order $(\rho_R^+)_{Me} > (\rho_R^+)_{Ph} > (\rho_R^+)_{NMe_2}$. This implies that, since the three families display the same sensitivity to inductive effects, the large electronic saturation brought about by the introduction of the first NMe_2 group essentially originates in the saturation of the conjugative ability of the carbonyl group.

Experimental Section

UV Measurements. These experiments have employed a Cary 219 spectrophotometer with matched 1-cm silica window cells. The temperature was kept constant within 0.1 °C by means of water circulation provided by a Lauda LS-15 ultrathermostat.

Materials. The solvents were Merck Uvasol products, stored over molecular sieves (4 Å) and distilled immediately prior to use. The compounds ***N,N*-dimethylpivalamide** (I), **methyl *N,N*-dimethylcarbamate** (II), **phenyl *N,N*-dimethylcarbamate** (III), ***N,N*-diethylpivalamide** (IV), and ***N,N*-dimethyl-*N'*,*N'*-diethylurea** (V) have been obtained by addition of an excess of diethylamine or dimethylamine to an etheral solution of the corresponding chloride. After filtration and removal of the solvent and the excess amine, these materials were purified by low-pressure fractional distillation or by crystallization ($PhOCONMe_2$). ***N,N*-Dimethylcarbamoyl cyanide (VI)** was obtained by treating *N,N*-dimethylcarbamoyl chloride (32 g, 0.3 mol) with potassium cyanide (32.5 g, 0.5 mol) in dry methylene chloride (150 mL) containing a catalytic amount (0.1 g) of 18-crown-6 ether.[6] The mixture was vigorously stirred for 24 h at room temperature and then filtered. Following the evaporation of solvent, the title compound was purified by low-pressure fractional distillation [bp 110 °C (25 torr)]. The yield of pure material was 50%. All these compounds are known and, in every case, their physical and spectroscopic properties were in good agreement with the data reported in the literature.[7]

Registry No. I, 24331-71-3; II, 7541-16-4; III, 6969-90-0; IV, 24331-72-4; V, 14216-18-3; VI, 16703-51-8; *N,N*-dimethylcarbamoyl chloride, 79-44-7; iodine, 7553-56-2.

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Short Regioselective Synthesis of (±)-α-Cuparenone via Three-Carbon Annelation

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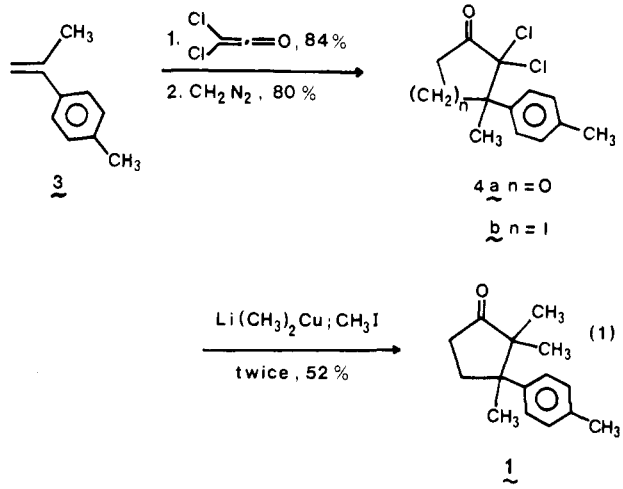
A great many of the syntheses of α- and β-cuparenones (**1** and **2**, from "mayur pankhi"[1]) and related compounds have been carried out primarily to demonstrate new methods of cyclopentanone formation and/or procedures for creating (vicinal) quaternary centers.[2] Nevertheless, there are to date relatively few efficient approaches to these deceptively simple molecules. In this paper we report a brief high-yield synthesis of (±)-α-cuparenone,[3] which is based on a novel reductive geminal dimethylation of α,α-dichlorocyclopentanone **4b**, itself readily produced by three-carbon annelation[4] of tolylpropene **3** (eq 1).



2-(*p*-Tolyl)propene[5] was converted to the α,α-dichlorocyclobutanone **4a** (mp 51–52 °C) in 84% yield through treatment with trichloroacetyl chloride and phosphorus oxychloride in ether in the presence of a zinc–copper couple.[6] None of the isomeric cyclobutanone could be detected. As expected from previous work,[4] ring enlargement of the cyclobutanone **4a** with diazomethane in ether–methanol also proved to be highly regioselective and yielded the α,α-dichlorocyclopentanone **4b** (mp 88–89 °C) in 80% isolated yield.

To complete the synthesis of **1**, replacement of the chloro substituents at the highly crowded α-position in **4b** with methyl groups was required. Previously, we had shown that α,α-dichlorocyclopentanones undergo clean reductive cleavage–methylation on treatment with lithium dimethylcopper followed by methyl iodide.[7] Dichloride **4b**, when subjected twice to these conditions, suffered the desired geminal substitutions[8] to produce in 52% overall

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(2) See: Halazy, S.; Zutterman, F.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 4385 and references therein. Gadwood, R. C. *J. Org. Chem.* **1983**, *48*, 2098. See also: Chandrasekaran, S.; Turner, J. V. *Tetrahedron Lett.* **1982**, *23*, 3799. Leriverend, M. L.; Vazeux, M. *J. Chem. Soc., Chem. Commun.* **1982**, 866.

(3) A synthesis of β-cuparenone (**2**) using a different approach has also been carried out and will be described separately (Greene, A. E.; Lansard J. P.; Luche, J. L.; Petrier, C., submitted for publication).

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(5) Eisenlohr, F.; Schulz, L. *Chem. Ber.* **1924**, *57*, 1808.

(6) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879. See also: Bak, D. A.; Brady, W. T. *Ibid.* **1979**, *44*, 107 and references therein. Chloromethylketene ($CH_3CHClCOCl$, $(C_2H_5)_3N$, cyclohexane, Δ) also underwent cycloaddition; however, the yield of the adduct was unsatisfactory.

(7) (a) Deprés, J. P.; Greene, A. E. *J. Org. Chem.* **1980**, *45*, 2036. (b) Greene, A. E.; Luche, M. J.; Deprés, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2435.

(8) Although reductive cleavage followed by enolate alkylation is a very well-known process, it apparently has not previously been applied iteratively in order to effect geminal dialkylation. See: House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972; p 565. See also footnote 6 in ref 7a. See, however: Coates, R. M.; Pigott, H. D.; Ollinger, J. *Tetrahedron Lett.* **1974**, 3955. Coates, R. M.; Shah, S. K.; Mason, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 2198. Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *Ibid.* **1982**, *104*, 4180.

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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.

(9) This can probably be attributed, at least in part, to the effect of the β-tolyl group and the presence of Cu(I) in the reaction medium. See: Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934. For examples of (less selective) cyclopentanone dimethylation reactions, see: Conia, J. M. *Rec. Chem. Prog.* **1963**, *24*, 43.

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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