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 NaNH₂ in liquid NH₃.¹ 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





Scheme 1. Reagents: i, MeI, DMF, 60 °C; ii, CsF, DMF, room temp.; iii, 10% KOH in EtOH, room temp.; iv, xylene, reflux; v, MeO₂CC=CCO₂Me, benzene, 50 °C.

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)].

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.

Recieved, 11th November 1987; Com. 1641

References

- D. Lednicer and C. R. Hauser, J. Am. Chem. Soc., 1957, 79, 4449; A. Benattar, D. Barbry, B. Hasiak, and D. Couturier, J. Heterocycl. Chem., 1981, 18, 63.
- 2 M. Nakano and Y. Sato, J. Chem. Soc., Chem. Commun., 1985, 1684, J. Org. Chem., 1987, 52, 1844; N. Shirai and Y. Sato, ibid., 1988, 53, 194.
- 3 C. R. Hauser and D. N. Van Eenam, J. Am. Chem. Soc., 1957, 79, 5512.
- 4 A. Padwa and J. R. Gasdaska, J. Org. Chem., 1986, 51, 2857.

† (**4a**), viscous oil (could not be distilled); ¹H n.m.r. δ (CDCl₃) 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); ¹³C n.m.r. δ (CDCl₃) 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); λ_{max}. (hexane) 318 (log ε 3.8); *mlz* 189.1520 (*M*⁺); C₁₃H₁₉N requires 189.1517.

J. CHEM. SOC., CHEM. COMMUN., 1988

370