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**Convenient Preparations of  
1,2,3,4,5-Pentamethylcyclopentadiene and  
1-Ethyl-2,3,4,5-tetramethylcyclopentadiene**

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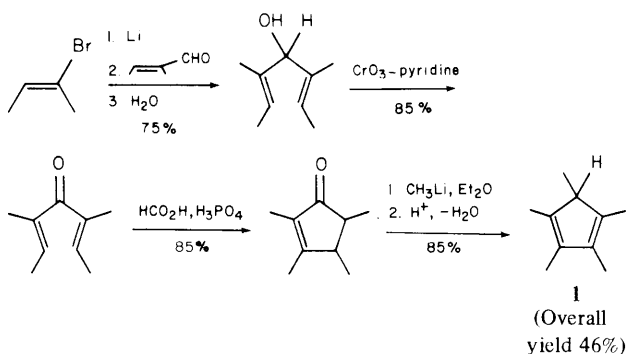
Pentamethylcyclopentadienyl ( $\text{Me}_5\text{Cp}$ ) anion is a useful cyclopentadienyl congener in transition metal chemistry.<sup>1,2</sup> Investigation of  $\text{Me}_5\text{Cp}$ -metal compounds has been hindered by the inaccessibility of pentamethylcyclopentadiene (**1**).<sup>1,3</sup> The most commonly used synthesis<sup>3</sup> (Scheme I) is inconvenient and expensive and the optimal experimental conditions<sup>4</sup> have not been widely disseminated. Although specialized reactions yield  $\text{Me}_5\text{CpM}$  derivatives,<sup>5,6</sup> no general, large-scale preparation of pentamethyl- or other polyalkylated cyclopentadiene derivatives has been available.

Burger et al. recently reported two short syntheses of  $\text{Me}_5\text{Cp}$  which are practical for large-scale preparations (Scheme II).<sup>7</sup> The starting material in the first of these syntheses, hexamethyl(Dewar benzene) (**2**) is expensive and sensitive. We have repeated the cleavage of **3** to **1** following the reported method<sup>7</sup> on a preparative scale and found it to be an efficient and convenient method. The second procedure provides an

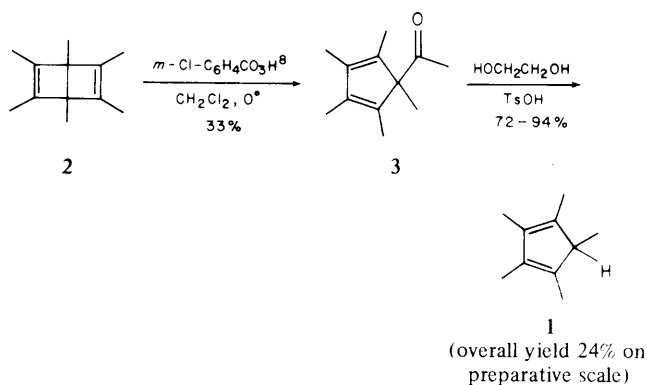
inexpensive route to tetramethylcyclopentenone (**4**), an intermediate also used in the previous synthesis.<sup>3</sup> We have not reproduced the second route.

Here we describe a fourth route to **1** and a particularly convenient preparation of 1-ethyl-2,3,4,5-tetramethylcyclopentadiene (**9**) (Scheme III). This synthesis of **1** is based on the work of Conia<sup>9</sup> and Eaton.<sup>10</sup> 2-Butyl tiglate (**6**) is prepared either by acid-catalyzed esterification of tiglic acid (**5**) or by allowing tigloyl chloride to react with 2-butanol. Compound **6** is cyclized and dehydrated to tetramethylcyclopentenone (**4**) using 1:10 solution of  $\text{P}_2\text{O}_5$  in methanesulfonic acid.<sup>10</sup> This medium proved superior to PPA for this cyclization (see the Experimental Section). Addition of methyllithium to **4** and dehydration of the resulting alcohol to **1** follow previous syntheses.<sup>3,7</sup> The synthesis of **9** begins with dimerization of 3-pentanone to 4,5-dimethyloctane-3,6-dione (**7**) by refluxing with lead dioxide.<sup>11</sup> This procedure is both more convenient and safer than that requiring acetyl peroxide,<sup>12</sup> and it is not necessary to isolate **7**. After simple distillation of excess 3-pentanone, a base-catalyzed internal aldol condensation converts **7** to **8**; addition of methyllithium and dehydration affords **9**. Compound **9** was characterized by NMR spectroscopy and by conversion to ethyltetramethylcyclopentadienyl ( $\text{EtMe}_4\text{Cp}$ ) derivatives of titanium and iron ( $(\text{EtMe}_4\text{Cp})_2\text{TiCl}_2$  and  $(\text{EtMe}_4\text{Cp})_2\text{Fe}$ ).

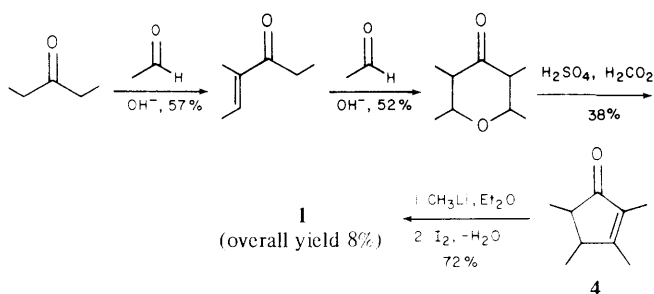
The relative merits of these new methods for preparation of pentaalkylcyclopentadienes are based on cost and convenience. The most convenient of these four preparations for large-scale work is that leading from 3-pentanone to **9** (method

**Scheme I.** Synthesis of Pentamethylcyclopentadiene (**1**) Based on Butenyllithium (Method 1)<sup>3,4</sup>**Scheme II.** Syntheses of Pentamethylcyclopentadiene Reported by Burger et al.<sup>7</sup>

## Method 2



## Method 3



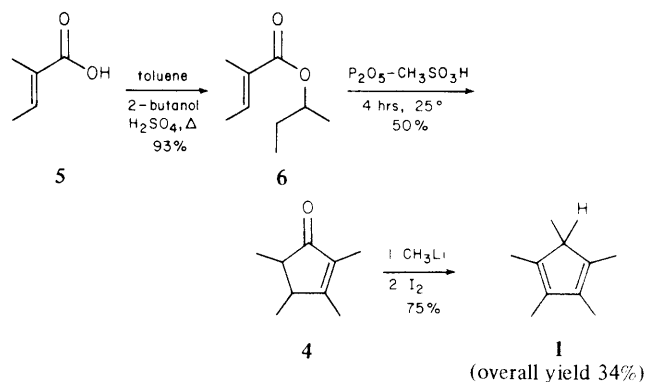
5). Starting materials are inexpensive and the procedure is easily carried out on a scale that yields 100–200 g of **9**. Although organometallic derivatives of  $\text{EtMe}_4\text{Cp}$  lack the aesthetic symmetry afforded by  $\text{Me}_5\text{Cp}$ , they have the compensating advantage of higher solubility ( $(\text{EtMe}_4\text{Cp})_2\text{TiCl}_2$  is soluble in both toluene and hexane while  $(\text{Me}_5\text{Cp})_2\text{TiCl}_2$  is insoluble in these solvents) and lower melting points ( $\text{Cp}_2\text{Fe}$ , 171°;  $(\text{Me}_5\text{Cp})_2\text{Fe}$ , 291–295°;  $(\text{EtMe}_4\text{Cp})_2\text{Fe}$ , 145°;  $\text{Cp}_2\text{TiCl}_2$ , 289–291°;  $(\text{Me}_5\text{Cp})_2\text{TiCl}_2$ , 273°;  $(\text{EtMe}_4\text{Cp})_2\text{TiCl}_2$ , 200–201°).

Hexamethyl(Dewar benzene) (**1**) is not an inherently expensive material and reduction of its current price would unquestionably render method 2 the best route to **1**. Both methods 2 and 4 produce **1** in comparable yields (24% and 34%, respectively), but method 4 has the disadvantage that an additional step is required. Tiglic acid is, however, less expensive than hexamethyl(Dewar benzene). Method 1 is clearly less convenient as a procedure to **1** than are methods 2 and 4. We have attempted to prepare 2-butyl tiglate (**6**) directly from 2-bromo-2-butene, carbon monoxide, and 2-butanol following the procedure of Heck et al.<sup>13</sup> but have not been able to produce more than trace amounts.

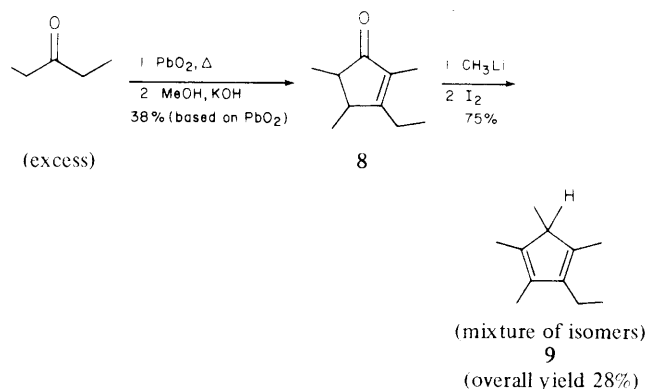
All of the methods discussed have particular applications as large-scale preparatory methods for pentaalkylated cyclopentadienes. Symmetrical cyclopentadienes are available

**Scheme III.** New Syntheses of Pentamethylcyclopentadiene (**3**) and Ethyltetramethylpentadiene (**9**)

## Method 4



## Method 5



from the appropriate starting materials in methods 3–5. Varying degrees of substitution may be induced in method 3 by variations of aldehyde and/or ketone used and in method 4 by use of analogues of tiglic acid and 2-butanol. Method 5 generates a product of lower symmetry than  $\text{Me}_5\text{Cp}$ . Of course, substituents may be varied in derivatives made by methods 3–5 by the addition of alkyl lithium compounds other than methyl lithium to the tetraalkylcyclopentenone, although steric hindrance may become a problem with the more highly substituted cyclopentenones.

We note finally that the procedure for preparation of metallocenes using lithium cyclopentadienide given in the Experimental Section is superior to those previously reported and is applicable to pentamethylcyclopentadiene as well.<sup>14</sup>

**Experimental Section**

The following chemicals were obtained from the indicated suppliers: tiglic acid, 3-pentanone, thionyl chloride, methanesulfonic acid (practical grade) (Eastman);  $\text{P}_2\text{O}_5$  (Mallinckrodt); 2-butanol (Aldrich); methyl lithium (in  $\text{Et}_2\text{O}$ ) and titanium trichloride (Alfa); lead dioxide (Fischer); polyphosphoric acid (MCB). Ir spectra were taken using a PE Model 567 spectrophotometer, and NMR spectra using a Varian T-60 spectrometer. Melting points, boiling points, and pressures are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J. Both  $\text{Me}_5\text{CpH}$  and  $\text{EtMe}_4\text{CpH}$  should be stored at  $-10^\circ$ .

**2-Butyl Tiglate (6).** **Method A.** A mixture of 400 ml of 2-butanol, 400 ml of toluene, 46 g (0.46 mol) of tiglic acid, and 10 ml of concentrated  $\text{H}_2\text{SO}_4$  was refluxed for 18 hr while separating water in a Dean-Stark trap. The mixture was cooled, extracted once with 100 ml of water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The resulting oil was distilled through a 30-cm heated Holzmann column giving 65.1 g (93%) of 2-butyl tiglate having bp 66° (8 Torr), lit.<sup>15</sup> bp 87.5° (27 Torr). NMR ( $\text{CDCl}_3$ ):  $\delta$  (TMS) 6.82 (m, 1), 4.53 (sextuplet, 1,  $J \approx 6$  Hz), 1.85 (s, broad, 6), 1.52 (q, 2,  $J \approx 6$  Hz), 0.90 (d, 3,  $J \approx 6$  Hz), 0.73 (t, 3,  $J \approx 6$  Hz).

**Method B.**<sup>16</sup> Tiglic acid (25 g, 0.25 mol) and thionyl chloride (37 g, 0.28 mol) were heated for 2 hr on a steam bath. Excess thionyl chloride was removed by evaporation at reduced pressure, 2-butanol

(25 ml) was added, and the mixture was heated until the evolution of HCl ceased. The resulting oil was distilled to give 35 g (89%) of **6**.

**2,3,4,5-Tetramethylcyclopent-2-enone (4).** **Method A.** 2-Butyl tiglate (15.6 g, 0.1 mol) was magnetically stirred with 150 g of a 1:10 P<sub>2</sub>O<sub>5</sub>-methanesulfonic acid mixture (prepared by mechanically stirring 1 part of P<sub>2</sub>O<sub>5</sub> into 10 parts of practical (95%) methanesulfonic acid)<sup>10</sup> for 4 hr at room temperature. The deep red mixture was added dropwise over 2 hr to 350 ml of water, and aqueous material was extracted with 300 ml of pentane. The pentane solution was washed once with 100 ml of saturated aqueous NaHCO<sub>3</sub> solution and once with 100 ml of saturated aqueous NaCl solution, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. Distillation gave 7.6 g of **4** as a mixture of isomers having bp 100° (30 Torr), lit.<sup>3</sup> bp 59.8° (3.3 Torr), which was 92% pure by glpc (50% yield).

**Method B.** A 2-l. flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer was charged with 600 g of PPA and 90 g (0.19 mol) of 2-butyl tiglate. The mixture was heated to 90° for 10 min<sup>17</sup> and then quenched by the careful addition of ice water. Its final color was deep red. The hydrolyzed reaction mixture was extracted with pentane (1 l.) and the pentane solution extracted with 250 ml of 1 N aqueous NaOH solution. From the aqueous base, 9.6 g of impure tiglic acid was recovered by acidification, extraction, and crystallization. The pentane solution was further extracted with water, saturated aqueous NaHCO<sub>3</sub> solution, and saturated aqueous NaCl solution. Drying (Na<sub>2</sub>SO<sub>4</sub>), concentration, and distillation gave 26 g of material having bp 51–58° (6 Torr) which was 81% **4** by GLC (26%). This material was contaminated by two higher boiling fractions. It was not necessary to remove these contaminants.

**1,2,3,4,5-Pentamethylcyclopentadiene (1).** To a solution of 26 g (0.15 mol) of crude **4** (from the above preparation) in 300 ml of ether maintained at 0° in an ice bath and magnetically stirred under nitrogen was added 120 ml of 2.2 M methylolithium (0.28 mol) using a syringe. The mixture was stirred overnight. Excess methylolithium was destroyed by cautious addition of 30 ml of 2-propanol. The solution was poured into water and extracted with ether, and the combined organic layers were treated with a few crystals (ca. 100 mg) of iodine.<sup>18</sup> Water was allowed to separate for 2 hr. The resulting solution was washed with 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solution (400 ml) and saturated aqueous NaCl solution (150 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration and distillation gave 15.6 g (75%) of **1** (bp 51° (7 Torr), lit.<sup>3</sup> bp 58.3° (13.5 Torr)). NMR (CDCl<sub>3</sub>): δ 2.5 (m, 1), 1.83 (s, broad, 15).

**Pentamethylcyclopentadiene (Method 2).**<sup>7</sup> A mixture of 20 g (0.112 mol) of 1-acetyl-1,2,3,4,5-pentamethylcyclopentadiene,<sup>6</sup> 20 ml (0.36 mol) of ethylene glycol, and 0.3 g of *p*-toluenesulfonic acid hydrate was refluxed overnight while separating water in a Dean-Stark trap. The mixture was cooled, extracted once with 100 ml of water, twice with 100-ml portions of saturated aqueous NaHCO<sub>3</sub> solution, and once with saturated aqueous NaCl solution, and dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration at reduced pressure and distillation gave 11 g (72%) of **3**, bp 47° (5 Torr).

**3-Ethyl-2,4,5-trimethylcyclopent-2-en-1-one.** A mixture of 1 kg (2.1 mol) of lead dioxide and 1.7 l. of 3-pentanone was mechanically stirred at reflux overnight. Yellow lead oxide was removed by filtration and excess 3-pentanone and water were removed by distillation. The residue was taken up in 1.5 l. of methanol and stirred overnight with 5 g of KOH. The base was neutralized with 7.5 ml of concentrated HCl, the methanol evaporated at reduced pressure, and the residue extracted with equal volumes of water, 1 N aqueous NaOH solution, saturated aqueous NaHCO<sub>3</sub> solution, and saturated aqueous NaCl solution and dried (Na<sub>2</sub>SO<sub>4</sub>). Distillation gave 87 g (38%) of **8**, as a mixture of isomers, bp 81–84° (6 Torr). Ir (CCl<sub>4</sub>): 1694 (C=O), 1642 (C=C) cm<sup>-1</sup>. This compound was not characterized further but was used directly.

**Ethyltetramethylcyclopentadiene (9).** Cyclopentenone **8** was dried immediately before use by passage through 40 g of crude Woelm alumina (activity I). A 2-l. round-bottomed flask equipped for magnetic stirring and fitted with a precalibrated addition funnel capped with a No-Air stopper was flame-dried and purged with dry nitrogen. After cooling, 174 g (1.15 mol) of freshly dried **8** and 450 ml of dry ether were added directly to the flask via cannula and then 735 ml (1.25 mol) of 1.7 M ethereal methylolithium was added to the addition funnel, again by cannula. The flask was immersed in an ice bath and the methylolithium added slowly over 2 hr. The mixture was allowed to warm to room temperature and stir overnight. Excess methylolithium was destroyed by the cautious addition of 2-propanol (20 ml) and the

ethereal solution was extracted with water. To the ether layer was added 0.5 g of iodine. Over 0.5 hr 18 ml of water separated. The ethereal layer was extracted twice with 100-ml portions of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solution and twice with 100-ml portions of saturated aqueous NaCl solution, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated to give 164.5 g of light yellow oil (95% crude yield). Distillation gave 130 g (75%) of **9** (EtMe<sub>4</sub>CpH) bp 59–61° (5 Torr), as a mixture of isomers. This material was not further characterized but used directly in the following reactions.<sup>19</sup>

**(EtMe<sub>4</sub>Cp)<sub>2</sub>Fe.** Ferrous chloride was prepared by stirring at reflux 0.97 g (6 mmol) of FeCl<sub>3</sub>, 0.169 g (3 mmol) of iron powder (electrolytically reduced, 300 mesh), and 20 ml of THF (distilled from benzophenone ketyl) for 5 hr under argon. A 0.052 M slurry of EtMe<sub>4</sub>CpLi was prepared by the addition of 150 ml of 1.70 M methylolithium to a solution of 13.0 g of EtMe<sub>4</sub>CpH in 20 ml of dry Et<sub>2</sub>O, evaporation of ether, and replacement with THF. An aliquot of this slurry (42 ml) was added to the ferrous chloride preparation at room temperature via syringe. The reaction was stirred overnight at reflux, quenched with water, and extracted with 200 ml of CHCl<sub>3</sub>. The organic layer was washed with saturated aqueous NaCl solution, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated to give 1.7 g (53% crude) of (EtMe<sub>4</sub>Cp)<sub>2</sub>Fe. Three recrystallization from CHCl<sub>3</sub>-MeOH gave clear yellow crystals (0.9 g), mp 145° (sealed tube). NMR (CDCl<sub>3</sub>): δ 2.16 (q, 2, *J* = 7.6 Hz), 1.70 (s, 24), 0.9 (t, 6, *J* = 7.6 Hz). Mass spectrum (70 eV): M<sup>+</sup> - 1, 353. Ir spectrum (KBr, cm<sup>-1</sup>): 2960, 2900, 2860, 1470, 1450, 1420, 1375, 1025. Anal. Calcd for C<sub>22</sub>H<sub>34</sub>Fe: C, 74.57; H, 9.67. Found: C, 74.72; H, 9.73.

**(EtMe<sub>4</sub>Cp)<sub>2</sub>TiCl<sub>2</sub>.** Titanium trichloride (15.4 g, 100 mmol) was transferred in a drybox into a dry, 1-l. three-necked flask fitted with No-Air stoppers and equipped for magnetic stirring. The flask was removed from the drybox, 175 ml of dry THF was added via a syringe, the flask was flushed with argon, and one stopper was replaced with a reflux condenser. A suspension of EtMe<sub>4</sub>CpLi in THF prepared as described above (375 ml, 300 mmol) was added via syringe at room temperature and the mixture was refluxed overnight. After cooling of the mixture to 0° in an ice bath, 500 ml of 12 N HCl was added, the resulting dark red solution was extracted with 1 l. of CHCl<sub>3</sub>, and the organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation gave 25.5 g (61%) of (EtMe<sub>4</sub>Cp)<sub>2</sub>TiCl<sub>2</sub>. Recrystallization from CHCl<sub>3</sub>-MeOH gave lustrous purple-brown crystals, mp 200.5–201°. NMR (CDCl<sub>3</sub>): δ 2.50 (q, 4, *J* = 7.6 Hz), 2.03 (s, 24), 0.95 (t, 6, *J* = 7.6 Hz). Mass spectrum (70 eV): M<sup>+</sup>, 416. Ir (KBr, cm<sup>-1</sup>): 2960, 2900, 1450, 1430, 1390, 1380, 1365, 1048, 1020. Anal. Calcd for C<sub>22</sub>H<sub>34</sub>Cl<sub>2</sub>Ti: C, 63.32; H, 8.21; Cl, 16.99. Found: C, 63.25; H, 8.48; Cl, 17.25.

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**Registry No.** Tiglic acid, 80-59-1; 2-butanol, 78-92-2; 2-butyl tiglate, 28127-58-4; 2,3,4,5-tetramethylcyclopent-2-enone, 54458-61-6; 1,2,3,4,5-pentamethylcyclopentadiene, 4045-44-7; methylolithium, 917-54-4; 1-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, 15971-76-3; 3-pentanone, 96-22-0; 3-ethyl-2,4,5-trimethylcyclopent-2-en-1-one, 57459-40-2; ethyltetramethylcyclopentadiene, 57459-41-3; (EtMe<sub>4</sub>Cp)<sub>2</sub>Fe, 57473-98-0; (EtMe<sub>4</sub>Cp)<sub>2</sub>TiCl<sub>2</sub>, 57473-99-1.

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- (16) E. B. Womack and J. McWhirter, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., p 714.
- (17) Yields and purities are highly susceptible to variations in temperature and stirring efficiency. The reaction is exothermic above 80°, and inefficient stirring in large-scale preparations can lead to very high internal temperatures with reduction in yield and concomitant loss of purity.
- (18) A few drops of 6 *N* HCl will also suffice and may result in a cleaner product.<sup>14</sup>
- (19) The material is obtained as a mixture of isomers, and extensive purification does not simplify the spectrum. Prominent NMR resonances (CDCl<sub>3</sub>) are observed at  $\delta$  2.45 (q, 2,  $J = 7$  Hz), 1.80 (s, 12, broad), 0.98 (t, 3,  $J = 7$  Hz).