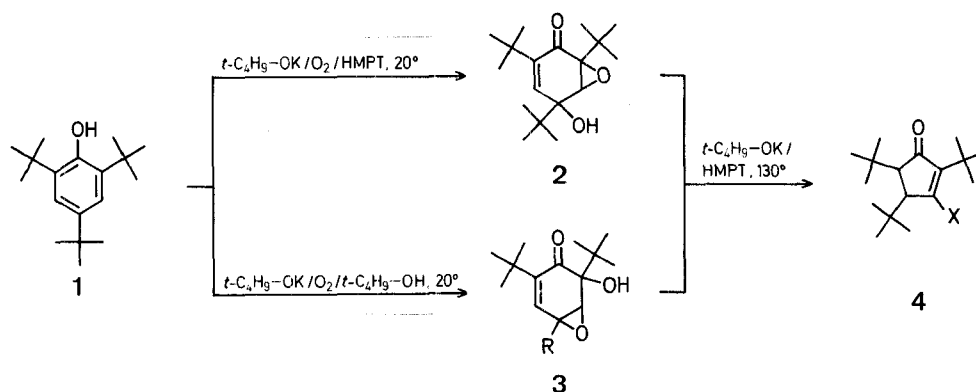


2,4,5-Tri-*t*-butyl-2-cyclopentenones from 2,4,6-Tri-*t*-butylphenol

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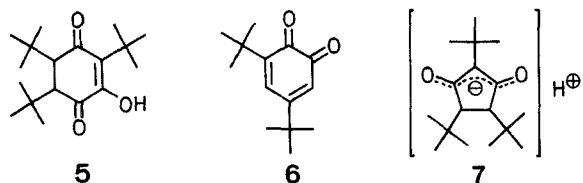
Recently, we reported that the base-catalyzed oxygenation of 4-aryl-2,6-di-*t*-butylphenols provides a novel route to 3-aryl-2,5-di-*t*-butylcyclopentadienones; it was suggested that the reaction involves the base-promoted rearrangement of intermediately formed epoxy-*o*-quinols¹ (**3a**, R = Ar). To the contrary, we now find that the base-promoted rearrangement of 4,5-epoxy-6-hydroxy-2,4,6-tri-*t*-butyl-2-cyclohexenone (**3b**, R = *t*-C₄H₉) and 5,6-epoxy-4-hydroxy-2,4,6-tri-*t*-butyl-2-cyclohexenone (**2**) [both compounds obtained in quantitative yield from 2,4,6-tri-*t*-butylphenol (**1**) by potassium *t*-butoxide-catalyzed oxygenation in *t*-butanol or hexamethylphosphoric triamide, respectively^{2,3}] affords 2,4,5-tri-*t*-butyl-2-cyclopentenone derivatives in good yield. Heating **3b** with potassium *t*-butoxide in hexamethylphosphoric triamide (130°, 3 h, nitrogen atmosphere) affords 3-hydroxy-2,4,5-tri-*t*-butyl-2-cyclopentanone (**4a**, X = OH) in 85% yield, which is also obtained from **2** in 70% yield by the same reaction.



The reaction is largely affected by the nature of base used and reaction conditions (Table 2). Thus, use of potassium

methoxide in hexamethylphosphoric triamide results in the formation of 2,4,5-tri-*t*-butyl-2-cyclopentenone (**4b**, X = H) in 80% yield whereas **3b** gives mainly 3,5-di-*t*-butyl-*o*-benzoquinone (**6**) under the same conditions.

The structure of compound **4a** (X = OH) was confirmed by the elemental analyses and spectral data of this compound and of its derivatives **4c** and **4d** (Table 1). Since the reaction at a little lower temperature (115°) gives 3-hydroxy-2,5,6-tri-*t*-butyl-2-cyclohexene-1,4-dione (**5**) besides **4a** (Table 2) which is assumed to proceed via **5** as an intermediate.



Some interesting observations were made in the spectra of 3-hydroxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4a**, X = OH). The I.R. absorptions ν_{OH} and ν_{CO} appear in regions close to those of the carboxy group and carboxylate ion, respectively, and the 1H -N.M.R. spectrum in protic solvents shows that C-4 and C-5 are equivalent. These observations strongly suggest that in crystalline form and in protic solvents compound **4a** is present, at least partially, in the ionic form **7**. The dissociation of **4a** to **7** may be explained by the steric repulsion of the *t*-butyl groups by which the unsaturation of **4a** is delocalized along the atom sequence O—C—C—C—O. This effect is not observed in the case of analogous cyclopentane-1,3-diones.

3-Hydroxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4a**, X = OH):

A solution of 4,5-epoxy-6-hydroxy-2,4,6-tri-*t*-butyl-2-cyclohexenone (**3b**, R = *t*-C₄H₉; 1.00 g, 3.4 mmol) and potassium *t*-butoxide (2.0 g, 17.9 mmol) in hexamethylphosphoric triamide (10 ml) is heated at 130° for 3 h under a nitrogen atmosphere. The mixture is then poured into excess ice-cold dilute hydrochloric acid. Com-

pound **4a** which separates is isolated by filtration; yield of crude product: 0.95 g (quantitative); colorless plates from chloroform, m.p. 190–192°.

C ₁₇ H ₃₀ O ₂	calc.	C 76.64	11.35
(266.4)	found	76.20	11.46

The same procedure is applied to the conversion **2**→**4a**.

2,4,5-Tri-*t*-butyl-2-cyclopentenone (**4b**, X = H):

A solution of 4-hydroxy-2,4,6-tri-*t*-butyl-2-cyclohexenone (**2**; 0.4 g, 1.4 mmol) and potassium methoxide (0.5 g, 7.1 mmol) in hexamethylphosphoric triamide (5 ml) is heated at 130° for 3 h under a nitrogen atmosphere. The mixture is then poured into excess ice-cold dilute hydrochloric acid and extracted with ether. The extract is dried with sodium sulfate and evaporated to give a yellow oily residue which is purified by column chromatography on silica gel (petroleum ether as eluent); yield: 0.282 g (74%); colorless plates from methanol, m.p. 56–57°.

C ₁₇ H ₃₀ O	calc.	C 81.53	H 12.08
(250.4)	found	81.35	11.92

3-Acetoxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4c**, X = OAc):

A solution of 3-hydroxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4a**; 0.08 g, 0.3 mmol) in acetic anhydride (3 ml) containing pyridine (1 ml) is allowed to stand at room temperature for 24 h. The mixture is then poured into ice water and extracted with ether. The extract is dried with sodium sulfate and evaporated to give **4c** as solid product; yield: 90 mg (97%); colorless needles from methanol, m.p. 58–59°.

C ₁₉ H ₃₂ O ₃	calc.	C 73.98	H 10.48
(308.5)	found	74.18	10.26

3-Methoxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4d**, X = OCH₃):

To a solution of 3-hydroxy-2,4,5-tri-*t*-butyl-2-cyclopentenone (**4a**; 0.15 g, 0.56 mmol) and sodium hydride (0.15 g, 6.3 mmol) in dimethyl sulfoxide, a solution of methyl iodide (0.45 g, 3.2 mmol) in dimethyl sulfoxide (5 ml) is added over a 5 min period, with stirring at room temperature. The mixture is allowed to stand for 30 min; it is then poured into ice-cold dilute hydrochloric acid and extracted with ether. The extract is dried and evaporated to give **4d**; yield: 0.15 g (95%); colorless needles from methanol, m.p. 63–64°.

Table 1. Spectral Data of 2,4,5-Tri-*t*-butyl-2-cyclopentenones (**4**)

4	X	I.R. (Nujol) ν_{max} [cm ⁻¹]	U.V. (ethanol) λ_{max} [nm] (ϵ)	1H -N.M.R. Solvent	δ [ppm] <i>t</i> -C ₄ H ₉	H-4 H-5 H-3		
a	OH	2700 (OH), 1570 (C=O)	26.2 (13500)	CDCl ₃	0.93, 0.97, 1.30	2.18	1.94	6.55 (OH)
				CDCl ₃ + D ₂ O	0.99 (18H), 1.30	2.10 (s, 2H)		
				CD ₃ OD	0.97 (18H), 1.27	2.10 (s, 2H)		
b	H	1695 (C=O)	23.3 (12000)	CDCl ₃	0.89, 0.91, 1.20	2.30 (d, <i>J</i> = 3 Hz)	1.90	6.17 (d, <i>J</i> = 3 Hz)
c	OAc	1770 (Ac), 1700 (C=O)	23.5 (13700)	CDCl ₃	0.94, 1.00, 1.13	2.75	2.06	2.23 (Ac)
d	OCH ₃	1680 (C=O)	25.3 (13000)	CDCl ₃	0.95, 0.95, 1.13	2.50	1.97	3.74 (CH ₃)

Table 2. Base-promoted Rearrangement of Epoxy-2,4,6-tri-*t*-butylquinols

Substrate	Solvent	Base	Reaction Temperature	Reaction Time [h]	Conversion [%]	Yield [%]			
						4a	4b	5	6
3b	DMF	<i>t</i> -C ₄ H ₉ —OK	20°	200	0				
	HMPT	<i>t</i> -C ₄ H ₉ —OK	130°	3	100	85	—	—	—
	HMPT	CH ₃ OK	130°	3	100	7	12	—	58
	HMPT	NaNH ₂	130°	3	0				
	HMPT/H ₂ O	NaOH	100°	3	0				
2	DMF	<i>t</i> -C ₄ H ₉ —OK	20	200	0				
	HMPT	<i>t</i> -C ₄ H ₉ —OK	130°	3	100	70	—	—	—
	HMPT	<i>t</i> -C ₄ H ₉ —OK	115°	4	100	50	—	18	—
	HMPT	CH ₃ OK	130°	3	100	—	74	—	—

$C_{18}H_{32}O_2$	calc.	C 77.09	H 11.50
(290.4)	found	77.10	11.27

3-Hydroxy-2,5,6-tri-*t*-butyl-2-cyclohexene-1,4-dione (5):

A solution of 5,6-epoxy-4-hydroxy-2,4,6-tri-*t*-butyl-2-cyclohexenone (**2**; 0.2 g, 0.68 mmol) and potassium *t*-butoxide (0.4 g, 3.6 mmol) in hexamethylphosphoric triamide (5 ml) is heated at 115° for 4 h under a nitrogen atmosphere. The mixture is then poured into excess dilute hydrochloric acid and the product which separates is isolated by filtration. It is chromatographed on a column of silica gel. Elution with benzene/petroleum ether (1:1) affords **4a** (0.11 g, 50%); further elution with benzene/ether (1:1) affords **5**; yield: 0.035 g (18%); light yellow needles from methanol, m.p. 97–98°.

$C_{18}H_{30}O_3$	calc.	C 73.43	H 10.27
(294.4)	found	73.33	10.43

I.R. (Nujol): ν_{\max} = 3220, 1660, 1650 cm^{-1} .

$^1\text{H-N.M.R.}$ (CDCl_3): δ = 0.89, 0.96, 1.37 (s, 9H, $t\text{-C}_4\text{H}_9$); 2.48, 2.78 (s, 1H, $\text{CH}=\text{CO}$); 7.62 ppm (s, 1H, OH, exchangeable with D_2O).

Received: March 29, 1976

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