A Stable Intermediate in the Sommelet–Hauser Rearrangement of 1-Methyl-2-phenylpiperidinium 1-Methylides: The Improved Sommelet–Hauser Rearrangement

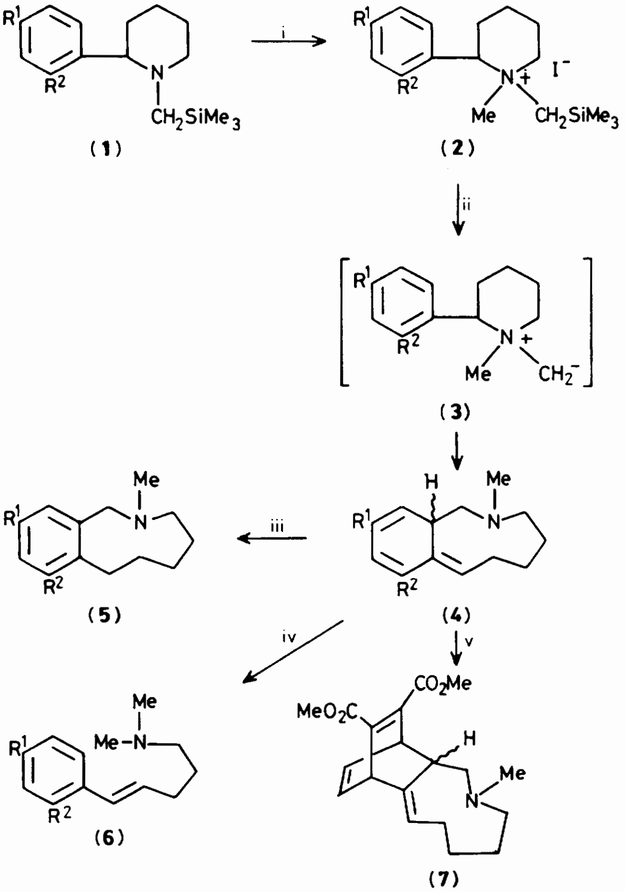
Naohiro Shirai, Fumihiko Sumiya, Yoshiro Sato,* and Mikiko Hori

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

Reaction of 1-methyl-1-(trimethylsilyl)methyl-2-(substituted phenyl)piperidinium iodides (**2**) with caesium fluoride gave high yields of 2-methyl-1,3,4,5,6,11a-hexahydro-2*H*-2-benzazonines (**4**) which are regarded as unstable intermediates in the Sommelet–Hauser rearrangement of ammonium ylides (**3**) to 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine derivatives (**5**).

The Sommelet–Hauser rearrangement of ammonium ylides is applicable to the synthesis of large ring cyclic amines. For example, the hexahydrobenzazonine (**5a**) was prepared in high yield by the reaction of 1,1-dimethyl-2-phenylpiperidinium iodide with $NaNH_2$ in liquid NH_3.[1] We previously reported the fluoride-ion assisted desilylation of (substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium halides to afford high yields of the Sommelet–Hauser rearrangement products in a non-basic medium at room temperature.[2] Application of this method to ring expansion reactions should offer a useful synthetic route to large ring cyclic amines having various functional groups.

When the 2-phenylpiperidine (**1a**) was quaternized with methyl iodide at 60 °C and then treated with caesium fluoride in *N*,*N*-dimethylformamide (DMF) at room temperature for 20 h, the hexahydrobenzazonine (**4a**) was obtained in 74% yield from (**1a**) instead of the expected Sommelet–Hauser rearrangement product (**5a**). The structure of (**4a**) was determined by 2-D COSY 400 MHz n.m.r., high resolution mass, and u.v. spectroscopy.† Although the triene (**4a**) is regarded as an unstable intermediate proceeding from (**3a**) to (**5a**) in the Sommelet–Hauser rearrangement, it was possible to store a hexane solution of (**4a**) without appreciable decomposition for more than a month in a refrigerator. Compound (**4a**) was isomerized to (**5a**) by proton migration in 10% KOH–ethanol at room temperature [yield 58% from (**1a**)], and to the ring-opened product (**6a**) on heating at 150 °C in xylene. Further, (**4a**) reacted with dimethyl acetylenedicarboxylate to give the Diels–Alder addition product (**7**) in benzene at 50 °C [35% from (**1a**)].



a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = Me$
c; $R^1 = Me, R^2 = H$

Scheme 1. *Reagents*: i, MeI, DMF, 60 °C; ii, CsF, DMF, room temp.; iii, 10% KOH in EtOH, room temp.; iv, xylene, reflux; v, $MeO_2CC{\equiv}CCO_2Me$, benzene, 50 °C.

Similar treatment of *ortho*- or *para*-methyl substituted analogues (**1b**) and (**1c**) gave the corresponding triene intermediates (**4b**) and (**4c**), both of which were isomerized to (**5b**) and (**5c**) by treatment with alkali [(**5b**), 47% from (**1b**); (**5c**), 47% from (**1c**)].

Hauser *et al.* isolated an exocyclic methylene cyclohexadiene having a triene structure similar to that of (**4**) by the reaction of (2,6-dimethylbenzyl)trimethylammonium halide with sodium amide in liquid ammonia.[3] However, this compound does not possess the hydrogen needed to restore ring resonance by proton migration. Recently, an interesting intermediate having a triene structure was isolated in a sulphur ylide rearrangement in dimethoxyethane by Padwa.[4]

The triene intermediates (**4a**—**c**) are unexpectedly stable, and their potential as intermediates in organic synthesis is being studied.

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References

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† (**4a**), viscous oil (could not be distilled); ^1H n.m.r. δ ($CDCl_3$) 1.28 (m, 1H), 1.50—1.65 (m, 3H), 2.10 (m, 2H), 2.35 (s, 3H), 2.45 (m, 2.92 (m, 1H), 3.45 (br. s, 1H), 5.64 (m, 3H), 5.87 (dd, 1H, *J* 5.5, 9.5 Hz), and 6.00 (d, 1H, *J* 9.5 Hz); ^{13}C n.m.r. δ ($CDCl_3$) 24.7 (t), 27.2 (t), 27.4 (t), 40.0 (d), 45.9 (q), 56.5 (t), 61.5 (t), 119.7 (d), 122.3 (d), 130.2 (d), 130.5 (d), 134.3 (d), and 138.4 (s); $\lambda_{max.}$ (hexane) 318 (log ε 3.8); *m/z* 189.1520 (M^+); $C_{13}H_{19}N$ requires 189.1517.