

A CONVENIENT SYNTHESIS OF ALKYL TETRAMETHYLCYCLOPENTADIENES AND PHENYL TETRAMETHYLCYCLOPENTADIENE

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Summary

A simple, large-scale synthesis of 1,2,3,4,5-pentamethylcyclopentadiene is reported. The method involves electrocyclic ring closure following dehydration of di-*s*-2-butenylmethylcarbinol, prepared from 2-butenyllithium and 0.5 molar equivalent of ethyl acetate. Ethyltetramethylcyclopentadiene, *n*-propyltetramethylcyclopentadiene, *n*-butyltetramethylcyclopentadiene and phenyltetramethylcyclopentadiene are also obtained in good yield by substitution of an appropriate ester for ethyl acetate. These polyalkylcyclopentadienes were converted to the lithium cyclopentadienides and added to iron, titanium, or zirconium yielding $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Fe}$, $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{TiCl}_2$, or $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{ZrCl}_2$, respectively.

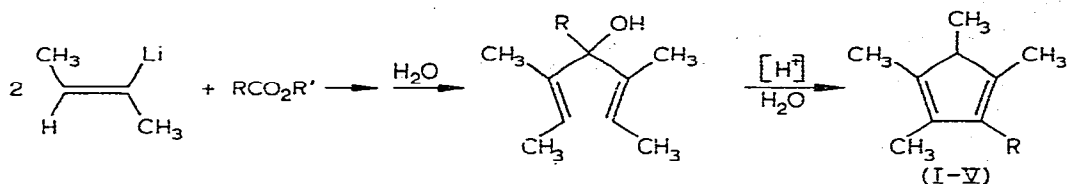
Transition metal compounds containing pentamethylcyclopentadienyl or ethyltetramethylcyclopentadienyl ligands are useful derivatives of the parent ($\eta^5\text{-C}_5\text{H}_5$) compounds by virtue of enhanced solubility and crystallizability [1]. In some cases, most notably for dicyclopentadienyl complexes of Ti and Zr, the fully methyl-substituted derivatives also exhibit higher stability [2-9].

The development of the chemistry of pentamethylcyclopentadienylmetal compounds has been rather slow, however, since no practical, large-scale synthesis of 1,2,3,4,5-pentamethylcyclopentadiene (I) was available. Feitler and Whitesides [1] recently evaluated the syntheses of I used previously and reported new routes to I and to 1-ethyl-2,3,4,5-tetramethylcyclopentadiene (II).

Here we report a much simpler synthesis of I, which is readily adapted to yield a variety of alkyltetramethylcyclopentadienes. The preparation of I fol-

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(I, R = CH₃; II, R = C₂H₅; III, R = *n*-C₃H₇; IV, R = *n*-C₄H₉; V, R = C₆H₅)

lows Scheme 1 (R = CH₃). 2-Butenyllithium prepared from 2-bromo-2-butene and lithium [10], is treated in situ with 0.5 molar equivalent of ethyl acetate to yield di-*s*-2-butenyl methylcarbinol. Subsequent treatment of the crude product of this reaction with a saturated diethyl ether solution of *p*-toluenesulfonic acid affords I in 75% overall yield (based on 2-bromo-2-butene). Since the final steps in the reaction involve an electrocyclic ring closure, we subsequently reviewed the literature and discovered that indeed Sorensen et al. [11] had prepared this carbinol by the same method and investigated the mechanism of its dehydration and closure to I. We wish to bring this method to the attention of those desiring I, since the original report may have escaped their notice as well as ours.

Substitution of one of the methyl groups of I by other alkyl groups is easily accomplished by using the appropriate ester in this reaction sequence. Thus II, III and IV were obtained in comparable yields following the same procedure, but substituting ethyl propionate, ethyl butyrate, and methyl valerate, respectively, for ethyl acetate. All our attempts to prepare *t*-butyltetramethylcyclopentadiene failed. Neither the synthesis of di-*s*-2-butenyl-*t*-butylcarbinol, nor its closure to the desired cyclopentadiene proceeded straightforwardly, probably due to steric constraints on these reactions. The preparation of di-*s*-2-butenyl-phenylcarbinol from 2 equivalents of 2-butenyllithium and ethyl benzoate was successful. It proved necessary to use a modification of the procedure for ring closure, since the use of *p*-toluenesulfonic acid yielded only small amounts of the ring-closed product. Thus careful addition of the carbinol to an excess of concentrated sulfuric acid at 0°C followed by quenching with Na₂CO₃ did afford V in 29% yield.

This method should be readily adaptable to the synthesis of any alkyltetramethylcyclopentadiene, providing the steric bulk of the alkyl group is not too large. All of the procedures are readily applied to large scale preparations.

The unsymmetrical cyclopentadienes II, III, IV, and V were obtained as a mixture of isomers. These were converted to the lithium cyclopentadienides by treatment with *n*-butyllithium, and their reactions with the appropriate metal chloride gave (η⁵-C₅Me₄R)₂Fe, (η⁵-C₅Me₄R)₂TiCl₂, or (η⁵-C₅Me₄R)₂ZrCl₂ in good yield following procedures described previously [1,8,12]. NMR, mass spectral, and analytical data are summarized in Table 1.

Experimental

2-Bromo-2-butene (*cis* and *trans* mixture) was obtained from Chemical Samples Company and used without further purification. Preparation of 2-lithio-2-butene was carried out under argon using diethyl ether which was freshly dis-

TABLE 1
ANALYTICAL, NMR, AND MASS SPECTRAL DATA

Compound	Analysis found (calcd.) (%)		¹ H NMR (δ, ppm)	Mass spectrum (75 eV) (m/e)	Melting point (°C)
	C	H			
C ₅ (CH ₃) ₅ H (I)			1.08d, 3H ^a 1.84(br)s, 12H 2.5m, 1H	M ⁺ 136(7) ^c 121(100) 105(35)	
C ₅ (CH ₃) ₄ (C ₂ H ₅)H (II)			1.0d, 3H ^a 1.02t, 3H 1.81s } 9H 1.78s } 1.65m, 2H 2.3m, 1H	M ⁺ 150(54) 135(100)	
C ₅ (CH ₃) ₄ (C ₃ H ₇)H (III)	87.59 (87.73)	12.40 (12.27)	0.95t, 3H ^b 1.0d, 3H 1.78(br)s, 9H 1.3m, 2H 2.2m, 3H	M ⁺ 164(32) 135(100)	
C ₅ (CH ₃) ₄ (C ₄ H ₉)H (IV)	87.34 (87.56)	12.37 (12.44)	0.95t, 3H ^b 1.0d, 3H 1.3m, 4H 1.77(br)s, 9H 2.2m, 3H	M ⁺ 178(34) 135(100)	
C ₅ (CH ₃) ₄ (C ₆ H ₅)H (V)			1.0m, 3H ^b 1.84m, 9H 2.5m, 1H 7.25(br)s, 5H	M ⁺ 198(100) 183(65)	
(η ⁵ -C ₅ Me ₄ Ph) ₂ Fe (VI)	80.06 (79.99)	7.61 (7.78)	1.70s, 6H ^a 1.76s, 6H 7.16m, 5H		153–154
(η ⁵ -C ₅ Me ₄ Ph) ₂ TiCl ₂ (VII)	70.13 (70.08)	6.70 (6.68)	1.89s, 6H ^a 2.05s, 6H 7.3m, 5H		215–216
(η ⁵ -C ₅ Me ₄ Et) ₂ ZrCl ₂ (VIII)	57.08 (57.36)	7.19 (7.44)	0.90t, 3H ^a 2.0s, 12H 2.40q, 2H		184–185
(η ⁵ -C ₅ Me ₄ Pr) ₂ ZrCl ₂ (IX)	59.09 (58.98)	7.90 (7.84)	0.92t, 3H ^a 1.25m, 2H 2.00s, 12H 2.4t, 2H		103–104
(η ⁵ -C ₅ Me ₄ Bu) ₂ ZrCl ₂ (X)	60.57 (60.43)	8.30 (8.19)	0.90t, 3H ^a 1.23m, 4H 1.92s, 6H 1.95s, 6H 2.45m, 2H		92–93

^a In CDCl₃. ^b In CCl₄. ^c Relative intensities given in parentheses.

tilled from LiAlH₄. Initiation of this reaction requires rigorously dry conditions.

Di-s-2-butenylmethylcarbinol. To a well-stirred mixture of 21 g (3.0 mol) of cut-up lithium wire in 3 l of dry diethyl ether was added a small portion of the 200 g (1.48 mol) 2-bromo-2-butene. After the reaction began, the remainder of the 2-bromo-2-butene was added at a rate sufficient to maintain gentle reflux. Following this addition, stirring was continued for an additional hour. Ethyl acetate (66 g, 0.75 mol) diluted with an equal volume of diethyl ether, then

was added dropwise. The resulting milky white mixture was poured into 2 l of saturated aqueous NH_4Cl . The ether layer was separated, and the pH of the aqueous layer was adjusted to ca. 9 with HCl . The water-solution was extracted three times with diethyl ether. The combined ether layers were dried over Na_2SO_4 and concentrated to 100–200 ml by rotary evaporation.

1,2,3,4,5-Pentamethylcyclopentadiene (I). The concentrate from above was quickly added to a mixture of 13 g *p*-toluenesulfonic acid monohydrate and 300 ml of diethyl ether in a 1 l 3-necked flask equipped with a reflux condenser and an addition funnel. Vigorous reflux began almost immediately and water separated. The mixture was stirred 5 additional minutes after reflux ended, then was poured into a solution of 7 g of Na_2CO_3 in a saturated solution of NaHCO_3 (800 ml). The ether layer was separated, and the aqueous layer extracted three times with diethyl ether. The combined ether layers were dried over Na_2SO_4 . Ether was removed by rotary evaporation and the crude product was transferred at 25°C using a vacuum line. The product was then vacuum distilled as described previously (b.p. $55\text{--}60^\circ\text{C}/13$ torr; reported $58.3^\circ\text{C}/13.5$ torr [13]; yield 75 g, 75%).

Ethyltetramethylcyclopentadiene (II). 2-Lithio-2-butene was prepared from 200 g of 2-bromo-2-butene and 21 g of lithium in 3 l of diethyl ether as described above. Ethyl propionate (76 g, 0.75 mol) diluted with an equal volume of diethyl ether, was added dropwise. Di-s-2-butenylethylcarbinol was isolated and converted to II following the same procedure as that used for I. The product was then vacuum distilled as described previously (b.p. $58\text{--}63^\circ\text{C}/5$ torr; reported $59\text{--}61^\circ\text{C}/5$ torr [1]; yield 72 g, 65%).

n-Propyltetramethylcyclopentadiene (III). 2-Lithio-2-butene was prepared from 200 g of 2-bromo-2-butene and 21 g of lithium in 3 l of diethyl ether as described above. Ethyl butyrate (87g, 0.75 mol) diluted with an equal volume of diethyl ether, was added dropwise. Di-s-2-butenylpropylcarbinol was isolated and converted to III following the same procedure as that used for I. The product was then vacuum distilled (b.p. $50\text{--}55^\circ\text{C}/2$ torr; yield 62 g, 51%).

n-Butyltetramethylcyclopentadiene (IV). 2-Lithio-2-butene was prepared from 200 g of 2-bromo-2-butene and 21 g of lithium in 3 l of diethyl ether as described above. 87 g (0.75 mol) of methylvalerate (87 g, 0.75 mol) diluted with an equal volume of diethyl ether, was added dropwise. Di-s-2-butenylbutylcarbinol was isolated and converted to IV following the same procedure as that used for I. The product was then vacuum distilled (b.p. $52\text{--}57^\circ\text{C}/2$ torr; yield 72 g, 54%).

Phenyltetramethylcyclopentadiene (V). 2-Lithio-2-butene was prepared from 200 g of 2-bromo-2-butene and 21 g of lithium in 3 l of diethyl ether as described above. Ethyl benzoate (105 g, 0.70 mol) diluted with an equal volume of diethyl ether, was added dropwise. Di-s-2-butenylphenylcarbinol was isolated following the same procedure as that used for di-s-2-butenylmethylcarbinol. The crude alcohol (110 ml) then was added to 250 ml of ice-cooled concentrated H_2SO_4 , maintaining the temperature below 10°C . The resulting dark red solution then was added as quickly as possible to a well-stirred mixture of 1 l CCl_4 , 300 g Na_2CO_3 and 1500 ml of ice-water slurry. The CCl_4 layer was separated and washed with 10% Na_2CO_3 solution, saturated NH_4Cl solution, and finally with a NaCl solution. The CCl_4 solution was dried over Na_2SO_4 and concentrated by

rotary evaporation. The remaining oil was vacuum distilled and the fraction distilling at 65–85°C/10⁻²–10⁻³ torr was collected. Yield 40 g, 29%.

Bis(phenyltetramethylcyclopentadienyl)iron. 10 g of iron powder was treated with excess anhydrous HCl under N₂ in 250 ml diethyl ether until all iron had reacted. The resulting white precipitate was dried under vacuum and transferred to a storage bottle in a N₂-filled box. Titration of a known weight of this material with KMnO₄ indicated 35.1% weight percent iron(II). V (2 g, 0.010 mol) was treated under N₂ with 4.0 ml 2.5 M n-C₄H₉Li (0.010 mol) in 150 ml of THF. FeCl₂ (700 mg) from above was added and the mixture was heated to reflux for 2 h. The solvents were removed under reduced pressure and the residue was extracted with 100 ml 30–60°C petroleum ether. The petroleum ether was concentrated by rotary evaporation and then cooled to –80°C to give 1 g of orange, crystalline product.

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