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ALKYLATION OF TRIMETHYLSILYLCYCLOPENTADIENIDE ANION WITH *tert*-BUTYL BROMOACETATE. A DESILYLATION REACTION ASSISTED BY A REMOTE STERIC REPULSION

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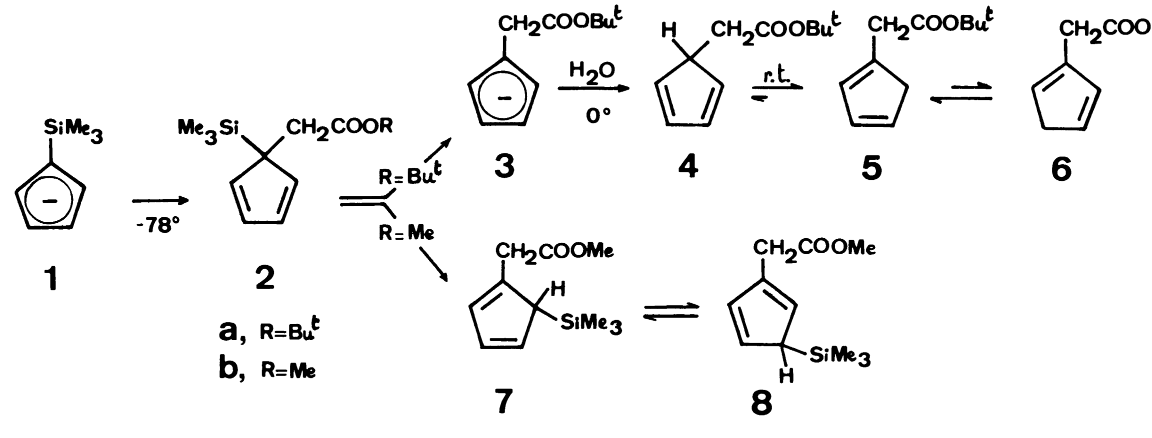
Alkylation of trimethylsilylcyclopentadienide anion with *tert*-butyl bromoacetate, in contrast with the alkylation with the corresponding methyl ester, proceeds with simultaneous elimination of the trimethylsilyl group. A peculiar, long-distance steric effect is postulated.

In connection with our studies on the synthesis of semibullvalene derivatives,[1] we were interested in the alkylation of trimethylsilylcyclopentadienide anion (1) with *tert*-butyl bromoacetate. When equimolar amounts of the bromo ester were added dropwise to 1, prepared from trimethylsilylcyclopentadiene[2] and sodium hydride, in THF at -78 °C, and the reaction mixture was allowed to warm up to 0 °C and finally treated with a cold buffered aqueous solution (pH~7), we isolated in 95% yield a crude product which was identified, by MS and comparison of its ^{1}H-NMR spectrum (δ 6.3, m, 3H; 3.23, d, J~1.3 Hz, 2H; 2.92, br s, 2H; and 1.42, s, 9H (CCl_4)) with those of the three possible methylcyclopentadienes,[3] as *tert*-butyl 1-cyclopentadienylacetate(5).[4] Furthermore, the compound was identical with a sample prepared by direct alkylation of cyclopentadienide anion with *tert*-butyl bromoacetate. In contrast with the corresponding methyl ester,[6] compound 5 (in fact, $5 \rightleftharpoons 6$)[4] may be evaporatively distilled at high vacuum (40-50 ºC, 0.03 Torr) and only dimerizes very slowly at r.t.

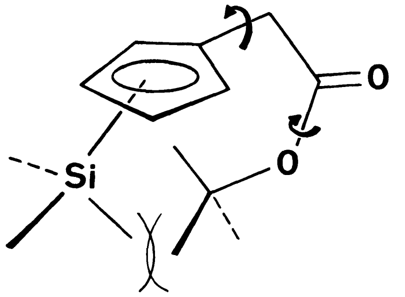


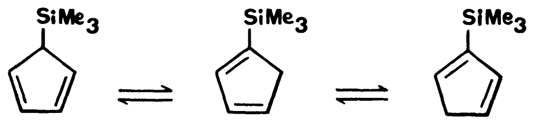
In principle, the fate of the trimethylsilyl group might be explained assuming an electrophilic attack of the bromoacetate at the *ipso* position[7] of the "aromatic six π-electron system"[8] of 1 to give the "Wheland σ-intermediate" 2a, followed by "reversion-to-type" by trimethylsilyl cation elimination (2a → 3).

On the other hand, alkylation of 1 with methyl bromoacetate, under the same conditions, afforded in good yield a product to which, on the basis of mass and NMR spectra (δ 6.4, br m, 3H; 3.59, s, 3H; 3.32, s, 2H;

2.95, m, 1H; and -0.08, s, 9H (CCl_4)), structures 7 and 8 may be assigned at first sight.[9] The postulated *ipso* attack (1 → 2) may be invoked again, the final reaction product being now the result of the 1,5-sigmatropic shifts of the trimethylsilyl group. So, the fate of the trimethylsilyl group in the case of the *tert*-butyl ester may be explained by a similar process, which could be followed by a nucleophilic attack of water on the bisallylic silicon atom; the departure of the trimethylsilyl group would be further assisted by the bulky *tert*-butyl group (see Figure below).[11]

In fact, the *ipso* attack is supported by MINDO/3 calculations,[12] as well as by thermodynamic considerations. It is well known[10,13] that trimethylsilylcyclopentadiene, in contrast with monoalkylated cyclopentadienes,[3] exists largely as the 5-substituted isomer (9a), with the 1- and 2-substituted isomers (9b and 9c) making up, at the equilibrium at 30 °C, only 7% and 3% of the mixture, respectively. Therefore, one would expect that of the three possible "Wheland σ-intermediates", the 5,5-disubstituted isomer (2) should be the more stable one. Moreover, assuming product-like transition states, the activation energy for the *ipso* attack, in which the highly favored double allylic position of trimethylsilyl group is preserved,[13] may be estimated to be *ca.* 6-9 kJ·mole^{-1} lower than that for the attack at anyone of the other positions.





9a 9b 9c

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4. If 5 is stored for a few days or distilled, a small signal at δ 5.9 and additional splittings near δ 3.2 are observed. It is likely[3,5] to attribute these peaks to isomer 6 (*tert*-butyl 2-cyclopentadienylacetate).
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9. As trimethylsilyl migrations are very rapid in the cyclopentadiene systems,[10] it can be suggested that a fast equilibrium among 2b, 7, and 8 occurs, the chemical shifts observed being average values of those of individual isomers (mainly 7 and 8 in the present case). The NMR spectrum also shows two small singlets at δ 0.01 and 0.10, corresponding most probably to isomers with the $SiMe_3$ group linked to olefinic carbon atoms.
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11. In our opinion, the relative stability of 5 towards dimerization also reflects such a steric hindrance.
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