

THALLIUM IN ORGANIC SYNTHESIS. XXI. DIRECT CONVERSION OF CHALCONES
INTO BENZILS WITH THALLIUM(III) NITRATE (TTN)

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The major factors which influence oxidation of olefins by thallium(III) salts were summarised in the preceding communication¹ and both the rate of reaction and the nature of the products shown to be largely dependent on the thallium reagent employed. Thus, in contrast to oxidation by thallium(III) acetate, which is slow and leads to mixtures of products, oxidation of simple olefins with thallium(III) nitrate (TTN) is complete within seconds at room temperature. Rearrangement during oxidation with TTN is the exclusive or predominant reaction pathway with olefins in which at least one of the substituent groups has a high migratory aptitude.

We are at present investigating the reactions of a variety of α,β -unsaturated compounds with thallium(III) salts and wish to report now that oxidation of chalcones with TTN in an aqueous acid/glyme medium results in formation of benzils. Thus, a solution of 0.03 mole of TTN in 20 ml of water and 5ml of 70% perchloric acid is added to a solution of 0.01 mole of chalcone in 15 ml of glyme, and the mixture stirred and heated under reflux for 2 hr. Thallium(I) nitrate is removed from the cooled reaction mixture by filtration and the filtrate poured into water. Extraction with chloroform and filtration of the extract through a short column of alumina removes traces of inorganic salts; evaporation of the eluate and crystallisation of the residue gives the pure benzil. Data for typical conversions are summarised in Table 1.

Three distinct oxidations are involved in this conversion (Scheme 1): (i) oxidative rearrangement of chalcone 1 gives the β -ketoaldehyde 2, which is

Table 1

Oxidation of Chalcones to Benzils with TTN



<u>Ar</u>	<u>Ar'</u>	<u>Yield, %^a</u>
C ₆ H ₅	C ₆ H ₅	61
4-BrC ₆ H ₄	C ₆ H ₅	55
C ₆ H ₅	4'-BrC ₆ H ₄	70
C ₆ H ₅	4'-CH ₃ C ₆ H ₄	49
4-CH ₃ OC ₆ H ₄	C ₆ H ₅	51
C ₆ H ₅	4'-CH ₃ OC ₆ H ₄	49
2-CH ₃ OC ₆ H ₄	C ₆ H ₅	52
C ₆ H ₅	4'-NO ₂ C ₆ H ₄	45

^aCalculated on pure recrystallised material

converted to deoxybenzoin 3 by acid-catalysed retro-Claisen cleavage; (ii) oxythallation of deoxybenzoin 3 (probably via the tautomeric enol 4) followed by nucleophilic displacement of thallium leads to benzoin 6; and (iii) oxidation of benzoin 6 gives benzil 8. We have examined each of these oxidations separately, and the results are compatible with the mechanism outlined in Scheme 1.

Formation of the β-ketoaldehyde 2 is fully consistent with reports by Ollis and his co-workers² that chalcones having activating substituents in ring A (e.g. 9b, Scheme 2) undergo slow oxidative rearrangement to the corresponding acetals, e.g. 10b, in low yield on prolonged heating with thallium(III) acetate in methanol. We have been able to show that rearrangement is complete in 1-2 hr with TTN in methanol containing a small amount of either perchloric acid or boron trifluoride; the acetals 10a, b can be isolated in 30-60% yield. Only chalcones having deactivating substituents in ring A (e.g. NO₂) fail to react readily. Retro-Claisen cleavage of these compounds to the corresponding deoxybenzoins proceeds smoothly in hot aqueous or methanolic perchloric acid.

Deoxybenzoins are rapidly oxidised to benzils by TTN: treatment of a solution of deoxybenzoin in glyme/aqueous perchloric acid with TTN gave benzil in 74%

formation and subsequent oxidation of benzoin, which can be derived from the oxythallation adduct 5 by either inter- or intra-molecular nucleophilic displacement of the thallium substituent. Oxidation of benzoin almost certainly proceeds via the enediol tautomer 7: enolisation has been shown to be the first step in the analogous oxidations of benzoin to benzil with both mercury(II) and lead(IV).^{4,5} Moreover, when enediol formation is impossible, oxidation is almost completely suppressed. Thus, treatment of benzoin methyl ether with TTN results in only 7% conversion to benzil during 2 hr; under identical conditions oxidation of benzoin gives benzil in 90% yield.

From the data in Table 1 it is evident that TTN oxidation of chalcones constitutes a simple and convenient procedure for the preparation of both symmetrical and unsymmetrical benzils. The reaction is unsuccessful only when substituent groups susceptible to oxidation by thallium(III) are present (e.g. OH, NH₂)⁶ or when both aromatic rings have electron withdrawing groups (e.g. NO₂). The latter restriction is a consequence of inhibition of the initial oxidative rearrangement process due to the poor migratory aptitude of deactivated aromatic systems. Preparation of benzils in which one of the rings is deactivated can readily be accomplished, however, by employing as starting material that chalcone in which the deactivated aromatic ring is alpha to the carbonyl group.

References

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