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LANTHANIDE REAGENTS IN ORGANIC CHEMISTRY. A CONVENIENT CATALYTIC OXIDATION OF BENZOINS TO BENZILS USING LANTHANUM NITRATES.

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The oxidation of benzoins provides one of the most direct synthetic route to benzils (2,3). It has been reported recently (4) that benzoins, desoxybenzoins and tolans are oxidised to benzils by thallium (III) nitrate (TTN) in aqueous glyme in the presence of $HClO_4$. We have found that the same oxidations can be simply carried out using catalytic amounts of lanthanide (III) nitrates and one equivalent of HCl in aqueous glyme. Benzil can also be obtained from desoxybenzoin or tolan using this method. Of the five lanthanide (III) nitrates we studied (La, Sm, Eu, Tm, Yb) ytterbium (III) nitrate was found to be the best catalyst, giving high yields from various benzoins (Table I). In contrast to the TTN oxidations, where thallium (III) is the oxidising agent (4), we suggest that in our system NO_3^- is the oxidising agent. In the presence of Yb^{3+} ion as a catalyst, the nitrite ion formed is then reoxidised to nitrate by molecular oxygen

This mechanism is supported by the following observations [Reactions were carried out under reflux in aqueous glyme containing HCl (Table I) unless otherwise stated] :

(i) Benzoin (0.01 mole) is oxidised to benzil (yield 18%) after refluxing with KNO_3 (0.01 mole) alone for 2 hr. However, in a similar reaction when $Yb(NO_3)_3$ (0.002 mole) was also present the yield was 75%.

(ii) Benzoin is oxidised to benzil by refluxing with $NaNO_2$ (1 equivalent) and $YbCl_3$ (0.2 equivalent).

(iii) $YbCl_3$ (0.2 equivalent) catalyses the oxidation of nitrite to nitrate (though the presence of acid was found not to be necessary in this step).

(iv) Yb^{3+}, alone in the absence of NO_3^- or NO_2^- does not catalyse the oxidation of benzoin.

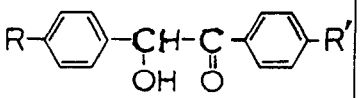
(v) When benzoin (0.01 mole) was refluxed with $Yb(NO_3)_3$ (0.002 mole) under an atmosphere of nitrogen the yield of benzil was very low.

(vi) In the oxidation step of benzoin by nitrate ion, the occurence of Ln^{3+} ion promotes the reaction, probably by chelation of the two oxygens atoms. In this reaction, conducted under nitrogen, higher yields were got using $yb(NO_3)_3$ instead of KNO_3.

(vii) We believe that Yb^{2+} does not take part in the catalytic process in view of the greater stabilities of tripositive lanthanide ions compared to dipositive ions in aqueous solutions (5) and since all dipositive lanthanide ions are readily reduced by hot water.

We are currently carrying out further studies of lanthanum salts as catalysts or modifiers for organic reactions since many are relatively cheap and safe reagents[6].

TABLE I - Oxidation of benzoins into benzils by $Yb(NO_3)_3$ [a]

		Benzil		
		Mp °C	Lit. Mp °C	Yield[b]
H	H	93-94	94-95	95
H	4Me	29-30	30-31	92
H	4MeO	61	62-63	85
4Me	4Me	103-104	104-105	93
4MeO	4MeO	131-132	133	92

a) Ytterbium (III) nitrate (0.002 mole) in aqueous glyme (30 ml, 1:1) was added to benzoin (0.01 mole) in glyme (10ml) and aqueous HCl (8ml, d = 1.19). The solution was refluxed for 5 hr, diluted with water and the product extracted with ether. The crude benzil was purified by recrystallisation.

b) calculated for the recrystallised product.

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References

(1) Equipe de Recherche associée au CNRS N° 559.

(2) G.S.HAMMOND and CHIN-HUA S.WU, J. Amer. Chem. Soc., 95, 8215 (1973).

(3) TSE-LOK HO, Chem. and Ind. (London) 807 (1972) and references therein.

(4) a) A.McKILLOP, B.P.SWANN, M.E.FORD, E.C.TAYLOR, J. Amer. Chem. Soc., 95, 3641 (1973).
b) A. McKILLOP, O.H.OLDENZIEL, B.P.SWANN, E.C.TAYLOR and R.L.ROBEY, ibid. 95, 1296 (1973).

(5) D.A. JOHNSON, J. Chem. Soc. Dalton, 1671 (1974).

(6) We note that although some reactions of lanthanum (III) salts in organic chemistry superficially resemble those of thallium (III) salts, there are also marked differences (e.g. $Ln(NO_3)_3$ salts do not react with olefins).