The Reduction of Triazolium and Tetrazolium Iodides with Sodium Borohydride

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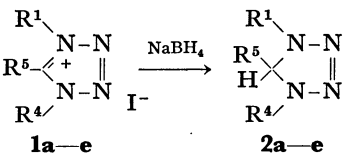
The sodium borohydride reduction of azolium iodides containing two, three, or four nitrogen atoms in the ring was studied. 1,4,5-Trisubstituted tetrazolium iodides gave Δ^2-tetrazolines, whereas 1,3,5-trisubstituted tetrazolium iodide yielded no reduction product. 1,3,4,5-Tetrasubstituted 1,2,4-triazolium iodides and 1,2-disubstituted 1,2,3-triazolium fluorosulfonate were reduced to Δ^2-1,2,4-triazolines and Δ^3-1,2,3-triazoline respectively, but 1,3,4,5-tetrasubstituted 1,2,3-triazolium iodides were not reduced at all. Both pyrazolium and imidazolium salts gave the corresponding azolidines. These results can be explained in terms of the characteristics of sodium borohydride, which reduces selectively the immonium moiety in azolium salts.

The reduction of pyridinium salts and these benzo-derivatives with sodium borohydride has been well-established and utilized as a synthetic tool useful in obtaining hydrogenated heterocycles.[1] With regard to the reduction of azolium salts, thiazolium halides[2,3] and pyrazolium perchlorate[4] give thiazolidines and pyrazolidine respectively in a protic solvent, and benzoisooxazolium[5] and benzoimidazolium salts[6] yield the corresponding benzoazolines. Imidazolium iodides are, however, reduced to ring-cleaved products, *N,N,N'*-trialkylethylene diamines.[7] These confused results prompted us to investigate the unknown behavior of triazolium and tetrazolium salts in the sodium borohydride reduction and to attempt to ascertain the common properties of azolium salts.

In general, azolium salts were treated with excess sodium borohydride in 95% ethanol at room temperature for several hours; the sole products were afforded in good yields when the reduction occurred. The reduction of 1,4,5-trisubstituted tetrazolium iodides (**1**) gave the corresponding Δ^2-tetrazolines (**2**). The analytically-pure Δ^2-tetrazoline (**2a**—**d**) could be isolated from the ethereal extract of the product without further purification.

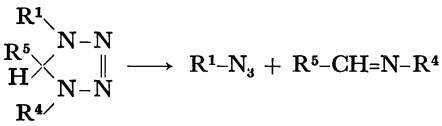
The structure of the novel type of Δ^2-tetrazoline was



1a—e **2a—e**

	a	**b**	**c**	**d**	**e**
R^1:	CH_3	CH_3	C_2H_5	CH_3	CH_3
R^4:	CH_3	C_2H_5	C_2H_5	C_6H_5	CH_3
R^5:	C_6H_5	C_6H_5	C_6H_5	CH_3	CH_3

elucidated by means of NMR and elementary analyses. The NMR spectra of **2a**—**c** displayed a singlet peak at around δ 4.61 ppm associated with the C^5-proton, while that of **2d** showed a quartet at δ 4.15 ppm and a doublet at δ 1.52 ppm assigned to the C^5-proton and the 5-methyl protons respectively. **2a** and **2d** are comparatively unstable to heat and are decomposed completely at 120°C in only a few minutes to give alkyl azides and Schiff's bases, whereas **2b** and **2c** are more stable and are scarcely decomposed at all on heating at 150°C. The formation of Schiff's bases was observed in the mass spectra of these tetrazolines.



In the reduction of 1,4,5-trimethyltetrazolium iodide (**1e**), the attempted isolation of the product, **2e**, was unsuccessful; however, the formation of **2e** was confirmed by the NMR spectrum of an aqueous solution of the reaction mixture. The spectrum revealed only two kinds of peaks, consisting of a singlet at δ 2.93 ppm and a doublet at δ 1.40 ppm. (A third peak might be hidden behind the absorption peak of water.) The peak at δ 2.93 ppm and the peak at δ 1.40 ppm can be assigned to, respectively, the *N*-methyl and 5-methyl protons of **2e** on the basis of the integral ratio and the chemical shifts, but the 5-methyl protons of the unreacted tetrazolium iodide, **1e**, also have a singlet peak at δ 2.93 ppm. For the further assignment of these peaks a similar reduction of **1e** was attempted in deuterium oxide; the reduced product, **5**, showed only a singlet peak at δ 2.93 ppm. Our previous report has revealed that the rapid hydrogen-deuterium exchange of the 5-methyl protons in 1,4,5-trimethyltetrazolium iodide, **1e**, occurred in a deuterium oxide solution, but no exchange of the 1- and 4-*N*-methyl protons was observed even under strongly basic conditions.[8] Therefore, the singlet peak at δ 2.93 ppm of **5** should be assigned to the 1- and 4-*N*-methyl protons. Similarly, the singlet peak at δ 2.93 ppm of **2e** should be associated not with the 5-methyl protons of the

1) R. E. Lyle and P. S. Anderson, "Advances in Heterocyclic Chemistry," Vol. 6, ed. by A. R. Katritzky and A. J. Boulton, Academic Press, New York and London (1966), p. 45.

2) G. F. Bovicine and D. J. Hennessy, *J. Amer. Chem. Soc.*, **79**, 6325 (1957); H. Hirano, *J. Pharm. Soc. Jap.*, **78**, 1387 (1958).

3) G. M. Clarke and P. Sykes, *J. Chem. Soc., C*, **1967**, 1269, 1141: *Chem. Commun.*, **1965**, 370.

4) A. V. El'tsov and N. M. Omar, *Zh. Org. Khim.*, **4**, 711 (1968): *Chem. Abstr.*, **69**, 2903 (1968).

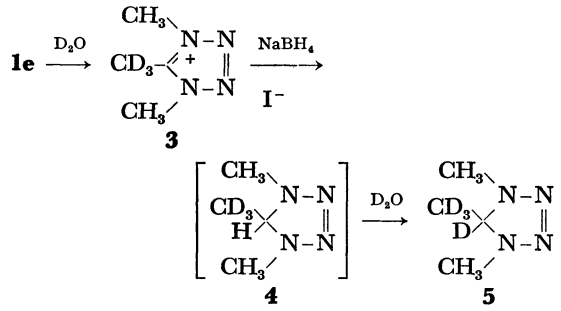
5) D. S. Kemp, *Tetrahedron*, **23**, 2001 (1967).

6) J. L. Aubagnac, *Bull. Soc. Chim. Fr.*, **1967**, 2184.

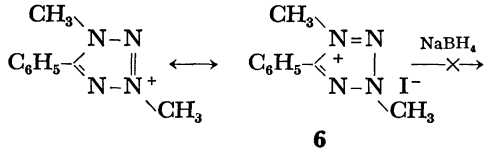
7) E. F. Godefroi, *J. Org. Chem.*, **33**, 860 (1968).

8) T. Isida, S. Fujimori, K. Nabika, K. Sisido, and S. Kozima, This Bulletin, **45**, 1246 (1972).

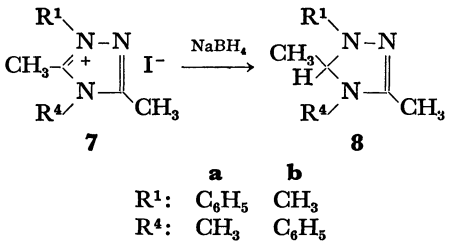
unreacted **1e**, but with the *N*-methyl protons of **2e**. The splitting of the peak of the 5-methyl protons of **2e** into a doublet suggested the presence of a C^5-proton peak hidden behind the absorption peak of water.



Our previous report[9] has shown that the reaction of 1-methyl-5-phenyltetrazole with methyl iodide gave a mixture of 1,3-dimethyl- and 1,4-dimethyl-5-phenyltetrazolium iodide (**6** and **1a**) at room temperature when the reaction continued for a long time. When a mixture of **1a** and **6**[10] was treated with sodium borohydride, the 1,4-dimethyl salt, **1a**, was reduced to 1,4-dimethyl-Δ^2-tetrazoline, **2a**, but the 1,3-dimethyl salt, **6**, remained unchanged.

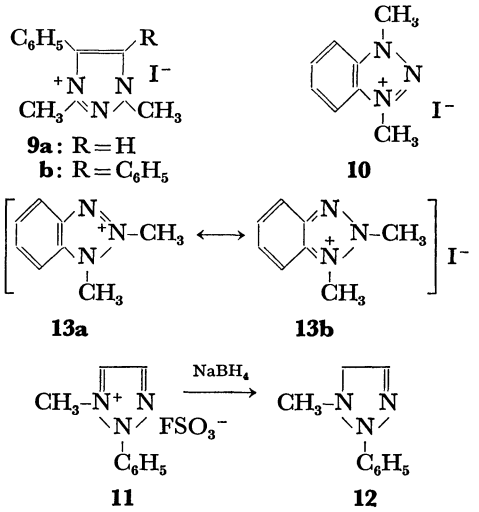


In the reduction of 1,3,4,5-tetrasubstituted 1,2,4-triazolium iodides (**7**),[11] the more electron-deficient 5-carbon atom was attacked by the hydride ion from sodium borohydride. The Δ^2-1,2,4-triazolines (**8**) thus formed showed the presence of the quartet peak of the C^5-proton and the doublet peak assigned to the 5-methyl protons in the NMR spectra.

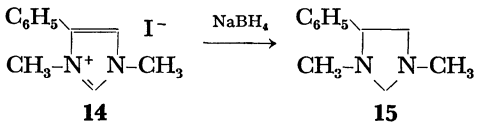


By contrast, the reaction of 4-phenyl- and 4,5-diphenyl-1,3-dimethyl-1,2,3-triazolium iodides (**9**),[12] or 1,3-dimethylbenzotriazolium iodide (**10**)[13] with sodium borohydride gave no reduction product, and each starting iodide was recovered.

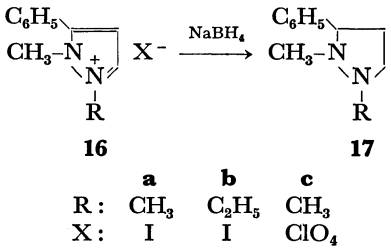
1-Methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (**11**)[14] was reduced to the corresponding Δ^3-triazoline (**12**), which was identified by the NMR spectrum and elemental analysis. However, 1,2-dimethylbenzotriazolium iodide (**13**)[13] yielded no reduction product.



Under conditions similar to those of the above reduction, the treatment of 1,3-dimethyl-4-phenylimidazolium iodide (**14**) gave only one product, 1,3-dimethyl-4-phenyl-imidazolidine (**15**), although Godefroi[7] reported the formation of a ring-cleaved product in the reduction of 1-benzyl-3-alkylimidazolium iodides.



Analogously, the reduction of 1-alkyl-2-methyl-3-phenylpyrazolium iodide (**16**) yielded 1-alkyl-2-methyl-3-phenylpyrazolidine (**17**). This finding is consistent with the finding of El'tsov in the reduction of pyrazolium perchlorate (**16c**).[4]



We can summarize the results of the sodium borohydride reduction of azolium iodides as follows. In the case of the tetrazolium iodides, the positions of the substituents at the nitrogen atoms of the tetrazole ring determined whether or not reduction occurred, as is shown by the fact that 1,4,5-trisubstituted tetrazolium iodides (**1**) yielded the partially-reduced Δ^2-tetrazolines, while 1,3,5-trisubstituted tetrazolium iodide (**6**) gave no reduction product. The reduction was more complicated in the cases of triazolium salts and benzotriazolium iodides. 1,2,4-Triazolium iodides (**7**) were

9) T. Isida, S. Kozima, K. Nabika, and K. Sisido, *J. Org. Chem.*, **36**, 3807 (1971).

10) 1,3-Dimethyl-5-phenyltetrazolium iodide (**6**) could not be separated from the salt mixture owing to its thermal instability.

11) G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *Chem. Ind.* (London), **1954**, 1458.

12) It was prepared by the reaction of 1-methyl-4-phenyl-1,2,3-triazole with methyl iodide. *Cf.* R. H. Wiley and J. Moffat, *J. Amer. Chem. Soc.*, **77**, 1703 (1955).

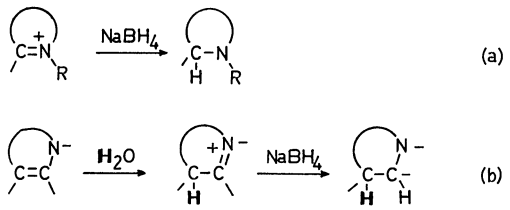
13) F. Krollpfeiffer, A. Rosenberg, and C. Muhlhausen, *Ann.*, **515**, 113 (1935).

14) M. Begtrup and K. V. Poulson, *Acta Chem. Scand.*, **25**, 2087 (1971): The quarterization of 1-substituted triazole with alkyl iodide gave only 1,3-dialkyltriazolium iodide,[12] and 2-substituted triazole gave no quarternary iodide with alkyl iodide.

readily reduced, and the occurrence of the reduction of 1,2,3-triazolium salts depended on the positions of the substituents at the nitrogen atoms, much as in the case of tetrazolium iodides. Δ^3-1,2,3-Triazoline was derived from 1,2-disubstituted 1,2,3-triazolium salt (**11**), whereas 1,3-disubstituted derivative (**9**) was unchanged. No reduction occurred in two kinds of benzotriazolium iodides (**10** and **13**). Both pyrazolium and imidazolium iodides (**14** and **16**) gave the corresponding diazolidine.

Many investigations of the sodium borohydride reduction of pyridinium salts[15] have revealed the mechanism for the formation of the tetrahydropyridines; Clark and Sykes proposed a similar pathway for the reduction of the thiazolium salts to thiazolidines.[3]

An analogous pathway could be applied to the sodium borohydride reduction of the azolium iodides. All of the azolium salts which can be reduced contain an immonium-ion moiety in the formula of the mesomerism, as is shown by the examples of **1**, **7**, **11**, **14**, and **16**. The other azolium salts (**6** and **9**) which cannot be reduced, by contrast, involve no immonium-ion moiety in the formula. The hydride ion derived from sodium borohydride attacks an electron-deficient carbon of the immonium-ion system in an azolium salt to form an azoline (Reaction a). When there remains an enamine moiety in the structure of a formed azoline, the enamine system re-forms an immonium-ion system with protonation by the protic solvent and is subsequently reduced to azolidine as the final product (Reaction b). The further reduction of both pyrazoline and imidazoline gave the corresponding diazolidines, but neither Δ^2-1,2,4- and Δ^3-1,2,3-triazolines nor Δ^2-tetrazolines could be reduced due to the lack of an enamine moiety in each ring system. The above pathway may be applied to the cases of benzoazolium salts, though the partial reduction product (benzoazoline) was not further reduced, because the C=C



double bond in the benzoazoline is included in the resonance system of the benzene ring and cannot be attacked by sodium borohydride in a protic solvent, much as in the case of dimethylaniline. These examples are typical of the reduction of benzoisooxazolium[5] and benzoimidazolium salts,[6] which gave the corresponding dihydrobenzoazoles. The fruitless reduction of 1,3-disubstituted benzotriazolium iodide (**10**) can be explained by the lack of the immonium-ion moiety in its canonical formula, so that it was not reduced with sodium borohydride and was recovered. One of the canonical formulae (**13b**) of 1,2-disubstituted benzotriazolium iodide (**13**) involves an immonium-ion moiety, but the absence of any reduction of **13** suggests that **13b** may contribute to its resonance in the salt scarcely at all.

15) A. R. Katritzky, *J. Chem. Soc.*, **1955**, 2586; and references in Ref. 1.

Experimental

The melting points were taken on Yanagimoto Seisakusho Micro Melting Point Apparatus, Serial No. 1417. The NMR spectra were obtained on a Japan Electron Optics C-60-H Spectrometer, operating at 60 MHz and with TMS (in $CDCl_3$) or DSS (in D_2O) as the internal reference. The UV spectra were measured in ethanol on a Shimadzu-MPS Spectrophotometer. The elemental analyses were performed by Mrs. K. Fujimoto of this labaratory on a Yanagimoto Autoanalyzer CHN Corder MT-1. The mass spectra were obtained on a Hitachi RMS-4 Mass Spectrometer.

*Reduction of 1,4-Dimethyl-5-phenyltetrazolium Iodide (**1a**) with Sodium Borohydride ($NaBH_4$).* To a solution of 395 mg (1.27 mmol) of **1a**[9] in 10 ml of 95% ethanol at room temperature, we added, portion by portion, 241 mg (6.35 mmol) of $NaBH_4$. After the mixture had ceased foaming, it was heated under reflux for 2 hr (or stirred for 5 hr at room temperature). The solvent was then removed *in vacuo*, and 10 ml of water was added to the residue. The aqueous layer was extracted twice with 20 ml portions of ether; the ether was then evaporated off to dryness *in vacuo* without heating to give 1,4-dimethyl-5-phenyltetrazoline (**2a**) as colorless crystals; 200 mg (89.5%); mp 53.0—53.5°C, NMR ($CDCl_3$) δ 7.46 (s, 5H, 5-phenyl), 4.48 (s, 1H, C^5-proton), 2.86 ppm (s, 6H, *N*-methyl).

Found: C, 61.49; H, 6.82; N, 31.57%. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.86; N, 31.80%.

UV (EtOH) λ_{max} 281 nm (ε_{max} 1160).

The heating of **2a** at 120°C for 5 min in a sealed tube gave *N*-benzalmethylamine quantitatively; it was identified by comparison with an authentic sample.[16] The evolved gas was determined to be methyl azide by means of presence in its mass spectrum of a parent ion at *m/e* 57. Similarly, the thermolysis of **2d** gave *N*-ethylideneaniline and methyl azide.

*Reduction of 1-Ethyl-4-methyl-5-phenyltetrazolium Iodide (**1b**).* An analogous treatment of **1b**[9] gave a liquid, **2b**, in a 66.8% yield. Tlc (silica gel) analyses displayed one spot; R_f= 0.50, 9:1 *n*-hexane–ethyl acetate. NMR ($CDCl_3$) δ 7.50 (m, 5H, 5-phenyl), 4.65 (s, 1H, C^5-proton), 3.15 and 1.17 (q and t, 2H and 3H, 1-ethyl), 2.85 ppm (s, 3H, 4-methyl).

Found: C, 63.36; H, 7.36; N, 29.28%. Calcd for $C_{10}H_{14}N_4$: C, 63.13; H, 7.42; N, 29.45%.

*Reduction of 1,4-Diethyl-5-phenyltetrazolium Iodide (**1c**).* An analogous treatment of **1c**[9] gave a liquid, **2c** (R_f=0.56, 9:1 *n*-hexane–ethyl acetate), in a 60.5% yield. NMR ($CDCl_3$) δ 7.45 (m, 5H, 5-phenyl), 4.80 (s, 1H, C^5-proton), 3.11 and 1.13 ppm (q and t, 4H and 6H, *N*-ethyl).

Found: C, 64.27; H, 8.18; N, 27.55%. Calcd for $C_{11}H_{16}N_4$: C, 64.67; H, 7.90; N, 27.43%.

*Preparation of 1,5-Dimethyl-4-phenyltetrazolium Iodide (**1d**).* The reaction of 2 g of 5-methyl-1-phenyltetrazole[17] with an excess of methyl iodide in a sealed glass tube at 100°C for 5 hr gave **1d**;[18] mp 205—206°C.

Found: C, 35.62; H, 3.53; N, 18.68%. Calcd for $C_9H_{11}N_4I$: C, 35.78; H, 3.67; N, 18.55%.

NMR (D_2O) δ 7.80 (s, 5H, 4-phenyl), 4.45 (s, 3H, 1-methyl), 3.00 ppm (s, 3H, 5-methyl).

16) R. B. Moffett, "Organic Syntheses," Vol. 34, 1954, p. 64.

17) E. K. Harvill, R. M. Herbst, E. C. Schreiner, and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

18) G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *Chem. Ind.* (London), **1955**, 1355.

*Reduction of 1,5-Dimethyl-4-phenyltetrazolium Iodide (**1d**).* An analogous treatment of **1d** gave a liquid, **2d** (R_f=0.45, 9:1 *n*-hexane–ethyl acetate), in a quantitative yield. NMR ($CDCl_3$) δ 7.35—6.95 (m, 5H, 4-phenyl), 4.15 (q, 1H, C^5-proton), 3.05 (s, 3H, 1-methyl), 1.52 ppm (d, 3H, 5-methyl). UV (EtOH) λ_{max} 304 nm (ε_{max} 3910), 222 nm (2980).

Found: C, 61.57; H, 6.89; N, 31.64%. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.86; N, 31.80%.

*Reduction of 1,4,5-Trimethyltetrazolium Iodide (**1e**) in H_2O and D_2O.* The reaction of **1e** with $NaBH_4$ was carried out at room temperature in an NMR tube. After 2 hr, the NMR spectrum showed two kinds of peaks, at δ 2.93 (s) and 1.40 ppm (d); their integral ratio was 2:1.

A solution of **1e** in D_2O was kept at room temperature in an NMR tube. After one week, the singlet at δ 2.93 ppm disappeared. To the above solution we then added $NaBH_4$, and it was kept at room temperature. After 2 hr, the remaining singlet at δ 4.30 ppm disappeared and the singlet at δ 2.93 ppm reappeared.

*Reaction of the Mixture of 1,4-Dimethyl and 1,3-Dimethyl-5-phenyltetrazolium Iodide (**1a** and **6**) with $NaBH_4$ in $CDCl_3$.* A mixture of **1a** and **6**[10] was treated with $NaBH_4$ in $CDCl_3$. After 5 hr, the peak at δ 4.28 ppm disappeared, and instead two peaks, at δ 4.48 and 2.87 ppm (1:6), of **2a** appeared. However, the two peaks at δ 4.75 and 4.52 ppm assigned to the 1- and 3-methyl protons of **6** remained.

*Preparation of 1-Phenyl-3,4,5-trimethyl-1,2,4-triazolium Iodide (**7a**).*[11] We obtained **7a** by heating a solution of 1-phenyl-3,5-dimethyl-1,2,4-triazole in excess methyl iodide in a sealed glass bottle at 100°C for 32 hr. After cooling, the reaction mixture was washed with benzene. The residue was dissolved in minimum acetone, and to the acetone solution we added hexane to precipitate crystals. By the additional precipitation procedure we obtained yellow crystals (mp 169—172°C) in a quantitative yield. NMR ($CDCl_3$) δ 7.67 (m, 5H, *N*-phenyl), 3.84 (s, 3H, 4-methyl), 2.74 (s, 3H, 5-methyl), 2.64 ppm (s, 3H, 3-methyl).[19]

Found: C, 41.96; H, 4.45; N, 12.89%. Calcd for $C_{11}H_{14}N_3I$: C, 41.92; H, 4.48; N, 13.33%.

*Reduction of **7a**.* The treatment of **7a** with $NaBH_4$ gave, in a 70% yield, an unstable liquid whose structure was determined to be 1-phenyl-3,4,5-trimethyl-1,2,4-triazoline (**8a**) by studying its NMR spectrum; δ 7.6—6.8 (m, 5H, 1-phenyl), 4.88 (q, 1H, C^5-proton), 2.73 (s, 3H, 4-methyl), 1.97 (s, 3H, 3-methyl), 1.52 ppm (d, 3H, 5-methyl), and the mass spectrum: a parent ion at *m/e* 189.

*Preparation of 1,3,5-Trimethyl-4-phenyl-1,2,4-triazolium Iodide (**7b**).* The treatment of 3,5-dimethyl-4-phenyl-1,2,4-triazole[20] with excess methyl iodide in a sealed glass bottle at 100°C for 24 hr gave colorless crystals; mp 106—107°C. NMR (D_2O) δ 2.37 (s, 3H, 3-methyl), 2.58 (s, 3H, 5-methyl), 4.07 (s, 3H, 1-methyl), 7.5—8.0 ppm (m, 5H, 4-phenyl).[21]

Found: C, 41.40; H, 4.51; N, 12.99%. Calcd for $C_{11}H_{14}N_3I$: C, 41.92; H, 4.48; N, 13.33%.

*Reduction of **7b**.* Similarly, an unstable liquid (86%) was obtained from **7b**. Its structure was determined to be 1,3,5-trimethyl-4-phenyl-1,2,4-triazoline (**8b**) by studying its NMR spectrum; δ 1.37 (d, 3H, 5-methyl), 1.80 (s, 3H, 3-methyl), 2.72 (s, 3H, 1-methyl), 4.45 (q, 1H, C^5-proton), 7.0—7.5 ppm (m, 5H, 4-phenyl), and the mass spectrum: a parent ion at *m/e* 189.

Attempts at the elemental analysis of **8a** and **8b** were given up because of their instability even at room temperature.

*Reduction of 1-Methyl-2-phenyl-1,2,3-triazolium Fluorosulfonate (**11**).*[14] The reaction of 120 mg (0.463 mmol) of **11** with 30 mg of $NaBH_4$ was also carried out at room temperature in 95% methanol. The conventional treatment of the reaction product gave a viscous liquid (R_f=0.85, 9:1 methylene chloride–ethyl acetate), which was identified as 1-methyl-2-phenyl-1,2,3-triazoline-Δ^3; 69 mg (92.2%); n_{26}^D 1.5738. NMR ($CDCl_3$) δ 2.67 (s, 3H, *N*-methyl), 3.76 (s, 2H, C^5-protons), 6.7—7.5 ppm (m, 6H, C^4-proton and *N*-phenyl).

Found: C, 67.00; H, 6.94; N, 26.06%. Calcd for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07%.

*Reduction of 1,3-Dimethyl-4-phenylimidazolium Iodide (**14**).* The treatment of **14** with excess $NaBH_4$ (for 5 hr at room temperature or for 2 hr under reflux) gave a thermally stable liquid. It was distilled at 120°C/20 mmHg (76.9%), and its structure was determined to be 1,3-dimethyl-4-phenylimidazolidine (**15**) by studying its NMR spectrum ($CDCl_3$); δ 7.30 (s, 5H, 4-phenyl), 2.40 (s, 3H, *N*-methyl), 2.20 (s, 3H, *N*-methyl), 2.40—3.90 ppm (m, 5H, ring protons) and the mass spectrum *m/e* 176 (M^+). Its picrate was recrystallized from ethanol; mp 165—167°C.

Found: C, 50.77; H, 4.99; N, 17.31%. Calcd for $C_{17}H_{19}N_5O_7$: C, 50.37; H, 4.72; N, 17.28%.

*Reduction of 1,2-Dimethyl-3-phenylpyrazolium Iodide (**16a**).* By an analogous treatment of **16a**, 1,2-dimethyl-3-phenylpyrazolidine (**17a**) (73.1%) was obtained; bp 140°C/21 mmHg (lit,[22] 80°C/1.2 mmHg); mass spectrum *m/e* 176 (M^+). The recrystallization of its picrate from ethanol gave yellow crystals; mp 178—180°C (lit,[22] 177—179°C).

19) In deuterium oxide solution of **7a**, the rate of H/D exchange reaction of methyl protons at δ 2.74 ppm was faster than that at δ 2.64 ppm, so that the former is assigned to the more electron-deficient 5-methyl protons and the latter is to the 3-methyl protons.

20) R. Meyer, Ger. 579944 (1933): *Chem. Abstr.*, **27**, 4541 (1933).

21) The assignment of the peaks was determined as similarly as **7a**.

22) J. L. Aubagnac, J. Elguero, and R. Jacquier, *Bull. Soc. Chim. Fr.*, **1969**, 3302.