Theophylline (IIc)——Yield: 97%. Needles (from H_2O), mp 265—268°. UV $\lambda_{max}^{H_2O}$ mμ (log ε): 272 (4.01); $\lambda_{max}^{0.1N\ NaOH}$ mμ (log ε): 275 (4.08); $\lambda_{max}^{0.1N\ HCl}$ mμ (log ε): 270 (3.99).

Reaction of Uric-8-^{14}C Acid with TMAF——A mixture of 0.35 g (0.0021 mole) of uric-8-^{14}C acid (5.55×10^8 dpm/mole) prepared from 4,5-diaminouracil and urea-^{14}C and 3.5 g (0.01 mole as HCO_2H) of TMAF was heated at 175—180° for 5 hr. The product obtained by usual treatment was repeatedly recrystallized from a large amount of water till its paper chromatogram (eluent: 16% aq. ammonium bicarbonate) gave a single spot. The resulting pure crystals were assayed for radioactivity (3.03×10^7 dpm/mole).

Radioactivity Measurement——The radioactivity was measured by Liquid Scintillation Counter Aloka LSC-601. Samples for the radioactivity measurement were prepared as follows. To 14 ml of the scintillator solution (4 g of DPO and 0.1 g of POPOP in 1000 ml of toluene) was added 1 ml of the solution of 5.427 mg of uric-8-^{14}C acid (or 5.266 mg of xanthine) and 5 ml of Hyamine 10X-10H. The counting efficiency was 74.7—77.0%.

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The Base-induced β-Elimination Reaction of 1,1,1-Trisubstituted Hydrazinium Salts

Yasumitsu Tamura, Jun-ichi Minamikawa, Osamu Nishikawa, and Masazumi Ikeda

Faculty of Pharmaceutical Sciences, Osaka University[1]

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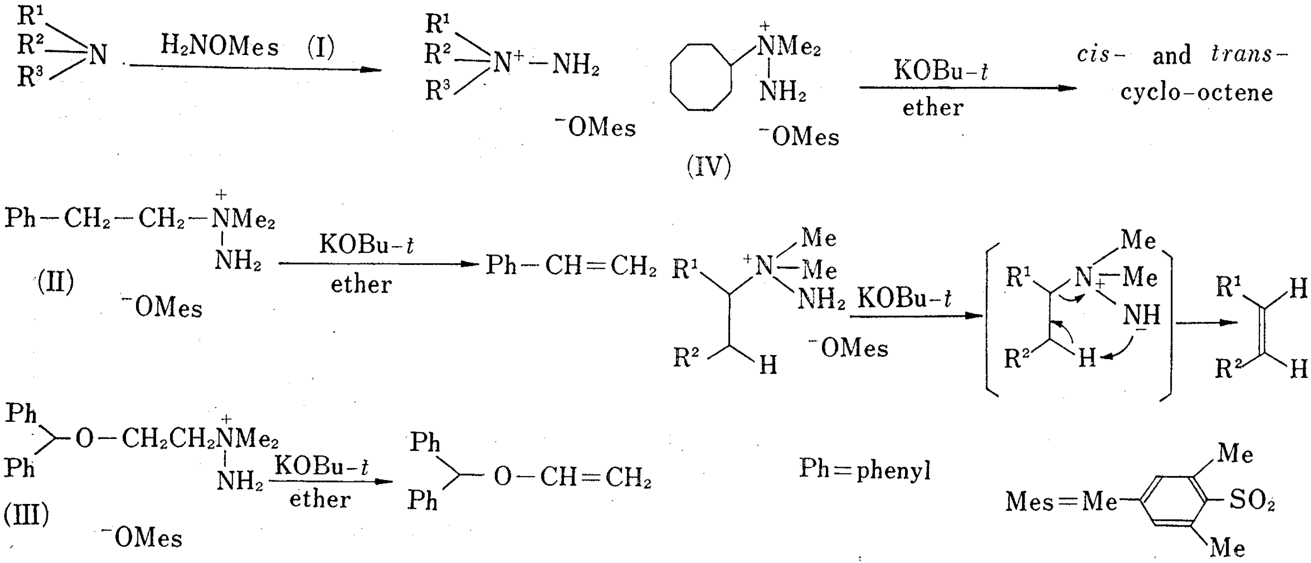
It has been established that pyrolysis of amine oxides[2] and amine imides[3] causes almost exclusively a *cis*-elimination *via* a five-membered cyclic transition state. However, there



Chart

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[1] Location: *6-1-1, Toneyama, Toyonaka, Osaka.*

[2] D.J. Cram and J.E. McCarty, *J. Am. Chem. Soc.*, **76**, 5740 (1954); R.D. Bach, D. Andrzejewski, and L.R. Dusold, *J. Org. Chem.*, **38**, 1742 (1973).

[3] D.G. Morris, B.W. Smith, and R.J. Wood, *J. Chem. Soc. Chem. Commun.*, **1971**, 1167.

has been no report appeared on the elimination mode of the related amine imines giving olefins. The present study of the base-induced β-elimination reaction⁴⁾ of 1,1,1-trisubstituted hydrazinium salts showed that the amine imine elimination also proceeds through a *cis*-elimination.

1,1-Dimethyl-1-(2-phenylethyl)hydrazinium mesitylenesulfonate (II), 1,1-dimethyl-1-(2-diphenylmethoxyethyl)hydrazinium mesitylenesulfonate (III) and 1,1-dimethyl-1-cyclo-octylhydrazinium mesitylenesulfonate (IV) were prepared from the parent amines and O-mesitylenesulfonylhydroxylamine (MSH) (I) according to the previously reported method.⁵⁾ Treatment of compounds (II, III and IV) with potassium *tert*-butoxide in ether gave styrene (39%), diphenylmethyl vinyl ether (41%) and cyclo-octene (41%), respectively. The cyclo-octene was found to consist of 96% *cis*- and 4% *trans*-cyclo-octene by gas chromatographic analysis on 15% dioctyl sebacate.

This result parallels those of pyrolysis of the corresponding amine oxides⁶⁾ and amine acetimides,³⁾ and established an intramolecular mechanism involving a five-membered cyclic transition state for the elimination of amine imines.

Experimental⁷⁾

Preparation of Hydrazinium Salts——General Procedure: An ice-cooled stirred solution of a tertiary amine (1 mmole) in CH_2Cl_2 (2—3 ml). The mixture was allowed to stand at room temperature for 5 min and a white precipitate was collected. The following hydrazinium salts were prepared:

1,1-Dimethyl-1-(2-phenylethyl)hydrazinium mesitylenesulfonate (II) was obtained from N,N-dimethyl-2-phenylethylamine, mp 212° (from CH_2Cl_2), in 77% yield. IR $\nu_{\max}^{\mathrm{KCl}}$ cm^{-1}: 3250, 3150 (NH_2). *Anal.* Calcd. for $C_{19}H_{28}O_3N_2S$: C, 62.62; H, 7.74; N, 7.69. Found: C, 62.59; H, 7.73; N, 7.58.

1,1-Dimethyl-1-(2-diphenylmethoxyethyl)hydrazinium mesitylenesulfonate (III) was obtained from diphenhydramine, mp 162° (from CH_2Cl_2), in 94% yield. IR $\nu_{\max}^{\mathrm{KCl}}$ cm^{-1}: 3250, 3150 (NH_2). *Anal.* Calcd. for $C_{26}H_{34}O_4N_3S$: C, 66.36; H, 7.28; N, 5.94. Found: C, 66.23; H, 7.22; N, 5.81.

1,1-Dimethyl-1-cyclo-octylhydrazinium mesitylenesulfonate (IV) was obtained from N,N-dimethyl-cyclo-octylamine, mp 199—200° (from CH_2Cl_2-$(C_2H_5)_2O$), in 96% yield. IR $\nu_{\max}^{\mathrm{KCl}}$ cm^{-1}: 3250, 3150 (NH_2). *Anal.* Calcd. for $C_{19}H_{34}O_3N_2S$: C, 61.59; H, 9.25; N, 7.56. Found: C, 61.78; H, 9.33; N, 7.48.

β-Elimination Reaction of Hydrazinium Salts——General Procedure: A suspension of a hydrazinium salt (1 mmole) and potassium *tert*-butoxide (1 mmole) in anh. ether (20 ml) was refluxed for 6 hr. After removal of a white precipitate, the filtrate was washed with 10% hydrochloric acid (5 ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residual oil was distilled to give a desired olefin.

The following olefins were prepared and identified by the comparison of their IR and NMR spectra with those of authentic samples.

Styrene was obtained from compound (II) in 39% yield.

Diphenylmethyl vinyl ether⁸⁾ was obtained from compound (III) in 41% yield. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640 (C=C). NMR ($CDCl_3$) τ: 2.70 (10H, singlet, aromatic), 3.55 (1H, doublet of doublets, $J=7$ and 14 Hz, ${}^{\underline{\mathrm{H}}}_{-\mathrm{O}}\rangle{=}\langle{}^{\mathrm{H}}_{\mathrm{H}}$), 4.18 (1H, singlet, $Ph_2C\underline{H}O$), 5.70 (1H, doublet of doublets, $J=2$ and 14 Hz, ${}^{\mathrm{H}}_{-\mathrm{O}}\rangle{=}\langle{}^{\mathrm{H}}_{\underline{\mathrm{H}}}$), 5.95 (1H, doublet of doublets, $J=2$ and 7 Hz, ${}^{\mathrm{H}}_{-\mathrm{O}}\rangle{=}\langle{}^{\underline{\mathrm{H}}}_{\mathrm{H}}$).

Cyclo-octene was obtained from compound (IV) in 41% yield. The product was found to consist of 96% *cis* and 4% *trans* cyclo-octene by GLC analysis on a 15% dioctyl sebacate column at 60°. Authentic *cis*- and *trans*-cyclo-octenes were obtained by Hofmann elimination of N,N,N-trimethylcyclo-octylammonium hydroxide.⁶⁾

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7) Melting points are uncorrected. Infrared (IR) spectra were measured on a Hitachi-EPI G2 spectrophotometer and nuclear magnetic resonance (NMR) spectra on a Hitachi R-20 instrument. Gas-liquid chromatography (GLC) analyses were carried out with a Hitachi gas chromatograph Model K53.

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