

DIRECT REMOTE OXIDATION
 OF ALIPHATIC KETONES TO γ - AND δ -DIKETONES

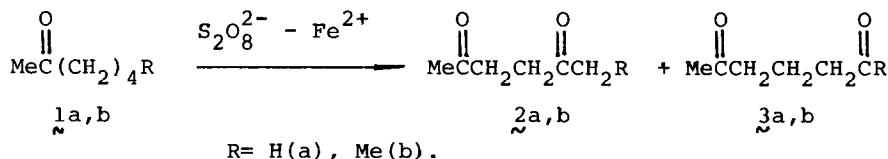
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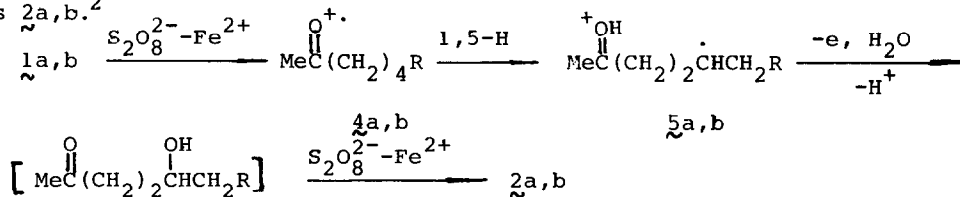
Summary. Aliphatic ketones are converted into γ - and δ -diketones in one-pot oxidation reaction on treatment with $\text{Na}_2\text{S}_2\text{O}_8$ in presence of Fe(II)-ions.

In context of our previous investigations of the remote oxidative functionalization of the alkanolic acids and their amides providing the new approach to γ -lactones¹, we have studied a Fe(II)-ions catalyzed oxidation of aliphatic linear and cyclic ketones by $\text{Na}_2\text{S}_2\text{O}_8$.

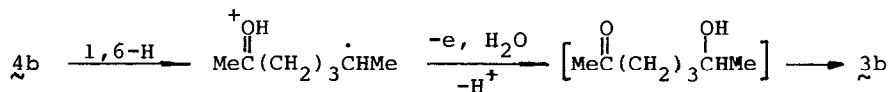
We have found that 2-hexanone 1a is converted on heating with $\text{Na}_2\text{S}_2\text{O}_8$ - FeSO_4 into 2,5-hexanedione 2a (yield 50% for converted 1a, conversion 44%). Under similar conditions 2-heptanone 1b is oxidized into a mixture of 2,5-heptanedione 2b and isomeric 2,6-heptanedione 3b in 1:1.15 ratio (total yield of diketones 2b, 3b is 50% for converted 1b, conversion 40%).



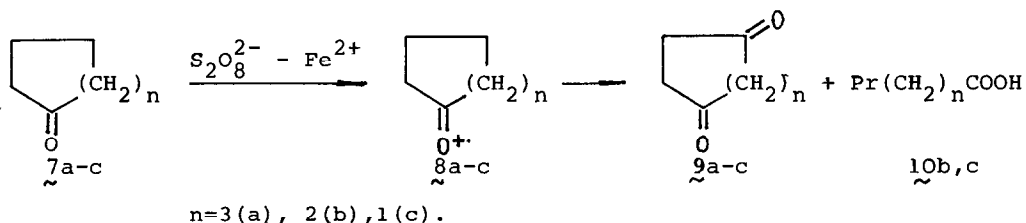
The suggested mechanism of the reaction involves initial generation of O-centered cation radicals 4a,b, that undergo 1,5-H shift to C-centered cation radicals 5a,b. Further oxidation of 5a,b via ketoles 6a,b leads to γ -diketones 2a,b.



δ -Diketone 3b is evidently formed by 1,6-H shift in 4b.



A reaction of oxidative functionalization at non-activated C-atom has been also observed for cycloalkanones $\underline{7a-c}$. Thus cycloheptanone $\underline{7a}$ is oxidized to 1,4-cycloheptanedione $\underline{9a}$ (yield 30% for converted $\underline{7a}$, conversion 66%)³ as a single product, while from cyclohexanone $\underline{7b}$ and cyclopentanone $\underline{7c}$ the mixtures of corresponding diketone $\underline{9b}$ or $\underline{9c}$ and acid $\underline{10b}$ or $\underline{10c}$ were obtained. The ratios $\underline{9b}:\underline{10b}$ and $\underline{9c}:\underline{10c}$ (based on PMR data) are 1:8 and 1:10, total yields of $\underline{9b}, \underline{10b}$ and $\underline{9c}, \underline{10c}$ 20 and 25%. In oxidation of cycloalkanones $\underline{7a-c}$ substantial amounts of tar have been also obtained.



The low yields of diketones $\underline{9b,c}$ could be ascribed to steric inhibition of H-migration in conformationally rigid cation radicals $\underline{8b,c}$ as compared with conformationally flexible $\underline{8a}$. Similar effect of the ring size has been noted in oxidative rearrangements of 1-cyanocycloalkanols.⁴

The studied reaction is, to our knowledge, the first example of remote functionalization at non-activated carbon of ketones caused by one-electron oxidant. Previously the remote acetamidation of alkanones has been observed in electrochemical oxidation in acetonitrile.⁵

Typical procedure. A solution of 4.76 g (0.02 mole) of $\text{Na}_2\text{S}_2\text{O}_8$ in 50 ml of water was added dropwise to a stirred mixture of 2.0g (0.02 mole) of $\underline{7a}$ and 0.83g (0.003 mole) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml of water at 80°. The mixture was kept at the same temperature for 6h, cooled to 20° and extracted with ether (2x100 ml) and CHCl_3 (100 ml), combined extracts were dried (MgSO_4). Distillation of the residue after solvent removal afforded 0.5g $\underline{9a}$ (yield 50% for converted $\underline{7a}$, conversion 44% (g.l.c. data)), b.p. 45°C (2 torr), ms: 114 (M^+); $^1\text{H NMR}$ (CDCl_3 , TMS, 100 MHz): 2.16 (s, 6H), 2.68 (s, 4H) ppm.

References and Notes.

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- For oxidation of alcohols by peroxydisulfates see e.g. A.R.Gallopo, J.O.Edwards, J.Org.Chem., 1971, **36**, 4089.
- All products have satisfactory $^1\text{H NMR}$ and mass spectral data; mixture of $\underline{2b}$ and $\underline{3b}$, b.p. 50-53°C (1.5 torr); $\underline{9a}$, b.p. 85-90°C (1 torr).
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