Cyclodienones. 7. Preparation and Reduction of 1-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)pyridinium Halides[1,2]

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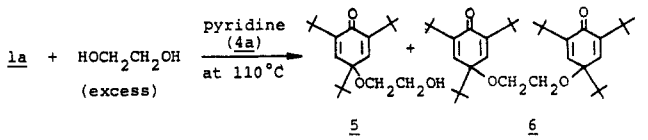
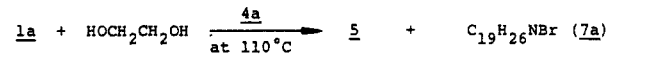
The reactions of 4-bromo- (**1a**) and 4-chloro-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one (**1b**) with compounds such as pyridine (**4a**), α- (**4b**), β- (**4c**), and γ-picoline (**4d**), and 3,5-lutidine (**4e**) were carried out under various conditions to produce the corresponding 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)pyridinium halides (**7**) or their intramolecular salts (**8**). The reduction of **7** and **8** with $NaBH_4$ in methanol afforded in good yields the corresponding tetrahydropyridine derivatives (**21**), which were reduced to *o*-piperidinophenols (**22**) by hydrogenation with Raney Ni (W2) catalyst in high yields. The reaction pathway of the formation of **7** is also discussed.

It has been previously reported that[3-5] 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one (**1a**, Scheme I) reacted with sodium phenolates, alcohols, and amines such as piperidine and morpholine to afford the corresponding 4-substituted 2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-ones (**2**) which were suitable starting materials for the preparation of 4-substituted phenols (**3**).

We have also found that[6] the reaction of **1a** with excess of ethylene glycol (EG) in the presence of pyridine (**4a**) afforded 2-(1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-oxy)ethanol (**5**) and a small amount of 1,2-bis[(1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-yl)oxy]ethane (**6**). However, when an equimolecular amount of EG to **1a** was used, **6** was not obtained, but an unidentified compound (**7a**) which contains a pyridine ring was formed.





This result strongly suggests that **1a** might directly react with **4a** to afford **7a**.

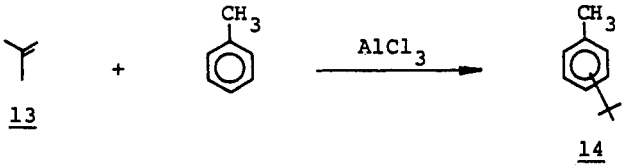
Accordingly, the present work is concerned with the reaction of 4-halo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-ones (**1**) with pyridines **4**.

Results and Discussion

Reaction of 1 with 4. The reactions of 4-bromo- (**1a**)[7,8] and 4-chloro-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one[8] (**1b**) with pyridine (**4a**), α- (**4b**), β- (**4c**), and γ-picoline (**4d**), and 3,5-lutidine (**4e**) were carried out under various conditions, and the results are summarized in Scheme II and Table I.

When a mixture of **1a** and **4a** in molar ratio of 1:2 without solvent was heated at 110 °C for 6 h under a nitrogen atmosphere, the expected compound **7a** was obtained in 20% yield together with known compounds, 2,4,6-tri-*tert*-butyl phenol (**9**),[9] 2,4,6-tri-*tert*-butyl-4-hydroxy-2,5-cyclohexadien-1-one (**11**),[10] 2,6-di-*tert*-butylbenzoquinone (**12**),[11] and isobutylene (**13**).

The compound **13** was generated during this reaction as a gaseous product which was entrained by the nitrogen stream into a mixture of toluene and a small amount of aluminium chloride to give *tert*-butyltoluenes (**14**).[12]



The structure of **7a** was confirmed as 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)pyridinium bromide by its elemental analysis, spectral data, and the chemical conversions described later.

It was also found that addition of EG in this reaction surprisingly increased the yield of **7a**. Adequate amounts of EG, **4a**, and **1a** for the maximum yield of **7a** seemed to be in a molar ratio of 1:2:1, for which the yield increased from 20% to 45% and the reaction time was shortened from 6 to 1 h in comparison with the reaction without EG (see runs 1 and 4 in Table I). Further addition of **4a** had no influence on both the yield of **7a** and the reaction time (run 5). The adequate reaction time was obtained by thin-layer analysis of the reaction mixture. Although the effect of some alcohols other than EG on the yield of **7a** in the reaction of **1a** with **4a** was examined (runs 6-9), these alcohols had less activity than did EG. It should be noted that the reaction of **1a** with **4a** without these alcohols for 1 h, which was enough time for the reaction in the presence of these alcohols; afforded **7a** only in 13% yield (run 10).

There was a possibility in the reaction of **1a** with **4a** in the presence of EG that compound **5** or **6** might be an intermediate for the formation of **7a**. However, the reaction of **5** or **6** with **4a** did not give any products.

Although, from the above results, it might be concluded

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[‡] Department of Molecular Science and Technology.

(1) A part of this paper was reported in a preliminary communication: M. Tashiro and G. Fukata, *Heterocycles*, **12**, 1551 (1979).
(2) Part 6: G. Fukata, N. Sakamoto, and M. Tashiro, submitted for publication in *J. Org. Chem.*
(3) M. Tashiro, H. Yoshiya, and T. Yamato, *Synthesis*, 399 (1978).
(4) M. Tashiro, G. Fukata, and H. Yoshiya, *Synthesis*, 988 (1979).
(5) M. Tashiro and G. Fukata, *Synthesis*, 602 (1979).
(6) G. Fukata and M. Tashiro, *Sōgōrikōgaku Kenkyuka Hōkoku*, **3**, 9 (1981).
(7) E. Müller, K. Ley, and W. Kiedaisch, *Chem. Ber.*, **87**, 1605 (1954).
(8) D. E. Pearson, S. P. Venkaturam, and W. E. Childers, Jr., *Synth. Commun.* **9**, 5 (1979).
(9) M. Tsubota, *Nippon Kagaku Zasshi*, **89**, 602 (1968); *Chem. Abstr.*, **69**, 106083 (1968).
(10) N. Nishinaga, T. Itahara, and T. Matsuura, *Bull. Chem. Soc. Jpn.*, **48**, 1683 (1975).
(11) A. McKillop and B. P. Swann, *Tetrahedron*, **26**, 4031 (1970).
(12) M. Tashiro, G. Fukata, and T. Yamato, *Org. Prep. Proced. Int.*, 8, 263 (1976).
(13) M. Tashiro, H. Yoshiya, and G. Fukata, *J. Org. Chem.*, in press.

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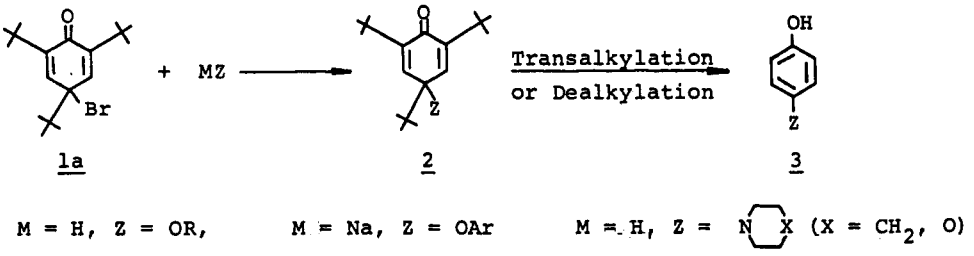
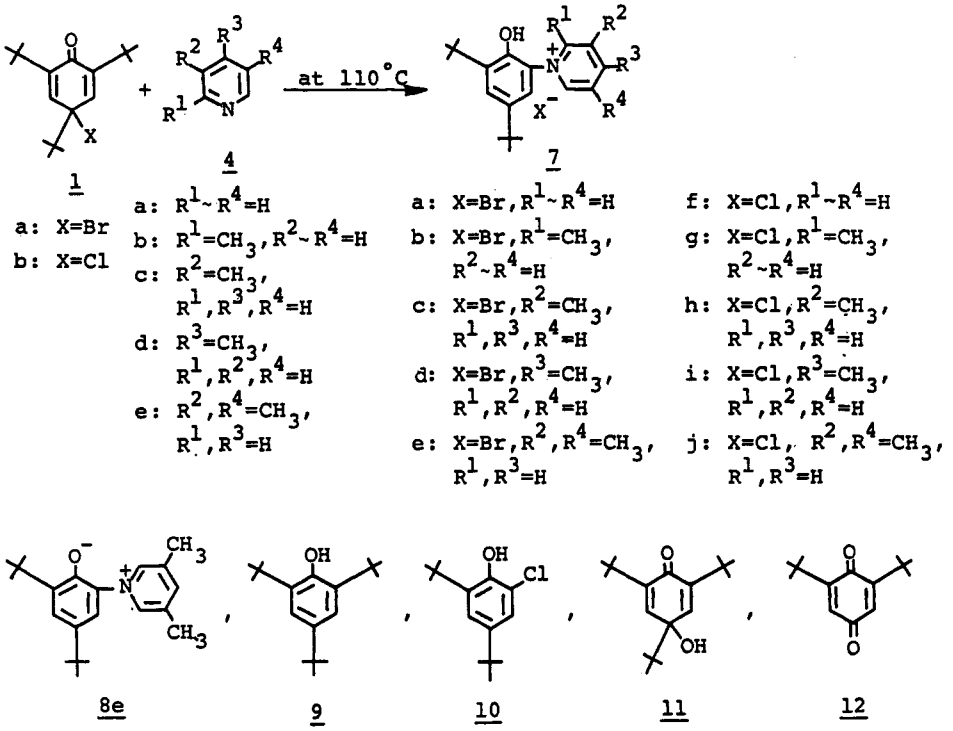
Scheme I



Scheme II



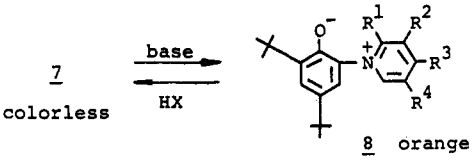
that addition of EG and the alcohols to the reaction of **1a** with **4a** affected the formation of **7a**, it is not clear why such different results are obtained.

The reaction of **1a** with **4b** and **4d** did not give the expected compounds **7b** and **7d**, respectively. In the former case, compounds **5**, **6**, **9**, **11**, and **12** were obtained as described in the previous report.[6] The latter case afforded **9** in good yield in the presence of EG (runs 15 and 16). It should be noted that the reaction of **1a** with **4b** in the absence of EG did not give any products, and **1a** was recovered in almost quantitative yield (run 11). It was also found in the reaction with **4e** that the expected **7e** was not obtained, but rather the intramolecular salt (**8e**) of **7e**. The compound **7e** was formed by treatment of **8e** with hydrobromic acid as described later.

Although **1b** reacted with **4a** to give the corresponding chloride **7f** together with 2,4-di-*tert*-butyl-6-chlorophenol (**10**),[13] the yield of **7f** was lower than that of **7a** (run 19). The reactions of **1b** with **4b** did not give the expected **7g** (runs 20 and 21). In contrast to **1a**, however, **1b** reacted with **4d** in the presence of EG to afford the expected **7i** and 27% yield. It was also found that the reaction of **1b** with **4e** afforded the salt (**7j**) but not **8e**, which was obtained by the reaction of **1a** with **4e**.

From the above results, it could be concluded that **1a** is more active for the reaction with **4** than **1b** except for the case of **4d**.

When the salt **7** was treated with bases such as DBU, NaOH, and $NaHCO_3$, the color changed immediately from colorless to orange-red or violet, and the corresponding intramolecular salts **8** were obtained in almost quantitative yields. Conversely, treatment of **8** with HX afforded again the corresponding **7** in almost quantitative yield.



a: R^1~R^4=H
c: R^2=CH_3, R^1,R^3,R^4=H
d: R^3=CH_3, R^1,R^2,R^4=H
e: R^2,R^4=CH_3, R^1,R^3=H

The compound **8a** was previously prepared by Reitz et al.[14] The structures of **8c–e** were confirmed by their elemental analyses and spectral data. The reversible conversion of **7** and **8** strongly supported the proposed structures for them.

In the ^1H NMR spectrum of **8d**, a quite interesting phenomenon was observed. When the spectrum was measured in $CDCl_3$, at first under usual conditions and then followed by treatment with D_2O, the signal for the methyl protons, which appeared in the expected region of δ 2.6 as a singlet peak with the correct integration ratio,

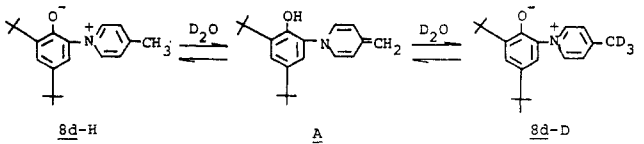
(14) G. Popp and N. C. Reitz, *J. Org. Chem.*, 37, 3646 (1972).

Table I. Reaction of 4-Halo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-ones (1) with Pyridines 4[a]

run	compd 1	compd 4	additional substance[b]	reaction time, h	product (% yield)[c]
1	a	a		6	7a (20), 9 (42), 11 (5), 12 (2)
2[d]	a	a		6	7a (21), 9 (42), 11 (9), 12 (2)
3[e]	a	a	EG	1	7a (33), 5 (20), 9 (20), 11 (4), 12 (2)
4	a	a	EG	1	7a (45), 5 (23), 9 (10), 11 (+), 12 (+)
5[f]	a	a	EG	1	7a (41), 5 (25), 9 (12), 11 (3), 12 (1)
6[g]	a	a	ME	1	7a (35)
7[g]	a	a	*n*-BA	1	7a (25)
8[g]	a	a	*t*-BA	1	7a (23)
9[g]	a	a	*i*-PA	1	7a (30)
10[g]	a	a		1	7a (13)
11	a	b		6	no reaction
12[h]	a	b	EG	6	5 (34), 6 (38), 9 (+), 11 (2), 12 (2)
13	a	c		6	7c (18), 9 (70)
14	a	c	EG	1	7c (40), 5 (31), 9 (10), 11 (3), 12 (2)
15	a	d		1	9 (80)
16	a	d	EG	1	9 (80)
17	a	e	EG	1	8e (60), 5 (15), 9 (8), 11 (+), 12 (+)
18	b	a		8	no reaction
19	b	a	EG	8	7f (24), 9 (+), 10 (38), 11 (3)
20	b	b		50	no reaction
21	b	b	EG	50	5 (48), 6 (17), 9 (+), 10 (5), 11 (2)
22	b	c		8	no reaction
23	b	c	EG	8	7h (35), 5 (42), 6 (7), 9 (+), 10 (+), 11 (6)
24	b	d		8	no reaction
25	b	d	EG	8	7i (27), 5 (11), 9 (15), 10 (6), 11 (2)
26	b	e		8	no reaction
27	b	e	EG	8	7j (33), 5 (37), 6 (10), 9 (+), 10 (4), 11 (2)

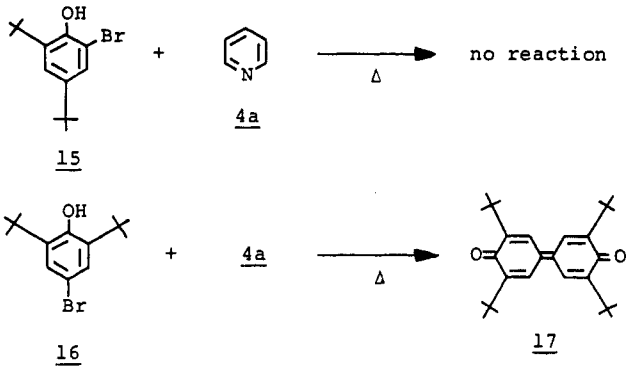
[a] Reaction at 110 °C (bath temperature) under a nitrogen atmosphere in the presence or absence of an additional substance; molar ratio of 1/4 of 1:2 unless otherwise indicated. [b] Equimolecular amount of the additional substance to 1 was added unless otherwise indicated: EG = ethylene glycol, ME = 2-methoxyethanol, *n*-BA = *n*-butyl alcohol, *t*-BA = *tert*-butyl alcohol, *i*-PA = isopropyl alcohol. [c] Isolated yields are shown and calculated based on 1; the plus (+) sign means less than 1%. [d] The molar ratio of 1a/4a of 1:6. [e] The molar ratio of 1a/4a/EG of 1:2:0.5. [f] The molar ratio of 1a/4a/EG of 1:6:1. [g] The yields of the products other than 1a were not analyzed. [h] From the literature.[6]

disappeared. On the basis of the observation mentioned above, it might be suggested that the deuterium-exchange reaction of the methyl protons of **8d** presumably proceeds via an intermediate A in the equilibrium process as schematically shown below.



8d-H A 8d-D

It was also found that 2-bromo-4,6-di-*tert*-butylphenol (**15**) did not react with **4a** and that 4-bromo-2,6-di-*tert*-butylphenol (**16**) afforded in 85% yield 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone (**17**).[15] These results clearly suggest that bromophenols such as **15** and **16** are not intermediates for the formation of the compounds **7**.



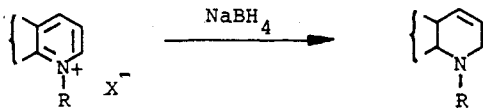
15 4a 16 4a 17

On the basis of the above results, our tentative mechanistic interpretation for the production of **7** is shown in Scheme III.

Tsubota[9] reported in the reaction of **1a** with triphenylphosphine that a radical was detected by ESR and proposed radical–cation intermediates in the reaction of **1a** with amines such as piperidine. These results should suggest that the reaction of **1** with **4** might proceed by a radical mechanism to produce radical–cation intermediates.

The debutylation at the 2-position of an intermediate like C might take place more easily than that at the 4-position of an intermediate like B; that is, $k_o \gg k_p$. The intermediate C should be less stable than the intermediate B due to its steric crowding. Therefore, the ortho isomer **7** was selectively formed but not the paraisomer **18**.

Reductions of 7 and 8. It is well-known that some pyridinium salts (**19**) are easily reduced with $NaBH_4$ to afford the corresponding tetrahydropyridine derivatives[16] (**20**). As is shown in Scheme IV and Table II compounds



19 20

7 and **8** were also reduced by $NaBH_4$ in MeOH solution to give the expected compounds **21** which were completely reduced to piperidino derivatives **22** by hydrogenation with Raney Ni (W2) catalyst.

Pyridinium bromide **7a** and pyridinio phenolate **8a** in methanol were reduced with sodium borohydride at room temperature for 0.5 h to give same product, 2,4-di-*tert*-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenol (**21a**) in 63% and 60% yields, respectively.

Pyridinium chloride **7i** was also reduced to form the corresponding product **21c** in 96% yield under the same conditions. In the case of **7c**, only when the reaction mixture was refluxed for 3 h, the corresponding **21b** was obtained in 80% yield with a small amount of an unidentified compound. Raney Ni (W2) catalyzed hydrogenation of the compounds **21a–c** afforded in high yields 2,4-di-*tert*-butyl-6-piperidinophenols **22a–c**, respectively. The structures of the products were deduced from their elemental analyses and spectral data (Table IV, supplementary material). Especially, the structure of 2,4-di-

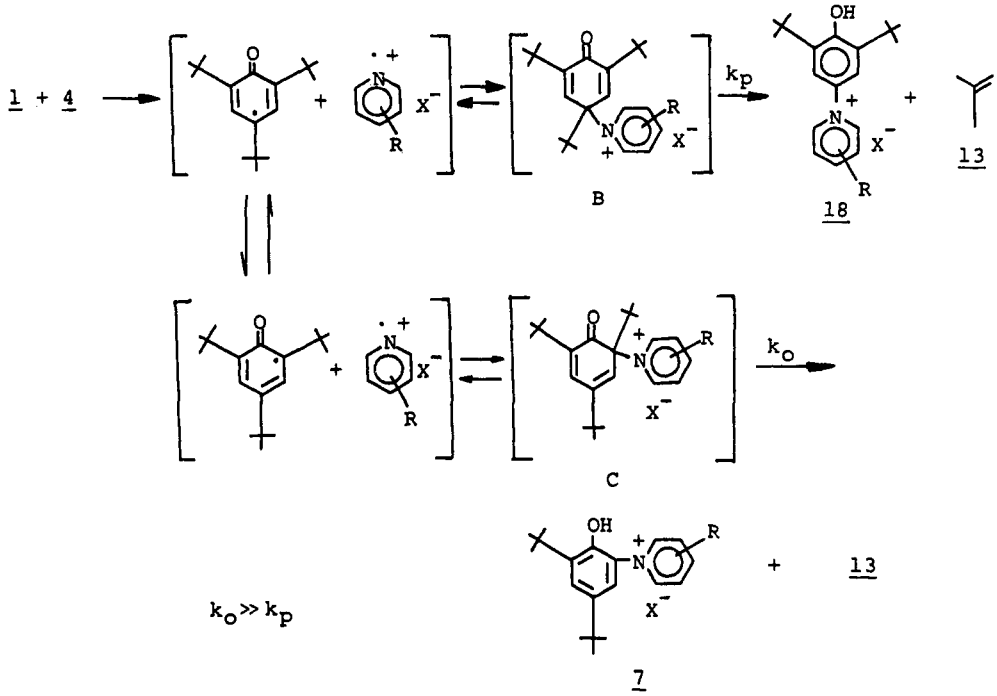
(15) M. Tashiro and G. Fukata, *J. Org. Chem.*, **42**, 428 (1977).
(16) P. S. Anderson, W. E. Krueger, and R. E. Lule, *Tetrahedron Lett.*, 4011 (1965). Y. Kikugawa, M. Kuramoto, I. Saito, and S. Yamada, *Chem. Pharm. Bull.*, **21**, 1914 (1973).

Table II. Preparations of Tetrahydropyridylphenols (21) and Piperidinophenols (22) from Pyridinium Compound (7 or 8)

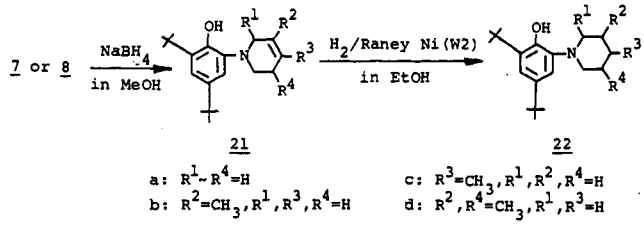
compd	product[i] (% yield)[a]	mp, °C[b] (appearance, solvent)	product[i] (% yield)[c]	mp, °C[b] (appearance, solvent)
7a	21a (63)	71-73 (colorless needles, MeOH-H_2O)	22a (82)	110-112 (pale blue needles, MeOH-H_2O)
8a	21a (60)			
7c	21b (80)	oil[d] (colorless, viscous)	22b (82)	69.5-70.5 (colorless needles, MeOH-H_2O)
7i	21c (96)	102-103 (light brown prisms, C_6H_6)	22c (89)	115-117 (colorless prisms, CH_3OH)
7e	21d[e]		22d (35)[f]	oil[h] (colorless, viscous)
8e	21d[e]		22d (34)[g]	

[a] Isolated yields, based on the pyridinium compound (7 or 8), are shown unless otherwise indicated. [b] Uncorrected. [c] Isolated yields, based on 21, are shown unless otherwise indicated. [d] HCl salt: mp 142-148 °C (pale yellow plates; C_6H_6-hexane). [e] Not isolated. [f] Based on 7e. [g] Based on 8e. [h] HCl: mp 178-181 °C (colorless prisms; MeOH-H_2O). [i] All compounds prepared gave satisfactory combustion analytical data.

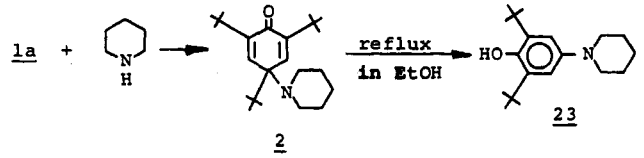
Scheme III



Scheme IV

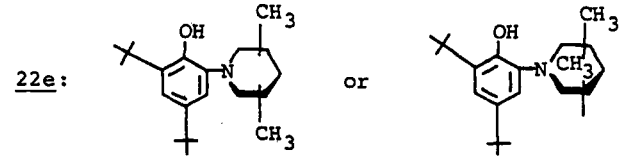


tert-butyl-6-piperidinophenol (**22a**, mp 110–112 °C) was further supported on comparison of its NMR, IR, and melting point data with the NMR and IR spectra and melting point (136–137 °C) of its isomer, 2,6-di-*tert*-butyl-4-piperidinophenol (**23**),[5] which had been synthesized as shown. In addition, the formation of **22a** gave a conclusive proof on the determination of the structure for the pyridinium bromide **7a**.



On the other hand, although the pyridinium compounds **7e** and **8e** were reduced with sodium borohydride in refluxing methanol to give same a complex mixture of reaction products, the expected product **21e** was not isolated because of difficulty in separating it from byproducts.

Therefore, the mixtures of the reaction products were each hydrogenated with Raney Ni (W2) catalyst to yield the same expected compound **22e** as an oily material in 35% and 34% yields, respectively, together with a small amount of an unidentified compound. The compound **22e** formed an HCl salt: colorless prisms; mp 178–181 °C. Although the structure of **22e** was deduced by means of elemental analysis and spectral data (Table IV), the stereochemistry of the two methyl groups on **22e**, as illustrated below, is not clear on the basis of the data at hand.



Experimental Section

All melting points are uncorrected. IR spectra were measured on a JASCO Model A-102 spectrophotometer as KBr pellets or as liquid films on NaCl pellets. ^1H NMR spectra were determined at 100 MHz on a JEOL FX-100 spectrometer with Me_4Si as an

internal reference. Mass spectra were obtained on a JEOL JMS-O1SG-2 spectrometer at 75 eV by using a direct inlet system. Gas chromatographic analyses were carried out by means of a Yanagimoto Yanaco G8 YR-101 (30% high-vacuum silicon grease; 2 m; temperature 110 °C; carrier gas, helium 50 mL/min).

The yields, melting points, appearances, solvents for recrystallizations, elemental analyses, and spectral data of the reaction products are summarized in Tables I–IV (Tables III and IV as supplementary material).

The dienones **1a** and **1b** were prepared by the reported method. Commercial grade pyridines **4a–e** were used without purification. **1a**: pale yellow prisms; mp 78–80 °C (petroleum ether, bp 40–60 °C) (lit.[7,8] mp 80 °C). **1b**: pale yellow needles; mp 94–95 °C (ethanol) (lit.[8] mp 94–95 °C).

Reaction of 1 with Pyridines 4a–e. Typical Procedure. A reaction mixture of **1a** (3.4 g, 10 mmol), pyridine (**4a**; 1.6 g, 20 mmol) and ethylene glycol (EG; 1.1 m, ca. 10 mmol) was heated in an oil bath at 110 °C for 1 h with stirring under a nitrogen stream to form a pale yellow mass with the evolution of isobutylene (**13**), which was carried by the nitrogen into a mixture of dry toluene (50 mL) contained aluminum chloride (0.05 g) which had been purified by sublimation just prior to use, giving *tert*-butyltoluenes (**14**, 25%). The isomer distribution of **14** was determined by gas chromatography to be 7:93 meta/para. The masses were washed with water, hexane, and benzene to give pyridinium bromide (**7a**) as fine colorless needles, which gave a satisfactory elemental analysis without further purification: 45% yield; mp ~300 °C dec. The organic layers were combined and washed with 10% HCl aqueous solution and then water. The organic layer was dried over sodium sulfate and then evaporated in vacuo to leave a residue. The residue was column chromatographed on silica gel (Wako gel C-300) with at first hexane (A), then benzene (B), and finally ethyl acetate (C) as eluants. The compounds **9** and **12** were obtained from fraction A, **11** was isolated from B, and **5** was eluted from fraction C. The IR spectra of known products **5**, **9**, **11**, **12**, and **14** were identical with those of the authentic samples.

Preparation of 8 from 7. Typical Procedure. To the compound **7a** (3.64 g, 10 mmol) in methanol (50 mL) was added aqueous 10% NaOH solution (10 mL) followed by addition of water (ca. 100 mL) to form the precipitate of **8a** as orange yellow needles. The elemental analysis of **8a** indicated that the monohydrate of **8a** ($C_{19}H_{25}NO{\cdot}H_2O$) was orange-red needles and the tetrahydrate orange-yellow needles.

Preparation of 7 from 8. Typical Procedure. To the monohydrate of **8a** (0.3 g, 1 mmol) in methanol (20 mL) was added aqueous 10% HBr solution (ca. 2 mL). The solution was then evaporated in vacuo to give white crystals of **7a**, 0.34 g (ca. 100%).

Sodium Borohydride Reductions of 7 and 8. Typical Procedure. To a solution of **7a** (1 g, 2.74 mmol) in methanol (20 mL) was added $NaBH_4$ (ca. 1.0 g) by portions over a 15-min period at room temperature. After the solution was allowed to stand for 15 min (in the cases of **7c,e** and **8e**, the solutions were refluxed for 3 h), the methanol was evaporated in vacuo to leave a crystalline residue. To the residue was added water (ca. 10 mL), and it was extracted with benzene 3 × 50 mL). The benzene layer was washed with aqueous 10% sodium bicarbonate solution and water. The organic layer was dried over sodium sulfate and evaporated in vacuo to give a residue which gave crude **21a** after washing with cold methanol. Recrystallization from a mixture of methanol and water gave colorless needles, 0.5 g (63% yield).

Catalytic Hydrogenations of 21. Typical Procedure. To a solution of **21a** (2.3 g, 8 mmol) in ethanol (100 mL) was added Raney Ni (W2) in ethanol (10 mL). The reaction mixture was then kept to stand at room temperature with stirring under hydrogen atmosphere. After the reaction was completed, the Raney Ni was taken off by filtration. The filtrate was evaporated in vacuo to leave pale blue crystals of crude **22a**. Recrystallization from a mixture of methanol and water gave pale blue needles, 1.9 g (82% yield).

Reaction of 16 with Pyridine (4a). After a solution of 1 g (3.5 mmol) of **16** in 5 mL of **4a** was refluxed for 1.0 h, the solution was evaporated in vacuo to leave orange-red residue. The residue was extracted with benzene. The benzene solution was washed with water and then dried over sodium sulfate. The organic layer was evaporated in vacuo to give orange-red crystals. Recrystallization of the crystals from methanol gave 0.61 g (85%) of **17** as orange needles, mp 241–243 °C (lit.[15] mp 241–243 °C).

Registry No. **1a**, 1988-75-6; **1b**, 5457-60-3; **4a**, 110-86-1; **4b**, 109-06-8; **4c**, 108-99-6; **4d**, 108-89-4; **4e**, 591-22-0; **5**, 73405-44-4; **6**, 78672-47-6; **7a**, 73405-43-3; **7c**, 78657-01-9; **7e**, 78657-02-0; **7f**, 78657-03-1; **7h**, 78657-04-2; **7i**, 78657-05-3; **7j**, 78657-06-4; **8a**, 35889-95-3; **8c**, 78657-07-5; **8d**, 78657-08-6; **8e**, 78657-09-7; **9**, 732-26-3; **11**, 4971-61-3; **12**, 719-22-2; *m*-**14**, 1075-38-3; *p*-**14**, 98-51-1; **16**, 1139-52-2; **17**, 2455-14-3; **21a**, 73405-45-5; **21b**, 78657-10-0; **21b**·HCl, 78657-11-1; **21c**, 78657-12-2; **21d**, 78657-13-3; **22a**, 78657-14-4; **22b**, 78657-15-5; **22c**, 78657-16-6; **22d**·HCl, 78657-17-7.

Supplementary Material Available: Tables III and IV showing the combustion analytical data and the NMR spectral data for **7a–j**, **8a–e**, **21a–c**, and **22a–d** (3 pages). Ordering information is given on any current masthead page.

Restricted Internal Rotations in Some Ortho-Substituted Diaryl Sulfides and Sulfones

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Restricted rotations about sulfur–aryl bonds were studied by ^1H NMR spectroscopy for a series of 2,6,2′,6′-tetrasubstituted diaryl sulfides (**3–6**) and sulfones (**7–11**) each of which bears at least two 2-hydroxy-2-propyl or 2-alkoxy-2-propyl substituents. Each shows two peaks for diastereotopic geminal methyl groups in its room-temperature NMR spectrum. Coalescence of the two methyl peaks was observed at higher temperature. The differing energy requirements for gear-meshing and gear-clashing modes of synchronous roatations of the two rings are invoked to explain these observations for **3–10**. A ring-inversion mechanism is proposed for **11**. Free energies of activation fall in the range 18.5–24.6 kcal mol^{-1} for the conformational interconversions responsible for the coalescence of the two methyl peaks in these compounds. The chirality of **3**, **5**, and **7** was demonstrated by using Pirkle's chiral alcohol as an NMR solvent.

In the course of our studies in persulfurane chemistry,[1] several diaryl sulfides and sulfones, in which both benzene rings are doubly ortho substituted, have been synthesized and characterized. Some of these highly substituted diaryl

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