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5-Methoxy-2,3,4,5-tetramethylcyclopent-2-enone, a Synthetic Equivalent For 2,3,4,5-Tetramethylcyclopentadienone: Application to the Synthesis of 1,2,3,4-Tetramethylfulvene.

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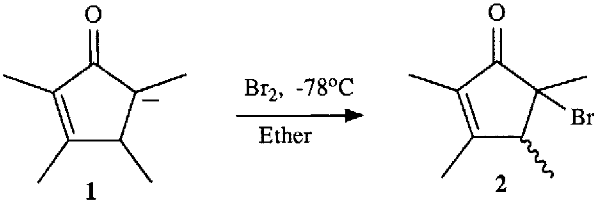
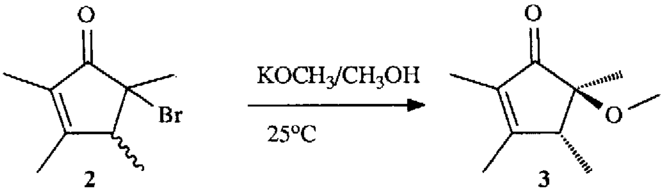
Summary. 5-Methoxy-2,3,4,5-tetramethylcyclopent-2-enone was synthesized and found to be a useful synthetic equivalent for 2,3,4,5-Tetramethylcyclopentadienone in the preparation of 1,2,3,4-Tetramethylfulvene.

The addition of nucleophiles to fulvenes has proven to be a successful route for the preparation of substituted cyclopentadienyl ligands[1]. We have recently reported the synthesis of 1,2,3,4,6-pentamethylfulvene and shown that it is a useful precursor to substituted tetramethylcyclopentadienyl ligands and substituted tetramethylcyclopentadienyl transition metal complexes[2]. In order to extend our previous work to the preparation of enantiomerically pure substituted tetramethylcyclopentadienyl ligands we needed a high yield method for the preparation of 1,2,3,4-tetramethylfulvene. We report here the synthesis of 5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone, a 2,3,4,5-tetramethylcyclopentadienone synthetic equivalent, and its conversion to 1,2,3,4-tetramethylfulvene.

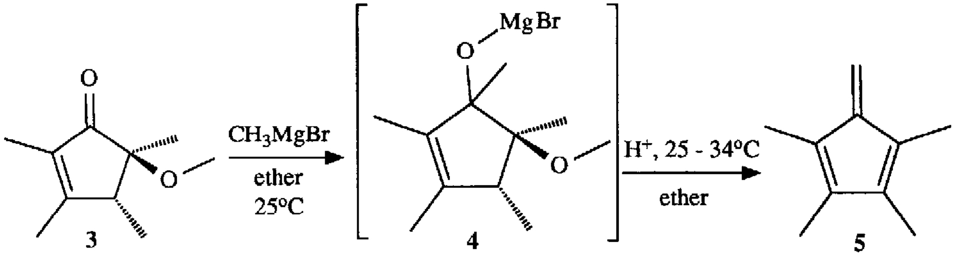
The reaction of 2,3,4,5-tetramethylcyclopent-2-enone enolate[3] **1** with Br_2 at - 78°C in ether gave an



approximately 40/60 mixture of cis and trans 5-bromo-2,3,4,5-tetramethylcyclopent-2-enone[4] **2** in 97 % yield. Compound **2** decomposes slowly, even at low temperature giving off HBr, and must be utilized immediately after preparation. Solvolysis of **2** with $KOCH_3/CH_3OH$ led to the formation of 5-methoxy-2,3,4,5-tetramethyl-



cyclopent-2-enone[5] **3** predominately as the cis isomer (> 90 %) in 94 % yield. The addition of methylmagnesium bromide to **3** in ether to give **4**, followed by acid catalyzed dehydration and elimination of methanol led to the



formation of 1,2,3,4-tetramethylfulvene[6] **5** in 81 % yield, 74 % yield overall from 2,3,4,5-tetramethylcyclopent-2-enone.

ACKNOWLEDGMENT

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4. Approximately 60/40 cis/trans mixture of isomers, ^1H NMR (C_6D_6) 0.65 (CH_3, d, 7.4 Hz); 1.07 (CH_3, d. 7.1 Hz); 1.41 (CH_3, s); 1.43 (CH_3, s); 1.54 (CH_3, s); 1.54 (CH_3, s); 1.58 (CH_3, s); 1.65 (CH_3,s); 3.02 (CH, q, 7.4 Hz); 3.28 (CH, q, 7.1 Hz). Mass Spec. m/e, assignment, % abundance: 218, $P^+(^{81}Br)$, 18 %; 216, $P^+(^{79}Br)$, 19 %; 137, $(P\text{-}Br)^+$, 100 %; 91, 14 %; 109, 51 %; 81, $^{81}Br^+$, 13 %; 79, $^{79}Br^+$, 15 %; 67, 36 %.
5. ^1H NMR (C_6D_6) 0.79 (CH_3, d, 7.6 Hz, 3H); 1.13 (CH_3, s, 3H); 1.51 (CH_3, s, 3H); 1.58 (CH_3, s, 3H); 2.57 (CH, q, 7.6 Hz, 1H); 3.17 (CH_3, s, 3H). Mass Spec. m/e, assignment, % abundance: 168, P^+, 2.3 %; 153, $(P\text{-}CH_3)^+$, 72 %, 138, $(P\text{-}2CH_3)^+$, 100 %; 137, $(P\text{-}C_2H_7)^+$, 43%, 123, $(P\text{-}3CH_3)^+$, 24 %; 109, $(P\text{-}4CH_3)^+$, 12 %.
6. ^1H NMR (C_6D_6) 1.69 (CH_3, s, 6H); 1.84 (CH_3, s, 6H); 5.32 (CH_2, s, 2H). Mass Spec. m/e, assignment, % abundance: 134, P^+, 34 %, 121, $(P\text{-}CH)^+$, 25 %; 119, $(P\text{-}CH_3)^+$ 100 %; 105, $(P\text{-}C_2H_5)^+$, 20 %; 91, $(P\text{-}C_3H_7)^+$, 38 %.

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