—152°C (X), NMR spectrum, a singlet at τ 9.00 (*t*-butyl group). λ_{max}^{MeOH} 217 mμ; log ε 3.92 (sh). ν_{max}^{KBr} 3077, 2915, 2833, 2632, 1873 cm^{-1}.

Found: C, 74.85; H, 10.59; N, 14.31%. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57%.

Dehydrogenation of the Mixture of VIIIa and VIIIb. Preparation of 6-*t*-Butyl-1, 3-Diazaazulene (XI). A solution of tetrachloro-*o*-benzoquinone (590 mg; 2.4 mm) in benzene (25 m*l*) was poured into a solution of the mixture of VIIIa and VIIIb (300 mg; 1.6 mm) dissolved in benzene (50 m*l*) and the resulted solution allowed to stand for 18 hr at room temperature. During standing, colorless crystals deposited. The reaction mixture was decomposed by adding dilute hydrochloric acid and the benzene layer separated was extracted with hydrochloric acid. The combined acidic portions were neutralized with sodium bicarbonate and extracted with chloroform. The chloroform-extract was passed through a column containing alumina (Grade 0-1; 50 g) and eluted with chloroform. Evaporation of the firstly eluted fraction afforded XI (90 mg) as a yellow oil, which, on being dried in desiccator, crystallized, but it again immediately turned to a yellow oil in air.

Found: C, 76.65; H, 8.03; N, 14.55%. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04%.

Compound XI afforded picrate, mp 238—240°C and styphnate, mp 207—208°C.

Found for picrate: C, 52.30; H, 4.03; N, 16.42%. Calcd for $C_{18}H_{17}O_7N_5$: C, 52.05; H, 4.13; N, 16.86%.

Found for styphnate: C, 49.83; H, 3.92; N, 16.43%. Calcd for $C_{18}H_{17}O_8N_5$: C, 50.12; H, 3.97; N, 16.24%.

The elution was continued with the same solvent and the next fraction, on evaporation, furnished VIIIa (183 mg), which, on recrystallization from cyclohexane, gave colorless crystals, mp 174—176°C. λ_{max}^{MeOH} 314 mμ; log ε (3.63). ν_{max}^{KBr} 3030, 2967, 2865, 2809, 2639, 1887 cm^{-1}.

Found: C, 76.22; H, 8.46; N, 14.38%. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88%.

Catalytic Reduction of VIIIa. Preparation of X. A solution of VIIIa (74 mg; 0.4 mm) dissolved in ethanol (5 m*l*) was hydrogenated in the presence of 10% Pd-C (25 mg). After two equivalents of hydrogen (22 m*l*) had been consumed, evaporation of ethanol afforded a pale yellow oil (75 mg), which crystallized. Recrystallization from water-ethanol gave colorless needles, mp 152—153°C, which were proved to be identical with X by mixed melting point method and by comparison of their infrared spectra.

Attempted Dehydrogenation of VIIIa. After a solution of VIIIa (100 mg; 0.53 mm) and tetrachloro-*o*-benzoquinone (197 mg; 0.80 mm) dissolved in benzene

(30 ml) had been refluxed for 3 hr, the solution was decomposed with 1 N hydrochloric acid. The acidic portions were neutralized with sodium bicarbonate and extracted with chloroform. The residue obtained from the chloroform-extract was dissolved in the same solvent and passed through a short column of alumina. Elution with chloroform followed by evaporation afforded colorless crystals (90 mg), mp 170—174°C. Recrystallization from cyclohexane gave mp 173—175°C, which was proved to be recovered VIIIa by mixed melting point method. When the same experiment was carried out in refluxing chlorobenzene in place of in refluxing benzene, VIIIa (40 mg) was recovered, although being accompanied by a fair amount of tar.

The authors thank to Professor T. Nozoe for his kind encouragement during the study. Financial supports by Sankyo Co. are also acknowledged.