yield (72%/step) α-cuparenone, without the formation of detectable amounts of any regioisomeric cyclopentanone or over-alkylated material.[9] The spectral data of 1 were in complete accord with the published values.[1,2]

A short, selective three-carbon annelation approach to racemic α-cuparenone is thus accomplished in 35% overall yield, which makes it competitive with the best currently available in the literature.

Experimental Section

Solvents were generally distilled prior to use. Tetrahydrofuran and ether were distilled from sodium hydride–lithium aluminum hydride, and hexamethylphosphoric triamide was distilled under reduced pressure from calcium hydride. Phosphorus oxychloride was distilled from potassium carbonate. Reaction mixtures were generally stirred under a nitrogen or argon atmosphere. Thin-layer chromatography was performed on Merck $60F_{254}$ (0.25 mm) sheets, which were visualized with molybdophosphoric acid in ethanol. Merck 70–230 silica gel 60 and Florisil 60-100 were employed for column chromatography. A Perkin-Elmer Model 298 or 397 spectrophotometer was used to record the IR spectra. A JEOL PMX-60 spectrometer was employed for the ^1H NMR spectra (Me_4Si as the internal reference in CCl_4 solutions). Mass spectra were obtained on a VG Micromass 70 70F instrument. Melting points were obtained with a Büchi-Tottoli apparatus and are not corrected. Microanalyses were performed by the Central Service of the CNRS.

2,2-Dichloro-3-methyl-3-(4-methylphenyl)cyclobutanone (4a). To a mixture of 10.0 g (ca. 154 mmol) of zinc–copper couple[6] and 4.12 g (31.2 mmol) of olefin 3[5] in 110 mL of dry ether, stirred under argon at room temperature, was added over 1.5 h a solution of 9.77 g (53.8 mmol) of trichloroacetyl chloride and 8.23 g (53.6 mmol) of phosphorus oxychloride in 55 mL of dry ether. After an additional 0.5 h, the ether solution was separated from the excess couple and added to hexane, and the resulting mixture was partially concentrated under reduced pressure in order to precipitate the zinc chloride. The supernatant was decanted and washed successively with a cold aqueous solution of sodium bicarbonate, water, and brine and then dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave the crude product, which was recrystallized from a small amount of cold pentane to yield 5.40 g of pure **4a**. Dry silica gel chromatography with ether–pentane of the material remaining in the mother liquor followed by recrystallization gave an additional 1.00 g (84% combined yield) of cyclobutanone **4a**: mp 51–52 °C (pentane); IR (Nujol) 1805, 1295, 1180, 1135, 990, 820, 780, 755, 720 cm^{-1}; ^1H NMR δ 1.66 (s, 3 H) 2.43 (s, 3 H), 3.50 (AB q, J = 16.5 Hz, $\Delta\nu_{AB}$ = 54.6 Hz, 2 H), 7.25 (s, 4 H). Anal. Calcd for $C_{12}H_{12}OCl_2$: C, 59.28; H, 4.97. Found: C, 59.03; H, 5.00.

2,2-Dichloro-3-methyl-3-(4-methylphenyl)cyclopentanone (4b). A 500-mg (2.06 mmol) sample of cyclobutanone **4a** dissolved in a minimum amount of ether was treated at room temperature with 20 mL (ca. 6 mmol) of ca. 0.3 M ethereal diazomethane followed by 1 mL of methanol.[4] After 1 h, a small amount of acetic acid was added to consume the excess diazomethane, and the solvents were removed under reduced pressure. Recrystallization of the crude material from cold pentane gave 397 mg of pure **4b**. Column chromatography on Florisil with ether–pentane of the material remaining in the mother liquor gave after some epoxide an additional 24 mg (80% combined yield) of cyclopentanone **4b**: mp 88–89 °C (pentane); IR (Nujol) 1760, 1130, 970, 890, 815, 760 cm^{-1}; ^1H NMR δ 1.37 (s, 3 H), 2.33 (s, 3 H), 1.7–3.0 (m, 4 H), 7.23 (AB q, J = 8 Hz, $\Delta\nu_{AB}$ = 19.4 Hz, 4 H). Anal. Calcd for $C_{13}H_{14}OCl_2$: C, 60.72; H, 5.49. Found: C, 60.54; H, 5.48.

2,2,3-Trimethyl-3-(4-methylphenyl)cyclopentanone [(±)-α-Cuparenone, (1)]. A 500-mg (1.95 mmol) sample of dichlorocyclopentanone **4b** in 2.5 mL of tetrahydrofuran was added over 5 min to a stirred solution at −78 °C of ca. 3.3 mmol of lithium dimethylcopper in tetrahydrofuran [from 640 mg (3.36 mmol) of cuprous iodide and 7.5 mL (6.75 mmol) of a 0.90 M solution of methyllithium in tetrahydrofuran, −30 °C, 5 min].[7] Following the addition, the reaction mixture was stirred for 20 min at −78 °C and was then treated with 5 mL of dry hexamethylphosphoric triamide followed by 3.5 mL (7.98 g, 56.2 mmol) of methyl iodide. The mixture was allowed to warm to −40 °C over 3.5 h and was then poured into rapidly stirred aqueous ammonium chloride–ether. The reaction product was isolated with ether and was filtered with ether–pentane through a small pad of Florisil to give 430 mg of a crude mixture of isomeric α-chloro α-methyl ketones. In a similar experiment run on the same scale, the crude mixture was separated by column chromatography on Florisil with ether–pentane to yield 69 mg (15%) of a more polar isomer [IR (Nujol) 1750, 1270, 1020, 820, 810, 740 cm^{-1}; ^1H NMR δ 1.20 (s, 3 H), 1.50 (s, 3 H), 2.33 (s, 3 H), 7.23 (AB q, J = 8 Hz, $\Delta\nu_{AB}$ = 10.2 Hz, 4 H)] and 246 mg (53%) of a less polar isomer: mp 84–85 °C (pentane); IR (Nujol) 1740, 1270, 1075, 1010, 810, 715 cm^{-1}; ^1H NMR δ 1.26 (s, 3 H), 1.66 (s, 3 H), 2.33 (s, 3 H), 7.25 (AB q, J = 8 Hz, $\Delta\nu_{AB}$ = 10.2 Hz, 4 H). Anal. Calcd for $C_{14}H_{17}OCl$: C, 71.02; H, 7.24. Found: C, 70.75; H, 7.31.

The above 430-mg crude sample of isomers in 5 mL of dry tetrahydrofuran was added over 5 min to a stirred solution at −78 °C of ca. 6.0 mmol of lithium dimethylcopper in tetrahydrofuran [from 1.15 g (6.04 mmol) of cuprous iodide and 13.0 mL (12.2 mmol) of a 0.94 M solution of methyllithium in tetrahydrofuran, −25 °C, 5 min]. Following the addition, the reaction mixture was allowed to warm to −50 °C over 1.25 h, recooled to −78 °C, and treated with 10 mL of dry hexamethylphosphoric triamide followed by 6.5 mL (14.82 g, 104.4 mmol) of methyl iodide. After being warmed to −50 °C over 1.25 h, the reaction mixture was poured into rapidly stirred aqueous ammonium chloride–ether. The product was isolated with ether and was purified by column chromatography on Florisil with ether in pentane to afford 218 mg (52% overall) of (±)-α-cuparenone (1)[1,2] as a low-melting solid: IR (film) 1740, 1380, 1375, 1275, 1100, 1055, 1020, 810 cm^{-1}; ^1H NMR δ 0.57 (s, 3 H), 1.13 (s, 3 H), 1.23 (s, 3 H), 2.37 (s, 3 H), 7.23 (m, 4 H). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32; M_r 216.15141. Found: C, 83.53; H, 9.60; M_r (mass spectrum) 216.15159.

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Registry No. (±)-1, 74183-95-2; 3, 1195-32-0; (±)-4a, 87306-59-0; (±)-4b, 87306-60-3; trichloroacetyl chloride, 76-02-8.

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Oxidation of Dihydroxy Aromatics by Hypervalent Iodine Oxides: A Facile Quinone Synthesis

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The quinone moiety plays an extremely important role in biological redox systems. A large number of oxidants have been used for preparations of *o*- and *p*-quinones from corresponding dihydroxy aromatics, i.e., silver oxide,[1] chromic[2] and nitric[3] acids, *o*-chloranil,[4] *N*-chlorosuccinimide,[5] etc.[6] Recently, hypervalent iodine oxides have

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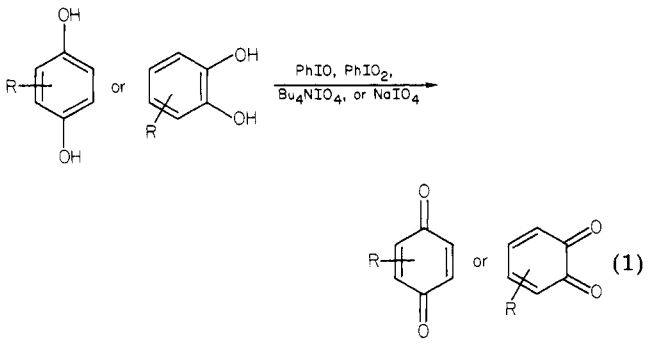
Table I. Quinone Preparation with PhIO, $PhIO_2$, Bu_4NIO_4, and $NaIO_4$ from Dihydroxy Aromatics[a]

substrate	isolated yield (yield by GC and TLC) of quinones, %			
	PhIO	$PhIO_2$	Bu_4NIO_4	$NaIO_4$
4-*t*-butyl-1,2-hydroquinone	(~100)[b]	(~100)[b]	(~100)[b]	95(~100)[b]
3,5-di-*t*-butyl-1,2-hydroquinone	78(~100)[b]	78(~100)[b]	88(~100)[b]	74(~100)[b]
4-chloro-1,2-hydroquinone				99
3-methoxy-1,2-hydroquinone	74			[c]
2-methyl-1,4-hydroquinone	91	61	48[d]	98
2,3,6-trimethyl-1,4-hydroquinone	95	75	72	78
2-*t*-butyl-1,4-hydroquinone				(97)[b,e]
2,5-di-*t*-butyl-1,4-hydroquinone				(~100)[b]
1,4-dihydroxynaphthalene	86[f]	86[f]	(95)[b,e]	98[e]
4,4'-dihydroxybiphenyl	75[g]	[h]	[h]	[i]

[a] The solvent used was CH_2Cl_2 for 1,2-hydroquinones and CH_2Cl_2/MeOH for 1,4-hydroquinones, because of the solubility of the substrates. [b] No byproduct was observed. [c] The reaction was too vigorous. [d] The yield decreases with prolonged reaction time. [e] The solvent was $CHCl_3$. [f] The solvent was $CHCl_3$/MeOH (9:1). [g] The reaction was carried out in THF for 5 h, and the product was precipitated from $CHCl_3$-acetone. [h] The reaction was very slow (no reaction for 1 h). [i] The product structure was not clear.

been found to be unique oxidants.[7,8] In our studies on oxygen transfer from iodosylarene (ArIO)[9] and tetrabutylammonium periodate (Bu_4NIO_4)[10] catalyzed by metalloporphyrins,[7c,d] these hypervalent iodine oxides as well as iodoxybenzene ($PhIO_2$)[11] and sodium periodiate ($NaIO_4$) were found to oxidize various dihydroxy aromatics to the corresponding quinones in high yields under very mild conditions.

When dihydroxy aromatics were treated with PhIO or Bu_4NIO_4 in CH_2Cl_2, $CHCl_3$, or CH_2Cl_2/MeOH (depending on substrate used) at room temperature (eq 1), the corresponding quinones were obtained in high yields in a few minutes. $PhIO_2$ required a slightly longer reaction time (20–30 min). $NaIO_4$ has been used to oxidize catechols in aqueous solutions.[12] We have found that a two-phase system is more suitable for this reagent. The reaction is accelerated greatly by addition of a phase-transfer catalyst such as benzyl trimethylammonium chloride. The quinone products are conveniently isolated directly from the organic layer.



Since the only product observable in TLC, GC, and NMR besides PhI was the quinone, purification with column chromatography on silica gel or recrystallization was very simple. In some cases, only washing the crude products with benzene or ether could remove PhI. Several types of quinones which have or do not have functional groups were obtained by simple treatment with these reagents in high yields. Results obtained for some stable quinones are summarized in Table I. 4,4'-Dihydroxybiphenyl was also oxidized to a quinoid structure product in good yield in a longer reaction time.

The procedures do not involve extraction, and all the reagents contain no heavy metals which require careful treatment. In the oxidation with PbO_2, $Pb(OAc)_4$, and Ag_2O as common oxidants the yields of quinones are not so high (30–80% for 3-methyl-1,2-hydroquinone, 4,4'-dihydroxybiphenyl, etc.).[6] Therefore, these oxidizing agents may be better than standard oxidizing agents for preparations of many quinones. $NaIO_4$ and Bu_4NIO_4 are the most useful of these reagents because they are easiest to purify. These reagents, however, were less effective for oxidation of phenol to quinone.[13]

Experimental Section

The dihydroxy aromatics, PhIO, Bu_4NIO_4, $NaIO_4$, and benzyl trimethylammonium chloride are commercially available. Bu_4NIO_4 was also prepared in 90% yield according to literature method:[10] colorless needles; mp 158 °C (lit.[10] mp 158–159 °C). Both PhIO and $PhIO_2$ were synthesized from iodobenzene by known methods.[9,11]

Preparation of Quinone. Examples of the preparative methods using 2,3,6-trimethyl-1,4-hydroquinone as a substrate are shown below (all procedures were carried out at room temperature).

(A) With PhIO. A solution of 242 mg (1.1 mmol) of PhIO and 152 mg (1.0 mmol) of the hydroquinone in CH_2Cl_2/MeOH (5:1, 12 mL) was stirred for 3 min. The residue after evaporation of the reaction mixture was subjected to the usual column chromatography on silica gel (benzene as an eluent). 2,3,6-Trimethyl-1,4-benzoquinone was eluted after iodobenzene. The pure quinone (142 mg, 95%) was isolated as yellow solid: mp 29 °C (lit.[14] mp 28–29.5 °C); ^1H NMR ($CDCl_3$) δ 2.05 (br s, 9 H, $3CH_3$), 6.57 (m, 1 H); IR ($CDCl_3$) 1640 cm^{-1} (C=O).

(B) With Bu_4NIO_4. The substrate (153 mg, 1.0 mmol) and a stoichiometric amount of Bu_4NIO_4 (433 mg, 1.0 mmol) were dissolved in CH_2Cl_2/MeOH (5:1, 12 mL) and stirred for 2 min. By a workup and purification procedure to that above, the pure quinone was obtained in 72% yield. Iodine sometimes formed

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(13) Oxidation of 2,4-di-*tert*-butylphenol with $PhIO_2$ gave 3,5-di-*tert*-butyl-1,2-benzoquinone in 82% yield.[8] However, the oxidations with PhIO, Bu_4NIO_4, and $NaIO_4$ under similar conditions afforded sluggishly complex product mixtures. In the case of Bu_4NIO_4, 29% of the quinone was obtaied along with some byproducts.

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during the reaction and was removed by washing the crude products with $Na_2S_2O_4$ solution prior to chromatography.

(C) With $PhIO_2$. A mixture of 0.6 mmol of $PhIO_2$ (142 mg) and 1.0 mmol (152 mg) of the substrate in CH_2Cl_2/MeOH (5:1, 12 mL) was stirred for 3 min. The purified product yield was 113 mg (75%) after chromatography.

(D) With $NaIO_4$. To 1.52 g (10 mmol) of the substrate dissolved in 50 mL of CH_2Cl_2 was added a solution of $NaIO_4$ (2.14 g, 10 mmol) in 10 mL H_2O. $PhCH_2NMe_3^+Cl^-$ (50 mg) was added to the mixture and the reaction mixture was stirred for 5 min. The product quinone from organic layer separated was isolated in 78% yield after chromatography. Without $PhCH_2NMe_3^+Cl^-$ vigorous stirring of the reaction with a magnetic stirrer gave the same results in 30 min.

The other quinones isolated, 2-methyl-1,4-benzoquinone,[15] 2,4-di-*tert*-butyl-1,2-benzoquinone,[16] 4-*tert*-butyl-1,2-benzoquinone,[17] 4-chloro-1,2-benzoquinone,[18] 3-methoxy-1,2-benzoquinone,[19] 2,5-di-*tert*-butyl-1,4-benzoquinone,[20] 2-*tert*-butyl-1,4-benzoquinone,[21] 1,4-naphthoquinone,[22] and bis(4-oxo-2,5-cyclohexadienylidene),[23] were identical with the known compounds.

Registry No. PhIO, 536-80-1; $PhIO_2$, 696-33-3; Bu_4NIO_4, 65201-77-6; $NaIO_4$, 7790-28-5; 4-*tert*-butyl-1,2-hydroquinone, 98-29-3; 3,5-di-*tert*-butyl-1,2-hydroquinone, 1020-31-1; 4-chloro-1,2-hydroquinone, 2138-22-9; 3-methoxy-1,2-hydroquinone, 934-00-9; 2-methyl-1,4-hydroquinone, 95-71-6; 2,3,6-trimethyl-1,4-hydroquinone, 700-13-0; 2-*tert*-butyl-1,4-hydroquinone, 1948-33-0; 2,5-di-*tert*-butyl-1,4-hydroquinol, 88-58-4; 1,4-dihydroxynaphthalene, 571-60-8; 4,4'-dihydroxybiphenyl, 92-88-6; 4-*tert*-butyl-1,2-benzoquinone, 1129-21-1; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9; 4-chloro-1,2-benzoquinone, 31222-02-3; 3-methoxy-1,2-benzoquinone, 60855-15-4; 2-methyl-1,4-benzoquinone, 553-97-9; 2,3,6-trimethyl-1,4-benzoquinone, 935-92-2; 2-*tert*-butyl-1,4-benzoquinone, 3602-55-9; 2,5-di-*tert*-butyl-1,4-hydroquinone, 2460-77-7; 1,4-naphthalenedione, 130-15-4; bis(4-oxo-2,5-cyclohexadienylidene), 494-72-4.

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Selective Oxidation of Steroidal Allylic Alcohols Using 3,5-Dimethylpyrazole and Pyridinium Chlorochromate

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3,5-Dimethylpyrazole complexed with chromium trioxide has been used for the oxidation of alcohols to carbonyl compounds[1] and for effecting benzylic oxidation.[2] In the steroid series, this complex has also been successfully used for the allylic oxidation of Δ^5- and $\Delta^{8(14)}$-steroids to the corresponding ketones.[3,4] Pyridinium chlorochromate has recently found wide use in organic synthesis for the oxidation of primary and secondary alcohols to carbonyl compounds.[5] This reagent in methylene chloride containing 2% pyridine at 2–3 °C was reported to effect the high-yield selective oxidation of the allylic hydroxyl function of a number of steroidal alcohols.[6] We now report that $Py{\cdot}HCrO_3Cl$, when used in conjunction with DMP, is a convenient and useful reagent for the rapid and selective oxidation of allylic alcohols.

The selectivity of this reagent was indicated by its failure to significantly oxidize saturated primary and secondary alcohols relative to allylic alcohols. Treatment of **9**, **10a**, and **10b** with 3.0 equiv. of $Py{\cdot}HCrO_3Cl$ in methylene chloride containing an excess of DMP (2%) at 2–3 °C results in a >90% recovery of starting material. Under similar conditions, several steroidal allylic alcohols were successfully oxidized to the corresponding α,β-unsaturated carbonyl compounds (Table I).

When DMP and $Py{\cdot}HCrO_3Cl$ (3 equiv) were used, the diol **1** could be selectively oxidized to testosterone (**2**) in 87% yield. Under identical conditions, sterols **3a**, **5a**, and **7** were oxidized to the corresponding unsaturated ketones in high yield. Several of the substrates contained saturated secondary hydroxyl groups that were not concomitantly oxidized during the reaction. The allylic hydroxyl function in these sterols is in the quasi-equatorial configuration, which makes them more amenable to chromate oxidation. The quasi-axial allylic alcohol **3b** was selectively oxidized, giving a mixture of the 7-keto sterol and starting material. These results are consistant with the slower rate of oxidation reported for allylic alcohols with a quasi-axial configuration.[7] Increasing the amount of $Py{\cdot}HCrO_3Cl$ to 6 equiv resulted in an increased yield of product (91%), indicating the ability to successively oxidize allylic alcohols in either configuration. In constrast to these results, the oxidation of the quasi-axial allylic alcohol **5b** resulted in the formation of a complex mixture of oxidation products (observed by thin-layer chromatography) from which only a low yield of the 7-keto sterol **6** was obtained. These results are similar to those observed when **5b** was oxidized by $Py{\cdot}HCrO_3Cl$ in a 2% pyridine solution of CH_2Cl_2.[6] Undesired side reactions during the chromate oxidation of allylic alcohols have been reported by other workers.[7] Also, the susceptibility of **5b** and its ester derivatives to rearrangement has been observed previously during treatment with acid, Oppenauer oxidation, and pyrolysis.[8,9]

Manganese dioxide of controlled activity has been widely used for the selective oxidation of allylic and benzylic alcohols. Unfortunately, undesired side reactions, long reaction times, and failure of the oxidation of hindered hydroxyl functions have been reported.[7,10,11] Other chromate oxidizing reagents[12-14] and DDQ[10,15] have been reported to selectively oxidize benzylic and allylic alcohols with varying degrees of success. In general, these reactions

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