6-chrysenol was established by acetylation and methylation.

**6-Acetoxychrysene.** A solution of pyridine (0.16 mL) and acetic anhydride (16 mL), both previously distilled, was refluxed for 15 min and cooled to room temperature. This was added to 30 mg of 6-chrysenol and stirred for 14 h at room temperature. The solution was concentrated, and the green solid obtained was dissolved in minimum of benzene and eluted through Florisil with 25-50% benzene-hexane. A tan yellow solid was obtained: 12 mg (34%); mp 111-113 °C (hexane); NMR ($CDCl_3$) $\delta$ 2.50 (s, 3 H, $CH_3CO_2$) (lit.[24] $\delta$ 2.50). The chemical shift is identical with that of the acetoxychrysene derived from the TsOH-catalyzed rearrangement of chrysene 5,6-oxide to chrysenol. Its mass spectrum (EI) showed $m/e$ 286 ($M^+$) and 244 ($M - CH_2{=}C{=}O$). The crude acetoxy compound before Florisil purification showed only one acetoxy peak at $\delta$ 2.50 in its $^1H$ NMR.

**6-Methoxychrysene.** To 30 mg of chrysenol (0.12 mmol) in 5 mL of dimethylformamide were added 1 mL of dimethyl sulfate and 1 g of barium oxide. The suspension was stirred for 19 h at room temperature. Concentrated $NH_4OH$ (5 mL) was added and stirring continued for 30 min. The mixture was taken up in 15 mL of ethyl ether, washed with water (4 × 15 mL), 5% HCl (2 × 15 mL), and $H_2O$ (1 × 15 mL), and dried ($MgSO_4$). Evaporation of solvent gave 20 mg of orange solid. Chromatography (Florisil) on elution with benzene gave yellow solid: 14 mg (43%); mp 115-119 °C (lit.[24] mp 121-122 °C); NMR ($CDCl_3$) $\delta$ 4.15 (s, 3 H, $OCH_3$) (lit.[24] $\delta$ 4.10). Its structure was confirmed by CI mass spectroscopy (isobutane): $(M + 1)^+$ at $m/e$ 259.

**9-Methylphenanthrene 9,10-Oxide (7).** To 80 mg of 9-methylphenanthrene (0.42 mmol) in 10 mL of $CHCl_3$ and 80 mL of hypochlorite (pH 8.6) equilibrated with a room-temperature water bath was added at once 0.15 g of tetrabutylammonium hydrogen sulfate (0.44 mmol) with vigorous stirring. After 0.3 min the reaction was quenched with 30 mL of $CHCl_3$. The aqueous phase was decanted off, and the organic layer was washed with an excess of ice cold water. Drying ($K_2CO_3$) and removal of solvent at ambient temperature gave 70 mg of brownish solid (81%). This was used at once because of its instability. Its NMR ($CDCl_3$) [$\delta$ 1.93 (s, 3 H, $CH_3$), 4.23 (s, 1 H, oxiranyl H) 4.50 (s, 2 H, $CH_2Cl$)] showed the product to be a mixture of 7 and 9-(chloromethyl)phenanthrene 9,10-oxide (8) in a ratio of 3:1. This is also in agreement with the mass spectrum (CI, isobutane), $m/e$ 243, 245 (3:1), 209.

**10-Methyl-9-phenanthrol.** 9-Methylphenanthrene 9,10-oxide (70 mg) in 2 mL of $CH_2Cl_2$ was added dropwise at 0 °C to 1.0 equiv of diethyl phosphate in 3 mL of $CH_2Cl_2$. After stirring for 5 min, the reaction was quenched with 5 mL of $CH_2Cl_2$ and washed with 10% $NaHCO_3$ (1 × 10 mL) and $H_2O$ (2 × 10 mL). Drying and removal of solvent at ambient temperature gave 50 mg of light brown solid (72%). Recrystallization ($CH_3OH$-$H_2O$) gave a white solid: mp 119-122 °C (lit.[26] mp 125 °C); NMR ($CDCl_3$) $\delta$ 2.67 (s, 3 H, $CH_3$), 3.80 (s, 1 H, OH); UV $\lambda_{max}$ (95% EtOH) 255 nm. No adduct with an ethoxy group was observed at all in the $^1H$ NMR. The same results were obtained from acid hydrolysis of the epoxide.

**Reactions of Phenanthrene 9,10-Oxide with Amine Salts of Dibenzyl Phosphate.** An equimolar amount of a freshly prepared sample of phenanthrene 9,10-oxide and 2,3-diphenylbutane (as an internal standard) were mixed, and the NMR ($CDCl_3$) was recorded. To a solution of the aniline derivative (1.4 equiv) and dibenzyl phosphate (1.1 equiv) in 1.0 mL of $CDCl_3$ was added a solution of the former two reagents in 1.0 mL of $CDCl_3$. The flask was stirred vigorously at room temperature for 5 min, an aliquot removed, and the NMR taken. We measured any change in the ratio of the 2-oxiranyl protons ($\delta$ 4.5) with respect to the methine protons of 2,3-diphenylbutane ($\delta$ 2.8). No reaction (i and ii, Table I) means no change was measured. Complete reaction (iii and iv) means the oxiranyl protons were absent in the NMR.

**Registry No.** 5, 585-08-0; 6, 15131-84-7; 7, 80641-44-7; 8, 80641-45-8; 11, 484-17-3; *p*-chloroanilinium dibenzyl phosphate, 80641-46-9; *m*-chloroanilinium dibenzyl phosphate, 80641-47-0; *m*-nitroanilinium dibenzyl phosphate, 80641-48-1; dibenzyl phosphate, 1623-08-1; diethyl phosphate, 598-02-7; phenanthrene, 85-01-8; chrysene, 218-01-9; 6-chrysenol, 37515-51-8; 6-acetoxychrysene, 7499-59-4; 6-methoxychrysene, 51361-87-6; 9-methylphenanthrene, 883-20-5; 10-methyl-9-phenanthrol, 16430-50-5.

(24) R. G. Harvey, S. H., Goh, and C. Cortez, *J. Am. Chem. Soc.*, **97**, 3468 (1975).
(25) F. Krasovec and J. Jan, *Croat. Chem. Acta*, **35**, 183 (1963).
(26) J. W. Cook, J. Jack, J. D. Loudon, G. L. Buchanan, and J. MacMillan, *J. Chem. Soc.*, 1397 (1951).

# Peroxy Esters. 7. Base-Catalyzed Reaction of 5-(Acylmethyl)-2,6-di-*tert*-butyl-4-oxa-2-cyclopentenones Derived Selectively from Acid Catalysis of 2,6-Di-*tert*-butyl-*p*-peroxyquinol Acetates[1]

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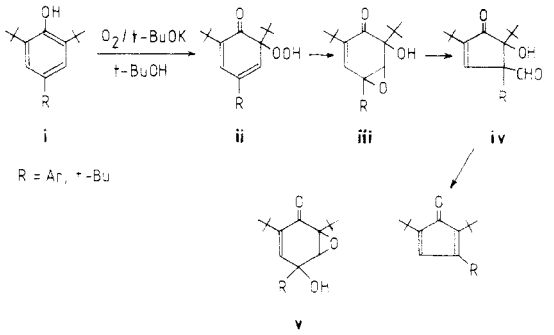
The reaction of 5-(acylmethyl)-2,5-di-*tert*-butyl-4-oxa-2-cyclopentenones, easily available from acid treatment of 2,6-di-*tert*-butyl-*p*-peroxyquinol acetates with *t*-BuOK in *t*-BuOH at 70 °C, gave 3-alkyl-2,5-di-*tert*-butyl-2,4-cyclopentadienones in good yield, providing a new convenient synthetic route to 3-alkyl-2,5-di-*tert*-butylcyclopentadienones from 4-alkyl-2,6-di-*tert*-butylphenols via oxygenation by which the phenols are selectively converted to the above *p*-peroxyquinols. Treatment of the 4-oxa-2-cyclopentenones with the same base in *t*-BuOH containing petroleum ether at 0 °C, on the other hand, led to the quantitative formation of 1,6-di-*tert*-butyl-8-oxabicyclo[3.2.1]octane-3,7-diones resulting from an intramolecular Michael addition of a carbanion generated on the acyl group of the acylmethyl group in the starting 4-oxa-2-cyclopentenones. Heating of these bicyclic products with *t*-BuOK in *t*-BuOH at 70 °C gave the cyclopentadienones quantitatively. A plausible mechanism involving equilibria among carbanions generated on the acylmethyl group is discussed.

Cyclopentadienones have received much attention because of their potential intermediacy in organic synthesis.[2] For example, many aromatic compounds including hetero aromatics have been synthesized by the Diels-Alder reaction with various cyclopentadienones as dienophiles as well as diene systems.[2] *tert*-Butylated cyclopentadienones have also been synthesized by rather complicated methods.[3-5] Recently, we have reported a one-step method to

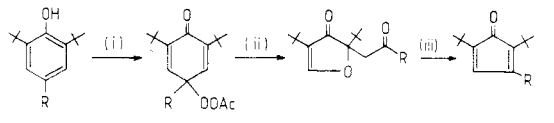
(1) Peroxy Esters. 6: Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1981**, *22*, 3261.
(2) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261.
(3) Krüerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.

0022-3263/82/1947-1431$01.25/0 

Scheme I




Scheme II[a]




[a] a, R = Me; b, R = Et; c, R = *n*-Pr; d, R = *i*-Pr; e, R = cyclopentyl; i, (1) $O_2$/KOH/EtOH/0 °C, (2) AcCl/Py; ii, $H^+$; iii, *t*-BuOK/*t*-BuOH/70 °C.

3-aryl- and 3-*tert*-butyl-2,5-di-*tert*-butylcyclopentadienones involving base-catalyzed oxygenation of 4-aryl- and 4-*tert*-butyl-2,6-di-*tert*-butylphenols (i) with *t*-BuOK in *t*-BuOH at 70 °C.[6] The mechanism of this reaction has been proven to involve regioselective oxygenation at the ortho position of the phenols, giving rise to *o*-hydroperoxides (ii) followed by intramolecular decomposition to epoxy-*o*-quinols (iii), which undergo ring contraction to give 4-formyl-5-hydroxy-2-cyclopentenones (iv) and subsequent elimination of formic acid under the reaction conditions (Scheme I).[6] The method is, however, applicable only to phenols (i) and not to 4-alkyl-2,6-di-*tert*-butylphenols (1) other than 2,4,6-tri-*tert*-butylphenol, because the oxygenation of 1 takes place only at the para position, and the resulting epoxy-*p*-quinols (v) are quite stable under the conditions where epoxy-*o*-quinols (iv) give cyclopentadienones.[7]

The present paper deals with a new route to cyclopentadienones from 4-alkyl-2,6-di-*tert*-butylphenols (1) which includes base-catalyzed reaction of 5-(acylmethyl)-2,5-di-*tert*-butyl-4-oxa-2-cyclopentenones (**3**), easily available from acid-catalysis of 4-alkyl-2,6-di-*tert*-butyl-*p*-peroxyquinol acetates (**2**),[8] which are in turn obtained conveniently by base-catalyzed oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols followed by acetylation.[9] It is now found that the reaction of **3** with *t*-BuOK in *t*-BuOH at 70 °C leads to the formation of 4-alkyl-2,5-di-*tert*-butylcyclopentadienones (**4**) in good yield (Scheme II). The reaction of **3** with *t*-BuOK at 0 °C, on the other hand, has been found to give 1,6-di-*tert*-butyl-8-oxabicyclo-[3.2.1]octane-3,7-diones.

## Results and Discussion

### 5-(Acylmethyl)-2,5-di-*tert*-butyl-4-oxa-2-cyclopentenones (3).

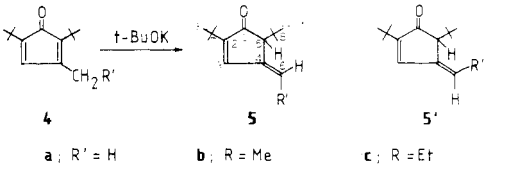
The compounds **3** were synthesized according to the method previously reported,[8] with minor modifications, involving treatment of **2** with trifluoroacetic acid. Addition of a small amount of water to the acid improved the yield of **3**. For the synthesis of **3**, it is no use to employ *p*-peroxyquinols instead of their acetates **2**, because acid treatment of the *p*-peroxyquinols gives a complex mixture resulting from protonation of both oxygen atoms of the hydroperoxy group.[8]

Table I. Base-Catalyzed Reaction of 3 at 70 °C[a]

| compd | *t*-BuOK/3 (mol/mol) ratio | reaction time, min | product yield,[b] % 4 | 5 |
|---|---|---|---|---|
| 3a[c] | 1 | 30 | 57 | 20 |
| 3a[d] | 1 | 40 | 69 | 24 |
| 3a | 2.3[e] | 30 | 0 | 100 |
| 3b | 1 | 30 | 96 | 0 |
| 3b | 2.3[e] | 30 | 44 | 42 |
| 3c | 1 | 30 | 91 | 7 |
| 3c | 2.3[e] | 60 | 0 | 96 |
| 3d | 1 | 150 | 81 | 0 |
| 3d | 2.3[e] | 90 | 84 | 0 |
| 3e | 1 | 150 | 91 | 0 |

[a] Reaction conditions: 3 (0.4 mmol), *t*-BuOK (0.4 mmol) in *t*-BuOH (20 mL) under $N_2$ unless otherwise noted; conversion, 100%. [b] Determined by $^1H$ NMR spectroscopy. [c] In this run, bicyclic product **6a** was obtained in 12% yield. [d] 3 (4 mmol), *t*-BuOK (4 mmol) in *t*-BuOH (200 mL). [e] 3 (0.4 mmol), *t*-BuOK (0.9 mmol) in *t*-BuOH (5 mL).

**Reaction of 3 with *t*-BuOK in *t*-BuOH at 70 °C.** A solution of *t*-BuOK in *t*-BuOH was added to a solution of **3** at 70 °C under a nitrogen atmosphere in 10 min, and the mixture was allowed to stand at the same temperature until the reaction was complete. The reaction time required was dependent on the nature of the substituent R in **3**. Chromatographic separation of the reaction mixtures gave the corresponding cyclopentadienones **4** as orange-red liquids, among which **4d** and **4e** were crystallized. The products **4** are volatile or sublimable. Therefore, careful manipulation is necessary in the isolation procedure. With **3a–c**, the isomeric products **5** were also obtained in addition to **4**. The yield of **5** depended on the amount of the base used: the use of an excess of the base increased the yield of **5** (Table I). Spectral data of **4** (Table II) are typical for cyclopentadienones.[5,6] In the $^1H$ NMR of **4**, a small coupling between the ring proton (C-4 H) and the $\alpha$-proton of the group R is observed (Table II). The product **5** should be a resultant of further base-catalyzed reaction of **4**. Actually, when **4a** and **4b** were treated with *t*-BuOK at 70 °C, **5a** and **5b** were obtained quantitatively.




Therefore, for the purpose of obtaining the cyclopentadienones **4** except for **4d** and **4e**, it is important to use an equimolar or less amount of the base. Analytical and spectral data of **5** are in good agreement with the structure. The decoupling technique with the $^1H$ NMR of **5a** revealed the chemical shifts of the individual olefinic protons and coupling constants between them. Thus, the signals at $\delta$ 5.11 (1 H, ddd, $J$ = 1.0, 0.8, 0.8 Hz), 5.30 (1 H, ddd, $J$ = 1.0, 0.6, 0.5 Hz), and 7.32 (1 H, dd, $J$ = 0.8, 0.6 Hz) were assigned for R'(H), C-6 H, and C-3 H, re-

(4) Hoogzand, C.; Hübel, W. *Tetrahedron Lett.* **1961**, 637.
(5) Maier, G.; Bosslet, F. *Tetrahedron Lett.* **1972**, 1025.
(6) Nishinaga, A.; Itahara, T.; Matsuura, T.; Rieker, A.; Koch, D.; Albert, K.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1826. Nishinaga, A.; Shimizu, T.; Matsuura, T. *J. Org. Chem.* **1979**, *44*, 2983.
(7) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978**, *100*, 1820.
(8) Nishinaga, A.; Nakamura, K.; Matsuura, T.; Rieker, A.; Koch, D.; Griesshammer, R. *Tetrahedron* 1979, *35*, 2493.
(9) Nishinaga, A.; Nakamura, K.; Yoshida, K.; Matsuura, T. *Chem. Lett.* **1977**, 303.

Table II. Physical Data of Cyclopentadienones 4 [m]

| compd | mp or bp, °C | IR, $cm^{-1}$ | $\lambda_{max}$, nm ($\epsilon$) | $^1H$ NMR ($CDCl_3$), δ | | |
|---|---|---|---|---|---|---|
| | | | | t-Bu | R | C=CH [a] |
| 4a | 85-86 [b] | 1700 [c] | 416 (410) | 1.13, 1.22 | 2.03 | 6.13 |
| 4b | 78-80 [b] | 1710 [c] | 416 (414) | 1.14, 1.23 | 1.09, [e] 2.44 [f] | 6.26 |
| 4c | 142-143 [b] | 1700 [c] | 416 (446) | 1.14, 1.22 | 0.99, [g] 1.42, [h] 2.41 [i] | 6.22 |
| 4d | 65-66 | 1710 [d] | 416 (475) | 1.14, 1.23 | 0.97, [j] 1.88 [k] | 6.24 |
| 4e | 47-49 | 1710 [d] | 416 (483) | 1.13, 1.24 | [l] | 6.37 |

[a] Broad signal due to a small coupling with the group R. [b] Boiling point at 2 mmHg. [c] Liquid film. [d] Nujol mull. [e] t, 3 H, $J$ = 7.7 Hz. [f] g, 2 H, $J$ = 7.7 Hz. [g] t, 3 H, $J$ = 7.5 Hz. [h] Sextet, 2 H, $J$ = 7.5 Hz. [i] t, 2 H, $J$ = 7.5 Hz. [j] d, 6 H, $J$ = 6.5 Hz. [k] Septet, 1 H, $J$ = 6.5 Hz. [l] δ 1.4-1.9 (m, 8 H), 3.3-3.7 (m, 1 H). [m] Satisfactory analytical data (±0.3% for C and H) for all compounds were submitted for review.

Table III. Physical Data of 1,6-Di-*tert*-butyl-8-oxabicyclo[3.2.1]octane-3,7-diones 6 and 7

| compd | mp, °C | IR (Nujol), $cm^{-1}$ | $^1H$ NMR ($CDCl_3$), ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | t-Bu | C-6 H | C-2 H | C-5 H | $R^1$ | $R^2$ |
| 6a | 92-94 | 1750, 1715 | 1.05 | 1.79 [a] | 2.46, [b] 2.54 [b] | 4.81 [c] | 2.31 [d] | 2.85 [e] |
| 6b | 94-95 [f] | 1745, 1710 [f] | 1.04, 1.06 | 1.78 [g] | 2.34, [h] 2.69 [h] | 4.80 [i] | 2.32 [j] | 1.37 [k] |
| 6c | 108-110 [l] | 1745, 1710 [l] | 1.04, 1.06 | 1.77 [g] | 2.36, [h] 2.63 [h] | 4.55 [m] | 1.68 [n] | 1.00 [o] |
| 6d | 92-93 | 1740, 1710 | 1.04 | 1.82 [g] | 2.28, [p] 2.77 [p] | 4.13 [g] | 1.01 | 1.37 |
| 6e | 99-100 | 1740, 1710 | 1.04, 1.05 | 1.67 [a] | 2.32, [p] 2.69 [p] | 4.20 [a] | 1.5-1.9 (m) | |
| 7b | 92-94 [f] | 1745, 1710 [f] | 1.05, 1.06 | 1.68 [g] | 2.40, [p] 2.57 [p] | 4.55 [m] | 1.00 [k] | 2.92 [q] |
| 7c | 108-110 [l] | 1745, 1710 [l] | 1.04, 1.06 | 1.68 [g] | 2.41, [p] 2.53 [p] | 4.64 [r] | s | s |

[a] d, $J$ = 1.4 Hz. [b] d, $J$ = 16.4 Hz. [c] ddd, $J$ = 1.4, 5.0, 1.6 Hz. [d] dd, $J$ = 16.4, 1.6 Hz. [e] dd, $J$ = 16.4, 5.0 Hz. [f] Data for the mixture of 6b and 7b obtained as a liquid; boiling point at 1 mmHg; IR with a liquid film. [g] d, $J$ = 2.0 Hz. [h] d, $J$ = 17.0 17.0 Hz. [i] dd, $J$ = 2.0, 0.5 Hz. [j] dq, $J$ = 0.5, 7.0 Hz. [k] d, $J$ = 7.0 Hz. [l] Data for the mixture of 6c and 7c. [m] dd, $J$ = 2.0, 1.5 Hz. [n] dt, $J$ = 1.5, 0.6 Hz. [o] t, 3 H, $J$ = 6.0 Hz. [p] d, $J$ = 16.0 Hz. [q] dq, $J$ = 7.0, 1.5 Hz. [r] dd, $J$ = 2.0, 4.8 Hz. [s] Not determined.

Table IV. Carbon-13 NMR Data of 6 and 7

| compd | shift, ppm | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | t-Bu |
| 6a | 87.4 | 46.1 | 206.1 | 48.2 | 72.4 | 61.7 | 214.3 | 35.3, 35.9, 28.3, 25.3 |
| 6b [a] | 88.2 | 44.9 | 209.7 | 51.4 | 76.9 | 57.8 | 213.9 | 34.4, 35.5, 28.0, 25.0 |
| 6c [b] | 87.1 | 43.3 | 208.7 | 58.5 | 74.9 | 61.1 | 213.8 | 34.9, 35.4, 27.9, 24.8 |
| 6d [c] | 87.5 | 41.6 | 209.9 | 87.5 | 80.8 | 57.6 | 213.7 | 34.5, 35.3, 28.0, 24.8 |
| 6e [d] | 87.8 | 42.3 | 209.6 | 61.6 | 79.9 | 59.4 | 214.4 | 34.7, 35.5, 28.3, 25.0 |
| 7b [e] | 87.3 | 42.7 | 207.6 | 49.5 | 76.8 | 41.4 | 213.6 | 34.0, 35.0, 28.9, 24.9 |
| 7c [f] | 88.0 | 45.1 | 208.6 | 58.0 | 75.1 | 61.0 | 213.4 | 34.4, 35.0, 28.0, 23.4 |

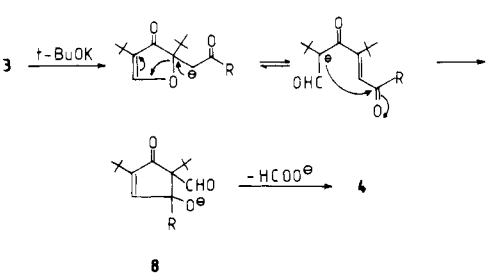
[a] Me group, 16.0 ppm. [b] Ethyl group, 19.9 and 11.3 ppm. [c] Methyl group, 24.1 and 19.1 ppm. [d] $(CH_2)_4$ group, 28.9, 25.5, 25.5, and 28.3 ppm. [e] Methyl group, 9.4 ppm. [f] Ethyl group, 17.5 and 13.4 ppm.

spectively. Coupling constants $J_{H_5-H_6}$, $J_{H_5-R'}$, $J_{H_5-H_6}$, $J_{H_5-R'}$, and $J_{H_5-R'}$ were determined as 0.8, 0.6, 0.8, 0.5, and 1.0 Hz, respectively. Coupling constants $J_{H_5-H_6}$ and $J_{H_5-H_6}$ observed for all the other compounds **5** were 1.0 and 0.8 Hz, respectively. These observations, therefore, exclude another possible geometry, **5′**. The exclusive formation of **5** may be due to steric repulsion between the groups R′ and *t*-Bu in **5′**. The steric control of the isomerization of **4** to **5** agrees with the fact that compounds **4d** and **4e** do not undergo such an isomerization.

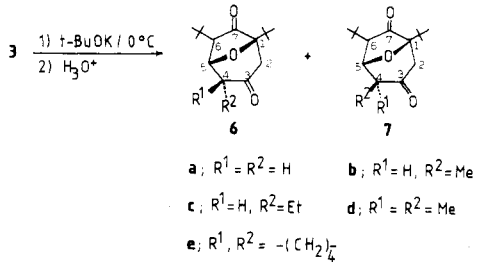
The present base-catalyzed formation of cyclopentadienones **4** from **3** may be rationalized by Scheme III. The intermediate **8** is analogous to the intermediate iv confirmed for the formation of cyclopentadienones from epoxy-*o*-quinols (iii, Scheme I). Attempts to isolate the intermediate **8** were, however, unsuccessful. The solvent effect on the formation of **4a** from **3a** has been examined, and *t*-BuOH was found to be the best one. In *N*,*N*-dimethylformamide, even with 1 equiv of *t*-BuOK, only **5a** was obtained (70 °C, 10 min; yield 99%). In ethanol or tetrahydrofuran, a complicated mixture including small amounts of **4a** and **5a** was obtained.

**Reaction of 3 with *t*-BuOK in *t*-BuOH at 0 °C.** The fact that a small amount of bicyclic compound **6a** was obtained in the base-catalyzed reaction of **3a** at 70 °C for 30 min (Table I) prompted us to examine the reaction of

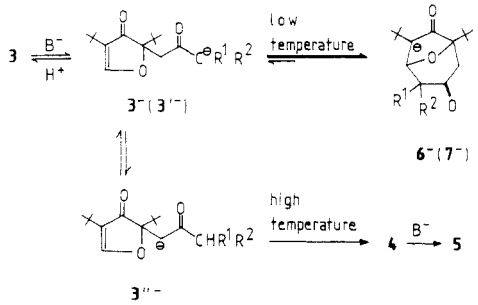
Scheme III




**3** with *t*-BuOK at a low temperature. Thus, in the reaction at 0 °C, compounds **3a,d,e** were found to give the corresponding 1,6-di-*tert*-butyl-8-oxabicyclo[3.2.1]octane-3,7-diones **6** quantitatively. Analytical and spectral data for

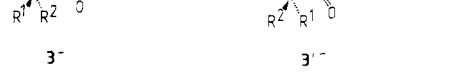


Scheme IV



6 are in good agreement with the structure. The IR spectra of 6 showed two carbonyl bands and no hydroxyl group. The $^1$H NMR spectra of 6 showed no signals in the olefinic region but a characteristic signal for an ethereal proton ($\delta$ 4.2–4.8, C-5 H) coupled with vicinal protons (C-4 H and C-6 H, Table III). The $^{13}$C NMR spectra of 6 also showed the existence of two carbonyl groups and two carbons attached to an oxygen atom (Table IV). With **3b** and **3c**, on the other hand, no single product was obtained. Analytical data and TLC of the products from **3b** and **3c** seemed to be consistent with the corresponding 6. The products were, however, shown to be a mixture of 6 and its stereoisomer 7 as judged by their $^1$H and $^{13}$C NMR spectra (Tables III and IV). Thus, **3b** gave **6b** (50%) and **7b** (50%), whereas **6c** (11%) and **7c** (89%) were obtained from **3c**. Attempts to separate these compounds 6 and 7 from the mixture were not successful.

The products 6 and 7 obviously result from the intramolecular Michael addition of the carbanions $3^-$ and $3'^-$



to the enone system of the ring. Therefore, 6 as well as 7 is expected to be a racemate (1*S*,6*R* and 1*R*,6*S*), because the configuration at the C-5 position is automatically controlled by the configuration at the C-1 position. Actually, the $^1$H and $^{13}$C NMR spectra of 6 and 7 are understood as those of a single racemate.

When **6a** was heated with *t*-BuOK in *t*-BuOH at 70 °C under nitrogen, a mixture of **3a** and **5a** was obtained: in a 5-min reaction, the conversion was 43% with the formation of **3a** (20%) and **5a** (50%), and the reaction was complete in 30 min to give **5a** (72%). The results indicate that the formation of 6 (7) from 3 is reversible, and under strong basic conditions the equilibrium between anions generated in 3 and 6 (7) is extremely shifted to the latter at 0 °C. At 70 °C, anion $3''^-$ which is reversibly formed undergoes an irreversible ring opening to give 4. Thus, the present reaction may be summarized as in Scheme IV, where an anion $6^-$ ($7^-$), among other seven-membered species obtainable in the equilibrated system, is simply depicted. The ring opening of $3''^-$ is obviously a rate-determining step.

Acid-treatment of 8-oxabicyclo[3.2.1]octane derivatives leading to tropolones[10] would suggest that compounds 6 and 7 may be converted to *tert*-butylated $\gamma$-tropolones. This would provide a new route to tropolones from phenols. Further studies on this possibility are underway.

## Experimental Section

All melting points were uncorrected. Elemental analyses were performed by the Analytical Center of the Pharmaceutical Department, Kyoto University. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer. Ultraviolet spectra were obtained with a Shimazu UV-200 spectrophotometer. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer. Carbon-13 magnetic resonance spectra were obtained with a Varian FT-80A spectrometer. Compounds 3 were synthesized by acid treatment of peroxyacetates 2 according to the method previously reported[8] with minor modifications: a solution of 3 (10 mmol) in dichloromethane (3 mL) was added dropwise to trifluoroacetic acid (15 mL) containing water (20 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, poured into ice-cooled water, and extracted with ether. The products 3 were isolated by chromatography as described in the literature.[8]

**Reaction of 3 with *t*-BuOK in *t*-BuOH at 70 °C.** A solution of 3 (0.4 mmol) and *t*-BuOK (0.048 g, 0.4 mmol) in *t*-BuOH (20 mL) was heated at 70 °C under a nitrogen atmosphere. After the reaction was complete (monitored by TLC), the mixture was poured into an aqueous $NH_4Cl$ solution and extracted with petroleum ether. The extract was dried ($Na_2SO_4$) and carefully evaporated to give a red oily residue. Yields of 4 and 5 were determined by $^1$H NMR of the residue (Table I). The products were separated by TLC (developed with a mixture of petroleum ether and dichloromethane (2:1) and purified by distillation under reduced pressure. Physical data for 4 are given in Table II.

**5a**: colorless oil; bp 81–82 °C (5 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 0.99 (s, 9 H), 1.21 (s, 9 H), 2.48 (dd, 1 H, $J$ = 0.8, 0.5 Hz), 5.11 (ddd, 1 H, $J$ = 1.0, 0.8, 0.8 Hz), 5.30 (ddd, $J$ = 1.0, 0.6, 0.5 Hz), 7.32 (dd, 1 H, $J$ = 0.8, 0.6 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 209.8 (C-1), 159.0 (C-2), 155.2 (C-3), 149.5 (C-4), 62.6 (C-5), 115.3 (C-6), 37.9 (C-7), 37.9 (C-8), 35.6 (C-9), 31.5 (C-10); IR (neat) 1710 cm$^{-1}$; UV (EtOH) $\lambda_{max}$ 272 nm (log $\epsilon$ 4.01). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.58; H, 10.92.

**5b**: colorless oil; bp 82–84 °C (2 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 0.96 (s, 9 H), 1.22 (s, 9 H), 1.90 (d, 3 H, $J$ = 7.3 Hz), 2.42 (d, 1 H, $J$ = 0.8 Hz), 5.57 (qdd, 1 H, $J$ = 7.3, 1.0, 0.8 Hz), 7.46 (d, 1 H, $J$ = 1.0 Hz); IR (neat) 1700 cm$^{-1}$; UV (EtOH) $\lambda_{max}$ 289 nm (log $\epsilon$ 4.00). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.49; H, 11.20.

**5c**: colorless oil; bp 105–106 °C (2 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 0.96 (s, 9 H), 0.97 (t, 3 H, $J$ = 7.0 Hz), 1.22 (s, 9 H), 2.33 (qd, 2 H, $J$ = 7.7, 7.0 Hz), 2.42 (d, 1 H, $J$ = 0.8 Hz), 5.53 (tdd, 1 H, $J$ = 7.7, 1.0, 0.8 Hz), 7.61 (d, 1 H, $J$ = 1.0 Hz); IR (neat) 1695 cm$^{-1}$; UV (EtOH) $\lambda_{max}$ 289 (log $\epsilon$ 4.04). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.75; H, 11.43.

**Reaction of 4 with *t*-BuOK.** To a solution of 4 (0.4 mmol) was added *t*-BuOK (0.9 mmol) at once at 0 °C under a nitrogen atmosphere, and the mixture was heated at 70 °C (reaction times: **4a**, 20 min; **4b**, 2 h; **4c**, 2 h). The mixture was poured into an ice-cooled aqueous $NH_4Cl$ solution and extracted with petroleum ether. The extract was dried ($Na_2SO_4$) and evaporated. $^1$H NMR and TLC analyses of the residue showed the quantitative formation of 5. No reaction took place with **4d** and **4e**.

**Reaction of 3 with *t*-BuOK in *t*-BuOH at 0 °C.** A solution of *t*-BuOK (0.224 g, 2 mmol) in *t*-BuOH (60 mL) containing petroleum ether (10 mL) was added dropwise to a solution of 3 (2 mmol) in petroleum ether (60 mL) in 10 min with stirring at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 30 min, poured into an ice-cooled aqueous $NH_4Cl$ solution, and extracted with petroleum ether. The extract was dried ($Na_2SO_4$) and evaporated to dryness. The $^1$H NMR of the resulting residue showed the quantitative formation of 6 from **3a**,**d**,**e**, which was crystallized and recrystallized from petroleum ether. The reaction of **3b** and **3c** gave a mixture of the corresponding 6 and 7, which could not be separated. The mixture of **6b** and **7b** was crystallized and recrystallized from petroleum ether, and that of **6c** and **7c** was distilled under reduced pressure. All the physical data are given in Tables III and IV. Analytical data are given below.

(10) Noyori, R.; Makino, S.; Okita, T.; Hayakawa, Y. *J. Org. Chem.* **1975**, *40*, 806 and references cited therein.

**6a**: colorless needles. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.50, H, 9.81.

**6b + 7b** (1:1): colorless prisms. Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.82; H, 9.84. Found: C, 71.89; H, 9.98.

**6c + 7c** (1:9): colorless oil. Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.07. Found: C, 72.55; H, 10.14.

**6d**: colorless prisms. Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.07. Found: C, 72.98; H, 10.32.

**6e**: colorless prisms. Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.52; H, 10.00.

**Registry No. 2a**, 62926-71-0; **2b**, 62926-72-1; **2c**, 75498-80-5; **2d**, 62926-73-2; **2e**, 80534-65-2; **3a**, 66483-14-5; **3b**, 69892-30-4; **3c**, 80534-66-3; **3d**, 69892-31-5; **3e**, 80534-67-4; **4a**, 80534-68-5; **4b**, 80534-69-6; **4c**, 80534-70-9; **4d**, 80534-71-0; **4e**, 80534-72-1; **5a**, 80534-73-2; **5b**, 80534-75-4; **5c**, 80534-74-3; **6a**, 80800-59-5; **6b**, 80800-60-8; **6c**, 80800-61-9; **6d**, 80800-62-0; **6e**, 80800-63-1; **7b**, 80844-91-3; **7c**, 80844-92-4.

# Synthesis and Chiroptical Properties of an Optically Active Doubly Bridged Allene[1]

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(±)-Bicyclo[10.8.1]heneicosa-1(21),12(21)-diene (**5**), the first synthesized member of doubly bridged allenes, was prepared by treatment of the dichlorocarbene adduct **21** with *n*-butyllithium at −78 °C. A partially asymmetric synthesis of **5** utilizing *n*-butyllithium in the presence of (−)-sparteine gave an optically active specimen of **5** [$[\alpha]_D$ +4.3° (optical purity ca. 2–4%)] whose CD spectrum indicated its *R* configuration.

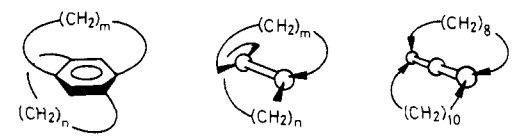
In the course of our synthetic investigations on twisted π-electron systems, we have prepared [8][8]- (**1**) and [8][10]paracyclophanes (**2**, Chart I) in optically active modifications and succeeded in determining their absolute configuration.[2] A logical extension of this study prompted us to undertake the synthesis of the ethylene analogues of **1** and **2**, which resulted in the successful preparation of the trans doubly bridged ethylenes **3** and **4**. The synthesis involved photochemical cis–trans isomerization of the cis percursors.[3] Recently we also have reported a partial photochemical asymmetric synthesis of the dextrorotatory modification of **3**.[4]

Another conceivable structural analogue of [*m*][*n*]-paracyclophane will be the doubly bridged allene **5** whose lower homologue **6** (Chart II) of $D_2$(V) symmetry was cited in Cahn, Ingold, and Prelog's classical paper[5] on specification of molecular chirality in a discussion of the axial nature of chirality inherent to this type of molecule. In this paper, we report the preparation of the doubly bridged allene **5**, the first member of this class of compound to be synthesized, as well as a partial asymmetric synthesis of its dextrorotatory enantiomer.

Before describing our synthetic approach, it seems pertinent here to give a brief survey on the bridged allenes of closely related types which have been obtained in optically active modification.

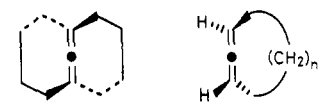
Cope and co-workers' optical resolution of 1,2-cyclononadiene (**7a**) through a chiral platinum complex provided them with (+)-**7a** (44% optical purity)[6] whose absolute configuration, once erroneously assigned to be *S*,[7]

Chart I



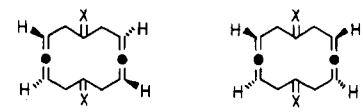

(1) m=n=8
(2) m=8, n=10
(3) m=n=8
(4) m=8, n=10
(5)

Chart II



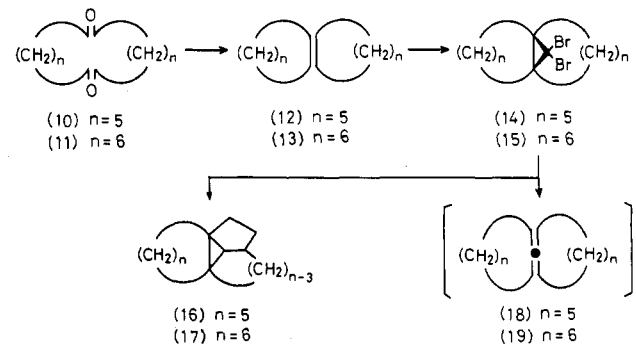

(R)-(6)
(+)-(R)-(7a) n=6
(7b) n=5

Chart III




(8) X = <OMe OMe (D2)
(9) X = <OMe OMe (C2h)

Scheme I




(10) n=5
(11) n=6
(12) n=5
(13) n=6
(14) n=5
(15) n=6
(16) n=5
(17) n=6
(18) n=5
(19) n=6

(1) For a preliminary report, see: Nakazaki, M.; Yamamoto, K.; Maeda, M. *Chem. Lett.* **1981**, 1035.

(2) Nakazaki, M.; Yamamoto, K.; Tanaka, S. *Tetrahedron Lett.* **1970**, 341. Nakazaki, M.; Yamamoto, K.; Itoh, M. *J. Chem. Soc., Chem. Commun.* **1972**, 433. Nakazaki, M.; Yamamoto, K. *Chem. Lett.* **1974**, 1051. Nakazaki, M.; Yamamoto, K.; Tanaka, S. *J. Org. Chem.* **1976**, *41*, 4081. Nakazaki, M.; Yamamoto, K.; Itoh, M.; Tanaka, S. *Ibid.* **1977**, *42*, 3468.

(3) Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Chem. Soc., Chem. Commun.* **1977**, 346; *J. Am. Chem. Soc.* **1979**, *101*, 147. Two reviews have appeared to survey this rapidly developing field: Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213. Nakazaki, M.; Yamamoto, K. *Yuki Gosei Kagaku Kyokai shi* **1981**, *39*, 624.

(4) Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Chem. Soc., Chem. Commun.* **1980**, 294. Nakazaki, M.; Yamamoto, K.; Maeda, M. *J. Org. Chem.* **1980**, *45*, 3229.

(5) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *6*, 385. Also see: Farina, M.; Morandi, C. *Tetrahedron* **1974**, *30*, 1819.

0022-3263/82/1947-1435$01.25/0 