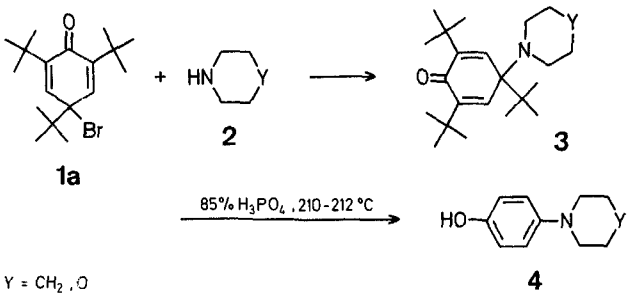
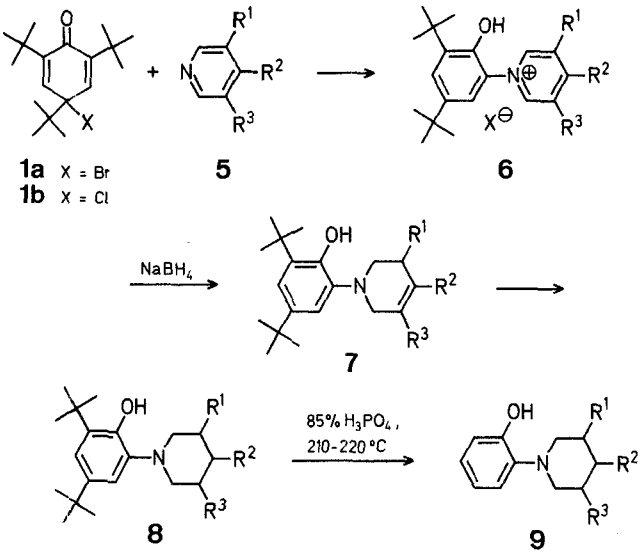


We now describe a related convenient preparation of several 2-piperidinophenols (**9**) from **1** in four steps.



The preparation of **8** from **1** and **5** was described in the previous paper[3]. When compounds **8a–d** were heated in 85% phosphoric acid for 3 h, the expected 2-piperidinophenols **9a–d** were obtained in good yields.

2-Piperidinophenols (9); General Procedure:

A mixture of the 4,6-di-*t*-butyl-2-piperidinophenol (**8**; 10 mmol) and 85% phosphoric acid (20 ml) is heated at 210–220 °C for 2 h, then allowed to cool to room temperature, and poured into water (100 ml). The mixture is made slightly alkaline with sodium carbonate and extracted with chloroform (4 × 100 ml). The extract is dried with sodium sulfate and evaporated in vacuo to leave crude **9**. Products **9a** and **9b** are purified by recrystallization from methanol/water; product **9c** is purified by column chromatography on silica gel (Wako gel C-300) using benzene as eluent followed by recrystallization from ethanol/water. The crude product **9d** is subjected to column chromatography on silica gel (Wako gel C-300) using benzene as eluent; the resultant oily **9d** is converted into its hydrochloride.

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Selective Preparations; 34[1]. A Convenient Preparation of 2-Piperidinophenols

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We recently reported[2] that 4-piperidino- and 4-morpholinophenols (**4**) can be prepared by acid-catalyzed de-*t*-butylation of the corresponding 4-amino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienones (**3**) which are readily obtained from the reaction of 4-bromo-2,4,6-tri-*t*-butyl-2,5-cyclohexadienone (**1a**) with the amines **2**.

Table. 2-Piperidinophenols (**9**)

9	R^1	R^2	R^3	Yield[a] [%]	m.p.[b] [°C]	m.p. (Lit.) or Molecular formula[c]	Appearance
a	H	H	H	95	70–72°	70–72°[4]	pale-yellow cubes from methanol/water
b	CH_3	H	H	88	51–53°	$C_{12}H_{17}NO$ (191.3)	colorless cubes from methanol/water
c	H	CH_3	H	33	82–84°	$C_{12}H_{17}NO$ (191.3)	colorless plates from ethanol/water
d	CH_3	H	CH_3	78	(hydrochloride: 265–268HO)	[$C_{13}H_{19}NO \cdot HCl$ (241.8)]	**9d**: viscous colorless oil (**9d**·HCl: colorless needles from ethyl acetate/methanol)

[a] Yield of isolated product.

[b] Uncorrected.

[c] The microanalyses (**9d** as hydrochloride) were in satisfactory agreement with the calculated values: C, ±0.08; H, ±0.24; N, ±0.17.

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[1] Part 33: M. Tashiro, Y. Fukuda, T. Yamato, *Heterocycles*, in press.
[2] M. Tashiro, G. Fukata, *Synthesis* **1979**, 602.
[3] G. Fukata, T. Itoh, M. Tashiro, *J. Org. Chem.*, submitted for publication.
[4] A. H. Sommers, S. E. Aaland, *J. Am. Chem. Soc.* **75**, 5280 (1953).

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