REDOX TROPONIZATION OF TRICHLOROMETHYLATED CYCLOHEXADIENONE BY THE ACTION OF ZERO-VALENCE PALLADIUM – A NEW METHOD FOR THE SYNTHESIS OF 2,4,6-CYCLOHEPTATRIEN-1-ONES

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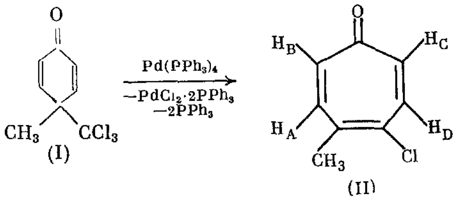
The great theoretical and practical importance of 2,4,6-cycloheptatrien-1-one (tropone) and its derivatives (troponoids) [1] has led to interest in the development of new pathways for the synthesis of this important class of compounds [1, 2]. In the present work, a new oxidation–reduction approach toward the formation of the troponoid system was proposed starting from available semiquinoid precursors, which permits the preparation of substituted tropones containing an active δ-ketodienyl halogen atom on the ring in one step and high yield. We found that the reaction of dienone (I) [3] with $Pd(PPh_3)_4$ [4] in benzene at 20°C for 24 h leads to the formation of trans-$PdCl_2 \cdot 2PPh_3$ (ν Pd–Cl 357 cm^{-1}) and 4-chloro-5-methyl-2,4,6-cycloheptatrien-1-one (II) in 65% yield, mp 75°C. The structure of (II) was shown by elemental analysis and its UV spectrum (λ_{max} 231 nm (log ε 4.23) and 320 nm (log ε 3.89)), mass spectrum (M^+ 156, 154, M^+, $M^+ - CO$ 128, 126, $M^+ - CO - Cl$ 91), and PMR spectrum taken on a Bruker WP-200SY spectrometer at 200 MHz in $CDCl_3$ (δ, ppm): 2.33 s (3H), 6.72 d.d ($1H_C$ or H_B, $^3J = 13$, $^4J = 3$ Hz), 6.78 d.d ($1H_B$ or H_C, $^3J = 13$, $^4J = 3$ Hz), 6.96 d ($1H_A$, $^3J = 13$ Hz), 7.61 d ($1H_D$, $^3J = 13$ Hz).



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