

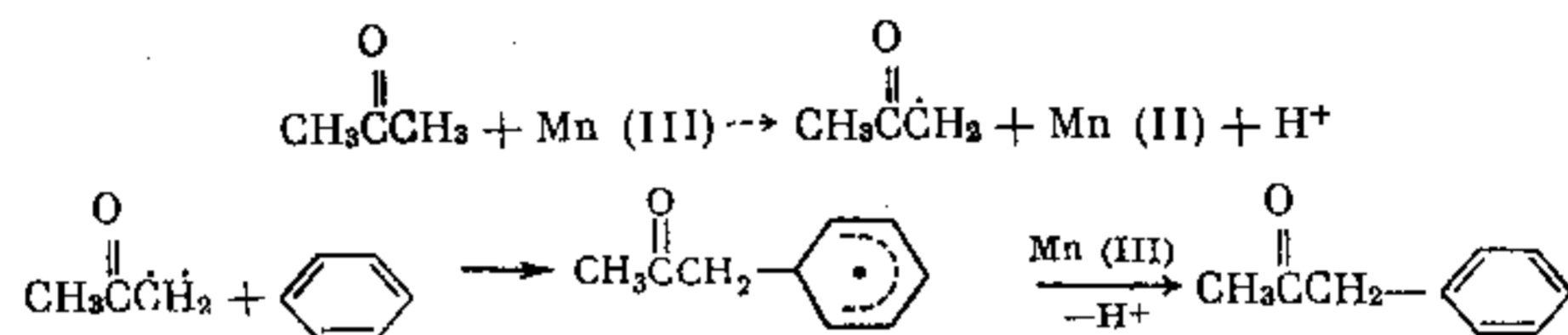
MANGANESE (III) ACETATE-INITIATED RADICAL REACTION OF ACETONE WITH BENZENE

M. G. Vinogradov, S. P. Verenchikov,
and G. I. Nikishin

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A simple method was recently proposed for the generation of acetyl 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:



The reaction of 0.1 mole of $\text{Mn}(\text{OOCCH}_3)_3 \cdot 2\text{H}_2\text{O}$ 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 $\text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$ with toluene under the same conditions takes two directions: the formation of tolylacetone (30%) and benzyl acetate (7%).

In contrast to $\text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$ radicals, sec- and tert- α -oxoalkyl radicals $\text{RR}'\dot{\text{C}}\text{COR}$ ($\text{R} = \text{alkyl}$, and $\text{R}' = \text{H}$ or alkyl) do not add to benzene but primarily recombine with one another. For example, $\text{CH}_3\text{CH}_2\text{COCH}_2 \cdot \text{C}_2\text{H}_5$ (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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2. E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 93, 524 (1971).