MANGANESE (III) ACETATE-INITIATED RADICAL REACTION OF ACETONE WITH BENZENE

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A simple method was recently proposed for the generation of acetonyl radicals by the one-electron oxidation of acetone by manganese (III) acetate [1, 2].

We have found that the radicals obtained are capable of adding to benzene:

$$\begin{array}{c|c} O & O \\ CH_3CCH_3 + Mn & (III) \longrightarrow CH_3CCH_2 + Mn & (II) + H^+ \\ O & O \\ CH_3CCH_2 + & O \\ \hline \\ CH_3CCH_2 - & O \\ \hline \\ O & Mn & (III) \\ \hline \\ -H^+ & CH_3CCH_2 - & O \\ \hline \end{array}$$

The reaction of 0.1 mole of $Mn(OOCCH_3)_3 \cdot 2H_2O$ with 2 mole of acetone and 0.5 mole of benzene in 100 ml of acetic acid at 70° yielded 0.018 mole (36%) of methyl benzyl ketone [here and elsewhere the yield based on Mn(III) is indicated in parentheses]. The reaction of CH_3COCH_2 with toluene under the same conditions takes two directions: the formation of tolylacetone (30%) and benzyl acetate (7%).

In contrast to CH_3COCH_2 radicals, sec- and tert- α -oxoalkyl radicals RR'CCOR (R = alkyl, and R' = H or alkyl) do not add to benzene but primarily recombine with one another. For example, $\text{CH}_3\text{CH}_2\text{COCH}_2$ \cdot C_2H_5 (2%) and ($\text{CH}_3\text{COCHCH}_3$)₂ (16%) were obtained by the reaction of methyl ethyl ketone with Mn(III) acetate in the presence of benzene. In the case of dipropyl ketone, only its dehydro dimer, viz., ($\text{C}_7\text{H}_{13}\text{O}$)₂ (32%), was isolated. The physical constants and spectral characteristics of the compounds obtained are in agreement with the literature data.

LITERATURE CITED

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