Tetrahedron Letters No. 36, pp 3193 - 3196, 1974. Pergamon Press. Printed in Great Britain.

FREE-RADICAL ADDITION REACTIONS INITIATED BY METAL OXIDES. I. ANTI-MARKOVNIKOV ADDITION OF ACETONE TO OLEFINS INITIATED BY ARGENTIC OXIDE

M. Hájek, P. Šilhavý and J. Málek*
Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences,
16502 Prague 6 - Suchdol, Czechoslovakia

(Received in UK 22 July 1974; accepted for publication 31 July 1974)

The reactions of argentic oxide[1] (AgO) with a wide variety of organic compounds have been a subject of numerous studies in recent years. When used in purely aqueous medium or in aqueous solvents, AgO has been found to oxidize readily alkylaromatic hydrocarbons to aldehydes or ketones, primary alcohols to aldehydes, secondary alcohols to ketones[2], α-aminoacids and α-aminoesters to aldehydes[3], aldehydes to acids[4] and amines to nitriles or aldehydes[4]. Oxidative decarboxylation of carboxylic acids by AgO[5,6] and oxidative cleavage of hydroquinone ethers in an aqueous acidic medium and in the presence of this reagent to yield quinones[7] have also been reported.

We now find that a dramatic change in the reactivity of AgO takes place if this agent is allowed to react with organic substances in a nonaqueous medium. When, for example, a suspension of AgO in acetone is heated under reflux, acetonylacetone can be isolated from the reaction mixture. If, however, to a suspension of AgO in acetone a terminal olefin is added in an appropriate ratio and the mixture is refluxed for several hours, the condensation of acetone is fully suppressed and a highly selective addition reaction of the anti-Markovnikov type occurs, leading, under essentially complete olefin consumption, to a formation of straight-chain methyl alkyl ketones in 73-83% yields (eq. 1):

$$RCH{=}CH_2 + CH_3COCH_3 \xrightarrow[55^\circ]{[AgO]} RCH_2CH_2CH_2COCH_3 \qquad (1)$$

where R is H or an alkyl group. Cycloalkenes give the corresponding acetonyl-

TABLE I

Addition of acetone to olefins initiated by AgO at 56°

Olefin	R[a]	Olefin conversion, %	Reaction time, h	Product	Yield[b] %
1-Pentene	100:1:0.8	100	29	2-octanone	73(64)
1-Hexene	200:1:0.4	98	38	2-nonanone	82(70)
1-Octene	50:1:0.4	78	33	2-undecanone	43
1-Octene	300:1:0.25	97	17	2-undecanone	79
1-Octene	300:1:0.7	100	10	2-undecanone	81
1-Octene	300:1:2.0	100	5	2-undecanone	83
1-Decene	200:1:0.4	97	35	2-tridecanone	80(76)
1-Decene	200:1:0.8	99	24	2-tridecanone	82(79)
Cyclohexene	200:1:2.0	90	33	acetonylcyclohexane	54

[a] Molar ratio: acetone/olefin/AgO on a 5-20 mmol olefin scale. [b] Product yields based on charged olefins and determined by vpc utilizing internal standardization; figures in parentheses indicate isolated yield.

cycloalkanes under these conditions. Gaseous olefins, e.g., ethylene, propylene and 1-butene are converted into 2-pentanone, 2-hexanone and 2-heptanone, respectively, by performing the reaction under a 0.1-5.0 at pressure. Internal olefins or cycloalkenes undergo the addition reaction with acetone less readily and at a lower rate.

In a typical reaction, where 1-octene (6.7g, 0.06mol) is added to a suspension of AgO (0.25g, 2.4mmol) in 825ml dry acetone (18mol) and the mixture is magnetically stirred under reflux in an atmosphere of nitrogen, a complete conversion of the olefin is achieved after 13 h; by filtration of the suspension[9] and simple distillation of the filtrate, one obtains a 81% yield of pure 2-undecanone[10]. Undistillable telomers are formed as by-products in an amount corresponding to remaining 19% of the olefin. Experimental conditions and examples of the addition reaction with other olefins are summarized in Table I.

All the reactions of olefins initiated by AgO were accompanied by telomerization, the extent of which, however, could be substantially suppressed by using a higher molar ratio of acetone to olefins. At least 20-25 mol % of AgO with respect to olefin concentration were required to obtain high yields of methyl alkyl ketones. Higher AgO concentrations (25-200 mol %) accelerated markedly the addition reaction but failed to increase the selectivity, which, on the other hand, was mainly dependent on the acetone to olefin ratio.

The reaction under discussion is analogous to known free-radical addition of ketones to olefins performed in the presence of organic peroxides or peroxy esters (10-20 mol %) as radical sources. However, additions of acetone to terminal olefins initiated, for example, by di-tert-butyl peroxide[11] or diisopropyl peroxydicarbonate[12] give, besides telomers and products of initiator disintegration, the corresponding methyl alkyl ketones only in 32-62% yields. A similar reaction performed in acetic acid as solvent and initiated by transition metal acetates leads to mixtures of the corresponding methyl alkyl ketones, unsaturated ketones and γ-ketoacetates as major products[13,14]. An analogous, Mn(III)acetate initiated reaction in the absence of acetic acid has been reported to give both undistillable products and methyl alkyl ketones without mentioning their yields from the corresponding olefins[15].

Four items of evidence suggest that the addition of acetone to olefins in the presence of AgO is also a free-radical process wherein AgO acts as a "heterogeneous" initiator: (a) The formation of acetonylacetone and water in the absence of olefins. (b) Silver-mirror formation on the reactor walls already at the beginning of the reaction at 56°, irrespective of the thermal stability of AgO (in water) up to 100° [16]. (c) Strong inhibition of the reaction by traces of α-naphthol or, to a lesser extent, of oxygen, both known to inhibit the free radical reactions. (d) Telomer formation. The most likely route to the 1:1 adducts of the anti-Markovnikov type appears therefore to involve initial hydrogen atom abstraction from acetone under action of AgO, followed by addition of the acetonyl radical to the olefin to give the intermediate acetonylalkyl radical; the interaction of this radical with acetone then produces the corresponding methyl alkyl ketone (eq. 2-4):

$$CH_3COCH_3 \xrightarrow{AgO} CH_3CO\dot{C}H_2 \qquad (2)$$

$$RCH{=}CH_2 + CH_3CO\dot{C}H_2 \longrightarrow R\dot{C}HCH_2CH_2COCH_3 \qquad (3)$$

$$R\dot{C}HCH_2CH_2COCH_3 + CH_3COCH_3 \longrightarrow RCH_2CH_2CH_2COCH_3 + CH_3CO\dot{C}H_2 \qquad (4)$$

In none of the AgO initiated reactions of terminal alkenes reported herein the isomers resulting from internal attack of the acetonyl radical were detected Further examination of the synthetic utility of this "heterogeneous" initiating system is in progress.

References and footnotes

1. R. N. Hammer and J. Kleinberg, *Inorg. Synth.*, **4**, 12 (1953).
2. L. Syper, *Tetrahedron Letters*, 4193 (1967).
3. T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *J. Chem. Soc. (C)*, 815 (1970).
4. T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *Tetrahedron Letters*, 5685 (1968).
5. J. M. Anderson and J. K. Kochi, *J. Org. Chem.*, **35**, 986 (1970).
6. J. M. Anderson and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 1651 (1970).
7. C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **94**, 227 (1972).
8. J. Málek, M. Hájek and P. Šilhavý, *Czechoslovak Patent Appl.*, 3917-74 (1974).
9. The collected inorganic precipitate and metallic silver deposited on the reactor walls can be quantitatively reused for the subsequent preparation of AgO.
10. Satisfactory analytical, infrared, NMR and mass spectral data have been obtained for this and following methyl alkyl ketones.
11. A. Rieche, E. Schmitz and E. Gründemann, *Z. Chem.*, **4**, 177 (1964).
12. J. C. Allen, J. I. G. Cadogan and D. H. Hey, *J. Chem. Soc.*, 1918 (1965).
13. E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **93**, 524 (1971).
14. M. G. Vinogradov, S. P. Verenchikov and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 200 (1971).
15. M. G. Vinogradov, S. P. Verenchikov and G. I. Nikishin, *Zhur. Org. Khim.*, **8**, 2467 (1972).
16. J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).