LITERATURE CITED

- 1. O. V. Bragin and A. L. Liberman, Usp. Khim., 39, 2122 (1970).
- O. V. Bragin, V. G. Tovmasyan, D. B. Furman, and A. L. Liberman, Izv. Akad. Nauk SSSR, Ser. Khim., 32 (1976).
- 3. J. K. A. Clarke, E. McMahon, and A. D. O. Cinneide, Proc. of the Fifth Int. Congress on Catalysis, North-Holland, Amsterdam-London (1973), preprint 47.
- 4. R. W. Maatman, Ind. Eng. Chem., 51, 913 (1959).
- 5. O. V. Bragin, Tao Lung Hsiang, and A. L. Liberman, Kinet. Katal., 8, 98 (1967).

GENERATION OF ACETONYL RADICALS BY ONE-ELECTRON OXIDATION OF ACETONE WITH METAL SALTS AND OXIDES IN NONAQUEOUS MEDIA

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When acetone reacts with the one-electron oxidizing agent Mn(III) acetate in nonaqueous media, CH_3COCH_2 radicals are generated [1, 2]. This reaction has found use in the synthesis of various carbonyl compounds [3-6]. More recently, AgO has been proposed for preparing acetonyl radicals from acetone [7]. In the present work, we have investigated the possibility of generating radicals from acetone using several simple oxidizing agents, viz., MnO_2 , $KMnO_4$, PbO₂, NiO₂, and Co(III), Pb(IV) and Ce(IV) salts. The free radicals formed by oxidation of the acetone were used in the following reactions: addition across a C=C bond; oxidative addition across a C=C bond in the presence of a Cu(II) salt; recombination; homolytic substitution in a benzene ring; and elimination of hydrogen from toluene.

The addition of acetonyl radicals to 1-heptene results in the formation of 2-decanone according to the scheme

The effectiveness of the above metal salts and oxides as radical initiators can be estimated from the yield of 2-decanone per g-equiv. of oxidizing agent (Table 1). The most active initiators are PbO_2 , MnO_2 , and Co(III) and Mn(III) acetate. The effectiveness of KMnO₄ is relatively low (10-20 g-eq of oxidizing agent are required to form 1 mole of 2decanone), but the yield of ketone based on olefin reacted is 40-60% under the conditions selected. This means that KMnO₄ can be used together with other, more selective initiators, for the preparation of higher ketones from acetone and olefins. The other oxidizing agents listed in Table 1 were relatively ineffective in this reaction.

The addition of AcOH to the acetone/l-heptene/oxidant system greatly accelerates the conversion of the oxidizing agent into its lower valence state. Thus, the duration of the reaction initiated by KMnO₄ at 100° is 20 h, but is complete in a few minutes when AcOH is added. It is also found that AcOH has a considerable effect on the yield of 2-decanone, the effect observed depending on the nature of the oxidizing agent. When the reaction is initiated by MnO₂, the ketone yield increases appreciably. When PbO₂ is used, on the other hand, the selectivity of the acid-catalyzed process is sharply reduced.

The effect of AcOH on the rate of the process and the yield of 2-decanone is connected with a change in the chemical nature of the reacting species. In experiments without AcOH addition, MnO_2 and $KMnO_4$ are reduced to MnO by reaction with the acetone. In the presence of AcOH, these oxidizing agents are converted to $Mn(OAc)_2$.

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TABLE 1. Radical Addition of Acetone to 1-Heptene

Oxidizing agent	Acetone: 1- heptene: oxidant ratio (mole: mole: g-eq)	Solvent*	Reaction conditions		Conversion, %		2-Decanone yield (%) based on reacted	
			т., ∘С	time, h	1-hep- tene	oxid- ant	1-hep- tene	oxidant†
$\begin{array}{c} {\rm PbO_2} \\ {\rm PbO_2} \\ {\rm PbO_2} \\ {\rm PhO_2} \\ {\rm MnO_2} \\ {\rm MnO_2} \\ {\rm MnO_4} \\ {\rm KMnO_4} \\ {\rm KMnO_4} \\ {\rm KMnO_4} \\ {\rm Mn(OAc)_3} \\ {\rm Co(OAc)_2OH} \\ {\rm ViO_2} \\ {\rm Ce(SO_4)_2} \\ {\rm NH_4)_2Ce(SO_4)_3} \end{array}$	$\begin{array}{c} 50:1:2\\ 50:1:2\\ 50:1:45\\ 50:1:45\\ 50:1:10\\ 50:1:2\\ 50:1:2\\ 50:1:5\\ 50:1:5\\ 50:1:5\\ 50:1:5\\ 50:1:2\\ 50:1:2\\ 50:1:3\\ 50:1:5\\ 50:1:5\\ 50:1:3\\ 50:1:5\\ 50:1:2\\ 50:1$	AcOH AcOH AcOH AcOH AcOH 	100 100 80 100 100 100 100 56 100 100 100 100	$\begin{array}{c} 20 \\ 2 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\$	97 70 77 22 96 55 86 99 100 92 	44 100 25 31 100 100 100 96 32 	$81 \\ 19 \\ 2 \\ 65 \\ 24 \\ 55 \\ 42 \\ 41 \\ 55 \\ 70 \\ 8 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 4 \\ 5 \\ 6 \\ 6 \\ 4 \\ 5 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6$	97 7 ~0,1 22 8 30 4 7 7 27 125 4 ** 1 ** 1 **

*10 vol.% of total solution.

 $\frac{1}{2}$ -Decanone, moles):(oxidant, g-eq) × 100.

[‡]Based on initial 1-heptene.

**Based on initial oxidant.

Analogously, PbO_2 is reduced to PbO in acetone but to $Pb(OAc)_2$ in an acetone/AcOH mixture. The considerable decrease in ketone yield observed when AcOH is added to the acetone/ 1-heptene/PbO₂ system is probably connected with the formation of acetate forms of Pb(IV) on the surface of the oxide. As we have shown (see Table 1), Pb(OAc)₄ has a low initiating power in the reaction in question.*

Reaction of acetone with MnO₂ in an acetic acid solution containing 1-heptene and Cu(II) acetate results in the oxidative addition of the radicals generated from the acetone to the olefin [3]. The products of this reaction are 5-decen-2-one (II) and trans-5-acetoxy-3-decen-2-one (III)



Under these reaction conditions, the β , γ -unsaturated ketone (I) is completely converted to the keto ester (III).

In the absence of olefin, the radicals generated from the acetone recombine to form 2,5-hexanedione. The use of benzene as solvent facilitates dehydrodimerization of acetone by metal oxides. In this case, the competing reaction of radical addition to the benzene ring plays an insignificant role: The oxidation of acetone with PbO_2 in benzene gives 2,5-hexanedione and methyl benzyl ketone in a ratio of 20:1 at an overall yield of 20% (based on oxidizing agent)

 $CH_{3}COCH_{2} + C_{6}H_{6} \rightleftharpoons CH_{3}COCH_{2} \xrightarrow{e} CH_{3}COCH_{2}C_{6}H_{5} + H^{+}$ (IV)

 $2CH_3COCH_2 \rightarrow CH_8COCH_2CH_2COCH_8$

^{*}Lead tetraacetate primarily gives rise to two-electron oxidation of ketones to acetoxy ketones. The preparation of the latter is based on this reaction [8].

In heterogeneous systems, the oxidation of the intermediate cyclohexadienyl radical (IV) by the metal oxides probably proceeds at a low rate, so recombination of the CH_3COCH_2 radicals predominates.*

When acetone is oxidized by PbO₂ in toluene, the acetonyl radicals remove hydrogen from the solvent. The resulting benzyl radicals recombine with one another or with $CH_3COCH_2^{\dagger}$ to form dibenzyl or benzylacetone

$\begin{array}{l} \mathrm{CH}_{3}\mathrm{CO\dot{C}H}_{2} \ + \ \mathrm{PhCH}_{3} \rightarrow \ \mathrm{Ph\dot{C}H}_{2} \ + \ \mathrm{CH}_{3}\mathrm{COCH}_{3} \\ \mathrm{CH}_{3}\mathrm{CO\dot{C}H}_{2} \ + \ \mathrm{Ph\dot{C}H}_{2} \rightarrow \ \mathrm{PhCH}_{2}\mathrm{CH}_{2}\mathrm{COCH}_{3} \\ \mathrm{2Ph\dot{C}H}_{2} \rightarrow \ \mathrm{PhCH}_{2}\mathrm{CH}_{2}\mathrm{Ph} \end{array}$

The oxidation of pinacolone with PbO_2 in toluene proceeds analogously [9].

Thus, various metal salts and oxides can be used to produce CH₃COCH₂ radicals from acetone; this extends the possibilities for using these radicals in organic syntheses.

EXPERIMENTAL

The PbO₂ (96%), MnO₂ (84%), KMnO₄, Ce(SO₄)₂·4H₂O, and (NH₄)₂Ce(SO₄)₃ were commercial reagents. The Mn(OAc)₃·2H₂O (97%) [10], Co(OAc)₂OH (90%) [11] and NiO₂ (5.5 g-eq/g) [12] were prepared by known methods.

The conversion of the oxidizing agents was determined by iodometry or cerimetry (salts), and the conversion of 1-heptene was determined by GLC (30% polyethylene glycol 300 on Chromosorb W, 80-100 mesh, $3 \text{ m} \times 3$ mm column, octane as internal standard).

Radical Addition of Acetone to 1-Heptene. a) Oxidizing agent PbO_2 . A mixture of 2.5 moles acetone, 0.05 mole 1-heptene and 0.1 mole PbO_2 was shaken in a sealed ampoule at 100° for 20 h. After leaving the suspension to stand, the solution was decanted and the excess starting materials distilled off. Distillation of the residue gave 6.2 g (80%) of 2-decanone, bp 40-42°/0.5 mm. Its properties and spectral characteristics were in agreement with literature data.

b) Oxidizing agent $KMnO_4$. A mixture of 5 moles acetone, 0.1 mole 1-heptene, 0.1 mole $KMnO_4$ and 50 ml AcOH was boiled while stirring in a slow stream of nitrogen until the solution became colorless (~5 h). The mixture was filtered to remove the $Mn(OAc)_2$ formed, and distilled to remove excess acetone and then most of the AcOH (at 40-50 mm). The residue was neutralized with Na₂CO₃ solution and extracted with ether. Distillation under vacuum gave 5.8 g (41%) of 2-decanone.

Radical Oxidative Addition of Acetone to 1-Heptene Initiated by $MnO_2-Cu(OAc)_2$. A mixture of 1 mole acetone, 0.1 mole 1-heptene, 0.2 g-eq MnO_2 , 0.01 mole $Cu(OAc)_2 \cdot H_2O$, and 40 ml AcOH was shaken in an ampoule at 100° until the dark-brown MnO_2 had been completely converted into almost colorless $Mn(OAc)_2$ (~1 h). The mixture was worked up as described above to give 1.3 g ($10\%^+$) of 5-decen-2-one, bp 40-41°/0.5 mm, and 2.7 g (30%) of trans-5-acetoxy-3-decen-2-one, bp 78-80°/0.5 mm. The spectral characteristics of these compounds were identical to those reported in [3].

Acetone Oxidation with PbO₂ in Toluene. A mixture of 2 moles acetone, 0.2 g-eq PbO₂ and 50 ml toluene was shaken in an ampoule at 125° for 20 h. After settling of the suspension, the solution was decanted. Iodometric analysis of the solid residue showed that the conversion of the oxidizing agent was 68%, while GLC analysis of the liquid phase (15% polyethylene glycol 1540 on Chromosorb W, 60-80 mesh, 2 m \times 3 mm column, 4-dodecanone as internal standard) showed that it contained 0.12 g of 2,5-hexanedione. After distilling off the excess acetone and toluene, the residue was washed with water and dried. Distillation gave 0.66 g of a fraction with a bp of 90-120°/5 mm. According to GLC, PMR, and IR data, this contained 40% benzyl acetone and 60% dibenzyl. The overall yield of products was 15% based on oxidant reacted.

*In acetic acid solutions of Mn(OAc)₃, addition of CH₃COCH₂ radicals to benzene is the major reaction, resulting in the formation of methyl benzyl ketone with a yield of 40% [4]. The driving force behind this process is the oxidation of the intermediate radical (IV) by Mn(III) ions to form a cation, which then undergoes proton elimination. [†]With respect to oxidant reacted, on the basis of the consumption of 2 g-eq of oxidant per mole of 5-decen-2-one and 4 g-eq of oxidant per mole of trans-5-acetoxy-3-decene-2-one.

CONCLUSIONS

1. Reaction of salts and oxides of Pb^{IV} , Mn^{III} , Mn^{IV} , Mn^{VII} , Ni^{III} , Ni^{IV} , Co^{III} , and Co^{IV} with acetone in nonaqueous media results in one-electron oxidation of the acetone and generation of acetonyl radicals. The most effective in this process are PbO_2 , MnO_2 , and Mn(III) and Co(III) acetate.

2. The radicals generated enter into typical dimerization, short-bond addition, and aromatic-ring addition reactions.

LITERATURE CITED

- 1. M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 200 (1971).
- 2. E. I. Heiba and R. M. Dessau, J. Am. Chem. Soc., 93, 524 (1971).
- 3. M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, Zh. Organ. Khim., <u>8</u>, 2467 (1972).
- 4. M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 1674 (1972).
- 5. M. G. Vinogradov, S. P. Verenchikov, T. M. Fedorova, and G. I. Nikishin, Zh. Organ. Khim., 11, 947 (1975).
- 6. R. M. Dessau and E. I. Heiba, J. Org. Chem., 39, 3457 (1974).
- 7. M. Hajek, P. Silhavy, and J. Malek, Tetrahedron Lett., 3193 (1974).
- 8. R. Criegee, Oxidation in Organic Chemistry, Part A, Academic Press (1965), p. 277.
- 9. R. Brettle, Chem. Commun., 342 (1970).
- 10. Handbook of Preparative Organic Chemistry [Russian translation], IL (1956), p. 672.
- 11. E. Koubek and J. O. Edwards, J. Inorg. Nucl. Chem., 25, 1402 (1963).
- 12. K. Nakagawa, R. Konaka, and T. Nakata, J. Org. Chem., 27, 1597 (1962).

ALKYLATION OF ALKALI METAL SALTS OF ALIPHATIC POLYNITRO COMPOUNDS -

A GENERAL METHOD FOR PREPARING DIFFERENT TYPES OF POLYNITRO

DERIVATIVES

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In alkylation reactions, the anions of aliphatic nitro compounds, which are ambidentate systems, are capable of undergoing attack at two nucleophilic centers, viz., the oxygen of the nitro group and the carbon bonded to it [1]. The reaction of alkylating agents with salts of mononitro compounds nearly always proceeds by an O-alkylation route to form unstable nitronate esters [1]. As far as the anions of polynitro compounds (PNC) are concerned, their alkylation has been studied practically only in the case of the Ag salts of polynitroalkanes until recently [2-4], and only recently have communications appeared concerning the use of mercury [5] and some other salts [6-8] in this reaction.

According to [9-11], when the Ag salts of polynitroalkanes are reacted with alkyl halides, either O-alkylation is exclusively observed or O- and C-alkylation take place simultaneously. This great tendency for the Ag salts of nitro compounds to undergo O-alkylation is evidently due to the very strong coordination of the silver cation with the halogen atom. This results in considerable polarization of the C-Hal bond in the halo derivative, as a result of which the transition state of the reaction acquires a partial carbonium character [9-11]. This increases the probability of attack at the most electronegative (the most "rigid") atom in the anion of the nitro compound, i.e., the oxygen of the nitro group. Ac-

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