Tetrahedron Letters No. 14, pp 1217 - 1218, 1975. Pergamon Press. Printed in Great Britain.

OXIDATIVE ADDITION OF KETONES TO OLEFINES IN THE PRESENCE OF CUPRIC SALTS

J.Y. LALLEMAND

Laboratoire de Chimie, Ecole Normale Supérieure (laboratoire associé au CNRS n° 32), 24, rue Lhomond, 75231 Paris Cedex 05, France.

(Received in UK 19 February 1975; accepted for publication 26 February 1975)

Oxidations of ketones and malonic esters by different metal ions (Mn^{III}, Pb^{IV}, Ag^{II}) have recently been reported to occur via radical intermediates, which can be trapped by an addition reaction with reactive double bonds [1-4].

We have examined the reaction of cyclopentanone (one of the most reactive ketones towards peroxides) and β-pinene[5] in the presence of various oxidants. We have found that cupric salts such as $Cu(OAc)_2$ are able to promote oxidative addition of cyclopentanone to β-pinene giving compound 5 accompanied by a small amount of 6 arising from hydrogen transfer on radical intermediate 4 (fig. 1).

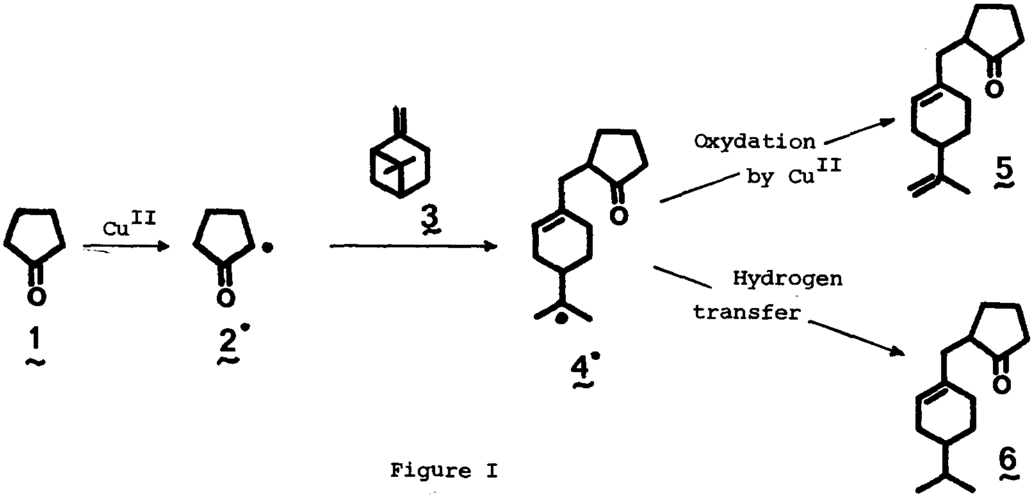

Figure I

Treatment of β-pinene 3 (10 mmoles) in cyclopentanone 1 (100 mmoles) with cupric acetate (20 mmoles) at 90°C for 4 hrs lead after work-up and distillation (97-100°C / 0.05 mm) to 5 (yield 44%, i.r. ν = 1750, 1650, 710 cm^{-1}, n.m.r. ^{1}H : 1.7 (m), 4.7 (s), 5.4 (m) δ, n.m.r. ^{13}C : sp^2 carbons : 108.2, 121.3, 122.0, 134.2 ppm ref. TMS) and 6 (Yield 12%, i.r. ν = 1750 cm^{-1}, n.m.r. ^{1}H : 0.9 (d), 5.5 (m) δ, n.m.r. ^{13}C : sp^2 carbons : 122.1, 134.7 ppm ref. TMS).

Replacement of $Cu(OAc)_2$ by $Mn(OAc)_3$ $2H_2O$ [1a] (20 mmoles), or by t-butyl perbenzoate (10 mmoles) or dibenzoylperoxide (10 mmoles) in the presence of a catalytic amount of copper salts furnished similar results. Pure 6 can be prepared by addition of cyclopentanone on β-pinene initiated by di-t-butyl peroxide[6].

An interesting improvement of the reaction can be realized by employing a catalytic amount of a mixture of copper salts[7] (CuCl, $Cu(OAc)_2$) reoxidized by a suitable reagent such as sodium bichromate[8] (7 mmoles), carefully added over a period of 2 hrs (solid or H_2O solution) in the presence of acetic acid (40 mmole) (yield : 55-75%, G.C. with internal reference). In the absence of copper salts, no 5 or 6 could be detected. This clearly indicates that cupric species are responsible for the hydrogen abstraction from cyclopentanone.

Yields are enhanced by the use of higher dilutions. The 5/6 ratio remains high even in the presence of a large excess of cyclopentanone (a good hydrogen donor in radical reactions) if the reaction mixture does not contain large quantities of solids. This result is consistent with Dessau's[1a] or Kochi's[9] observations on the remarkable ability of cupric salts to oxidize alkyl radicals. Addition of pyridine, or the use of DMF as solvent which are known to enhance the oxidation potential of cupric salts[10], does not afford drastic changes in the reaction course.

Analogous results were obtained with acetone and cyclohexanone. Ethyl acetate, acetic acid and acetonitrile are not oxidized under same reactions conditions.

We suspect that the formation of the radical intermediate 2 arises from the decomposition of a cupric enolate[11]. The same intermediate could also be involved in the oxidation or chlorination of the α-position of ketones by copper salts[12].

References and notes :

1 - a E.I. Heiba and R.M. Dessau, J. Amer. Chem. Soc., 93, 524 (1971).
b R.M. Dessau and E.I. Heiba, J. Org. Chem., 39, 3457 (1974)

2 - G.I. Nikishin, M.G. Vinogradov and T.M. Fedorova, J.C.S. Chem. Comm., 693, (1973) and references therein cited.

3 - M. Hajek, P. Silhavy and J. Malek, Tetrahedron Letters, 3193, (1974)

4 - M. Julia, J.M. Salard and J.C. Chottard, Bull. Soc. Chim. Fr., 2478, (1973)

5 - Addition on a common terminal double bond such as 1-octene leads a complexe mixture of cis- and trans-β- and α- unsaturated ketones (see ref 1 and 2).

6 - M. Cazaux, Thesis, Bordeaux (1969)

7 - J.K. Kochi, J. Amer. Chem. Soc., 84, 1572, (1962).

8 - $KMnO_4$ is also suitable but gives lower yields due to side reactions (decomposition into O_2 and MnO_2).

9 - J.D. Bacha and J.K. Kochi, J. Org. Chem., 33, 83, (1968)
J.K. Kochi and A. Bemis, J. Amer. Chem. Soc., 90, 4038 , (1968)
J.K. Kochi, Acc. Chem. Res., 7, 351, (1974).

10 - E.M. Kosower, W.J. Cole, G.S. Wu, D.E. Cardy and G. Meisters, J. Org. Chem., 28, 630, (1963).

11 - In the catalytic procedure we have replaced the cupric ion by other metal ions such as Co^{III}, Ce^{IV}, Fe^{III} and obtained only 6 with low yields.

12 - See for examples: Reagents for Org. Synthesis, L.F. Fieser and M. Fieser, 1, 159 and 2, 84.