Thallium in Organic Synthesis. XXXVIII. Oxidation of Chalcones, Deoxybenzoins, and Benzoins with Thallium(III) Nitrate (TTN)[1,2]

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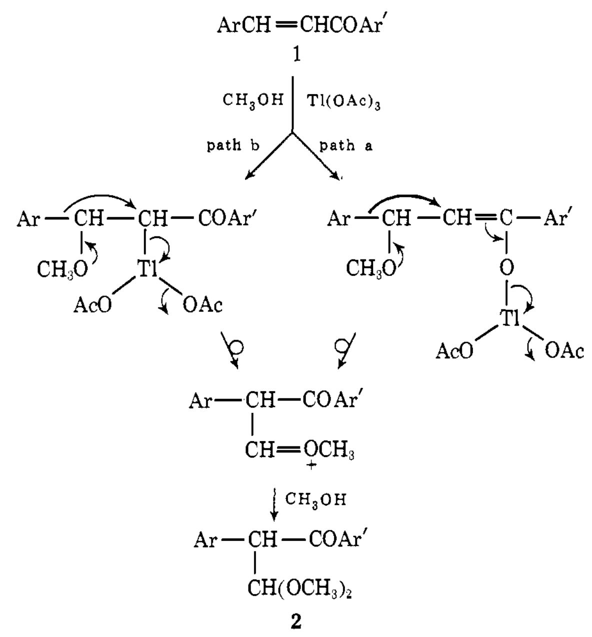
Abstract: Treatment of chalcones with 3 equiv of thallium(III) nitrate (TTN) in aqueous acidic glyme results in formation of benzils by means of a discrete series of three independent oxidations involving the intermediacy of deoxybenzoins and then benzoins. This reaction constitutes a simple and convenient method for the synthesis of unsymmetrical benzils from the readily accessible chalcones.

The oxidation products obtained on treatment of olefins with thallium(III) salts have been shown to depend on the structure of the olefin, the solvent, and the thallium(III) salt employed.[4] The predominant, and often exclusive, reaction pathway observed when simple disubstituted olefins are oxidized with a highly ionic thallium(III) salt such as the nitrate (TTN) is oxidative rearrangement, and the utility of this process for the synthesis of aldehydes and ketones has been described.[3] Little information is available on the reactions of thallium(III) salts with other than simple olefins; there are few reports in the literature dealing with oxythallation of α,β-unsaturated ketones, and these are contradictory. Uemura and his coworkers stated that α,β-unsaturated ketones did not react with thallium(III) salts,[5] but this conclusion was later shown to be incorrect by Ollis and his coworkers, who reported a novel synthesis of isoflavones based on oxidation of chalcones with thallium(III) acetate.[6] In an elegant adaptation of the oxidative rearrangement of olefins by thallium(III) salts, Ollis showed that treatment of highly activated chalcones such as the 4-methoxy derivative (**1**, Ar = $4\text{-}CH_3OC_6H_4$; Ar′ = C_6H_5) with thallium(III) acetate in methanol resulted in formation of the acetal **2** (Scheme I), and proved by standard labeling experiments that the reaction involved a 1,2-aryl migration. The two most probable mechanisms which are consistent with Ollis's results are shown in Scheme I (paths a and b), but it is not known which of these is preferred.

The synthetic utility of this interesting transformation was, however, severely limited: reaction conditions are unattractive (100 hr at reflux); both chalcone and the 4′-methoxy derivative were inert to thallium(III) acetate; and the yield of **2** was only 15%. The reasons for these limitations are now obvious: thallium(III) acetate is a poorly ionic salt and its efficacy as a reagent for oxidative rearrangement of olefins has been shown to be much inferior to more electrophilic salts such as the nitrate[4] and the perchlorate.[7] Indeed, by using TTN rather than thallium(III) acetate, Nógrádi has extended the Ollis procedure into a simple and effective preparation of isoflavones.[8]

Scheme I



As part of our survey of the reactions of TTN with unsaturated systems we have examined in detail the reactions of a variety of chalcones with thallium(III) nitrate (TTN) under different conditions and wish now to describe the results of this investigation.

Results

Oxidation of chalcone with 1 equiv of TTN in methanol containing a small amount of perchloric acid proceeded smoothly at room temperature and, after 18 hr, 93% of the theoretical amount of thallium(I)

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(1) Part XXXVII: E. C. Taylor, R. H. Danforth, and A. McKillop, *J. Org. Chem.*, **38**, 2088 (1973).

(2) Certain of these results were communicated in preliminary form: A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron Lett.*, 5281 (1970).

(3) (a) University of East Anglia; (b) Princeton University.

(4) A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, **95**, 3635 (1973).

(5) S. Uemura, R. Kito, and K. Ichikawa, *Nippon Kagaku Zasshi*, **87**, 986 (1966); *Chem. Abstr.*, **65**, 19962 (1966).

(6) (a) W. D. Ollis, K. L. Ormand, and I. O. Sutherland, *Chem. Commun.*, 1237 (1968); (b) W. D. Ollis, K. L. Ormand, and I. O. Sutherland, *J. Chem. Soc. C*, 119 (1970); (c) W. D. Ollis, K. L. Ormand, B. T. Redman, R. D. Roberts, and I. O. Sutherland, *ibid.*, 125 (1970).

(7) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

(8) L. Farkas, A. Gottsegen, M. Nógrádi, and A. Antus, *J. Chem. Soc., Chem. Commun.*, 825 (1972).

nitrate had precipitated. Filtration of the reaction mixture and evaporation of the filtrate gave an oil from which a colorless, crystalline solid was isolated. This was readily identified as the acetal **2** (Ar = Ar′ = C_6H_5); oxidation had therefore proceeded in the manner described by Ollis for 4-methoxychalcone. The yield of **2** (Ar = Ar′ = C_6H_5) was low (<20%) but could readily be raised to ~50% by use of BF_3–CH_3OH as solvent. Examination of the reactions of a variety of chalcones established that this rearrangement could be effected by TTN provided that no deactivating substituents were present in the migrating aryl group. Yields of the acetals **2** were moderate (20–70%), but this method represents the only one currently available for the synthesis of these interesting compounds.

The moderate yields of acetals obtained in these transformations can readily be explained; hydrolysis of the ketals **2** and subsequent acid-catalyzed retro-Claisen cleavage would be expected to give deoxybenzoins.[9] Direct glpc examination of the reaction mixture obtained on oxidation of chalcone with TTN showed that deoxybenzoin was indeed present together with other compounds including benzil. This latter compound appeared to represent the ultimate oxidation product, and both by a consideration of probable reaction mechanisms and the systematic variation of the relative stoichiometries of the reactants it was found that conversion of chalcone into benzil proceeded in maximum yield when 3 equiv of TTN was employed. Moreover, the reaction was found to be general and to proceed best in an aqueous glyme–perchloric acid medium. Experimental data for representative conversions are summarized in Table I.

Table I. Oxidation of Chalcones to Benzils with TTN–H_3O^+

$$ArCH{=}CHCOAr' \longrightarrow ArCOCOAr'$$

Ar	Ar′	Time, hr[a]	Yield, %[b]	Mp, °C	Lit. mp, °C
C_6H_5	C_6H_5	2	61	93	94–95[c]
4-BrC_6H_4	C_6H_5	6	55	88–89	89–90[d]
C_6H_5	4-BrC_6H_4	4	70	88–89	89–90[d]
4-$CH_3C_6H_4$	C_6H_5	2	62	29–30	30–31[e]
C_6H_5	4-$CH_3C_6H_4$	2	49	29–30	30–31[e]
4-$CH_3OC_6H_4$	C_6H_5	1.5	51	61–62	62–63[c]
C_6H_5	4-$CH_3OC_6H_4$	2	49	61–62	62–63[c]
2-$CH_3OC_6H_4$	C_6H_5	2	52	66–67	71–72[c]
C_6H_5	4-$NO_2C_6H_4$	7	45	140–141	142[f]
C_6H_5	2-C_4H_3S	2	44	61–62	59–60[g]

[a] Optimum reaction times were determined by standard glc sampling techniques. [b] Calculated on pure, recrystallized material. [c] N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, **71**, 2997 (1949). [d] E. P. Kohler and N. K. Richtmyer, *ibid.*, **50**, 3092 (1928). [e] H. H. Hatt, A. Pilgrim, and W. J. Hurran, *J. Chem. Soc.*, 93 (1936). [f] F. D. Chattaway and E. A. Coulson, *ibid.*, 1083 (1928). [g] J. H. Biel, E. P. Sprengeler, H. A. Leiser, J. Horner, A. Drukker, and H. L. Friedman, *J. Amer. Chem. Soc.*, 77, 2250 (1955).

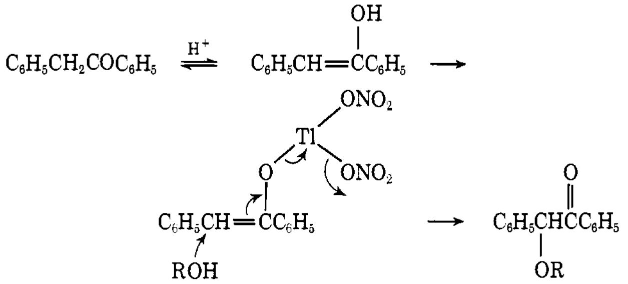
Discussion

The overall mechanism for the oxidation of chalcones to benzils is complex, but it was readily established that three distinct oxidations are involved, namely (i) conversion of the chalcone into the deoxybenzoin; (ii) oxidation of the deoxybenzoin to the benzoin; and (iii) conversion of the benzoin into the benzil. We have examined each of these oxidation steps separately with the following results.

(i) Chalcone to Deoxybenzoin Conversion. The initial product of oxidative rearrangement of chalcone by TTN in aqueous glyme–perchloric acid is presumably α-benzoylphenylacetaldehyde (*cf.* Scheme I). Under the aqueous acidic reaction conditions, however, retro-Claisen cleavage of this compound would be expected to occur readily to give deoxybenzoin. The same overall process is involved in reactions carried out in acidic methanol solution except that elimination of the formyl group can occur only after the original acetal **2** (Ar = Ar′ = C_6H_5) has been hydrolyzed. Reactions in methanol solution were slower than in aqueous acidic glyme, and this was due largely to the surprisingly slow rate of hydrolysis of the acetals **2**; using preformed acetals, it was found that their conversion into deoxybenzoins *via* hydrolysis and retro-Claisen cleavage required several hours reflux in methanolic perchloric acid.

(ii) Deoxybenzoin to Benzoin Conversion. The yield of benzil obtained on oxidation of chalcone with TTN varies with the solvent employed; it is 35–40% in methanol solution, but 60–65% in aqueous acidic glyme, and it was readily established that this discrepancy originated entirely in the oxidation step involving deoxybenzoin. Thus, treatment of deoxybenzoin with 2 equiv of TTN in methanol gave a mixture of four products which were easily identified as benzil (39%), benzoin methyl ether (40%), benzaldehyde (10%), and methyl benzoate (10%). The two minor components of the mixture and benzil are mainly derived from benzoin, whereas formation of benzoin methyl ether represents a side reaction which results in a decrease in the yield of benzil. Conversion of deoxybenzoin into benzoin methyl ether (**4**, R = CH_3) can readily be explained as shown in Scheme II.[10]

Scheme II



3 4

Further oxidation of benzoin methyl ether to benzil, presumably in a manner exactly analogous to that shown in Scheme II, was found to take place only very slowly, however, and in independent experiments oxidation of **4** (R = CH_3) to benzil by TTN in methanolic perchloric acid was found to be only 7% completed after 2 hr (88% of **4** (R = CH_3) was recovered unchanged; benzaldehyde (2%) and methyl benzoate

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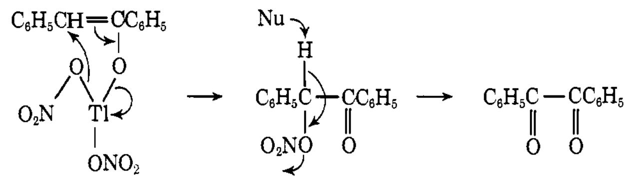
(9) TTN is a trihydrate, and hence moderately strong concentrations of nitric acid build up during the reaction.

(10) Oxidation of cyclohexanone by thallium(III) acetate in acetic acid has been shown to occur *via* rate-determining, acid-catalyzed enolization (J. S. Littler, *J. Chem. Soc.*, 827 (1962)). Oxidation of deoxybenzoin to benzil by chromic acid in acetic acid has also been shown to proceed *via* enolization (K. B. Wiberg, O. Aniline, and A. Gatzke, *J. Org. Chem.*, 37, 3229 (1972)).

(3%) accounted for the material balance). Thus, the significantly lower yield of benzil obtained in methanol, as opposed to aqueous glyme, derives from the ability of methanol to function as a nucleophile in the oxidation step **3** → **4**.

Oxidation of deoxybenzoins to benzoins under aqueous acidic conditions can occur as shown in Scheme II (R = H).[11] Alternatively, direct oxidation of deoxybenzoins to benzils may occur as shown in Scheme III. The ester **5** could readily be isolated as the major product formed on treatment of deoxybenzoin with 1 equiv of TTN in aqueous acidic glyme at room temperature, and standard control experiments demonstrated the ease with which it was converted into benzil. Thus, conversion of the ester **5** into benzil occurred smoothly and in high yield under the same reaction conditions as were employed for the oxidation of deoxybenzoins to benzils, *i.e.*, treatment with a mixture of thallium(I) nitrate and TTN in hot aqueous glyme. Benzil was also obtained in high yield when the ester **5** was heated in aqueous acidic glyme alone or in the presence of either thallium(I) nitrate or TTN.

Scheme III



3 **5**

(iii) Benzoin to Benzil Conversion. As indicated above, benzils may be formed either directly from deoxybenzoins or *via* the intermediacy of benzoins, and conversion of each of these types of substrate into benzils was checked independently. Oxidation of a variety of deoxybenzoins with 2 equiv of TTN in aqueous acidic glyme proceeded smoothly, and yield data for benzils obtained in this way are summarized in Table II. Oxidation of benzoins to benzils with 1 equiv of TTN under similar conditions proceeded rapidly, and experimental data for typical conversions are listed in Table III.

Table II. Oxidation of Deoxybenzoins to Benzils with TTN–H_3O^+

$$ArCH_2COAr' \longrightarrow ArCOCOAr'$$

Ar	Ar′	Yield, %[a]	Mp, °C	Lit. mp, °C
C_6H_5	C_6H_5	74	93–94	94–95[b]
C_6H_5	$4\text{-}BrC_6H_4$	69	88–89	89–90[c]
$2\text{-}ClC_6H_4$	$4\text{-}CH_3C_6H_4$	70	123–124	*d*
$2\text{-}ClC_6H_4$	$4\text{-}CH_3OC_6H_4$	44	102–104	104[e]
$4\text{-}CH_3OC_6H_4$	$4\text{-}BrC_6H_4$	48	136–137	*f*
$4\text{-}BrC_6H_4$	$4\text{-}BrC_6H_4$	76	226	228–229[g]
C_6H_5	$2,5\text{-}(CH_3)_2C_6H_3$	68	Bp 117 (3 mm)	*h*
$4\text{-}NO_2C_6H_4$	C_6H_5	66	139–140	141–142[i]

[a] Calculated on pure redistilled or recrystallized material. [b] Footnote *b*, Table I. [c] Footnote *c*, Table I. [d] *Anal.* Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.30. Found: C, 69.36; H, 4.25. [e] R. Stierlin, *Chem. Ber.*, **22**, 376 (1889). [f] *Anal.* Calcd for $C_{15}H_{11}BrO_3$: C, 56.40; H, 3.45. Found: C, 56.21; H, 3.74. [g] H. Biltz, *Chem. Ber.*, **41**, 1756 (1908). [h] *Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.50; H, 5.84. [i] Footnote *e*, Table I.

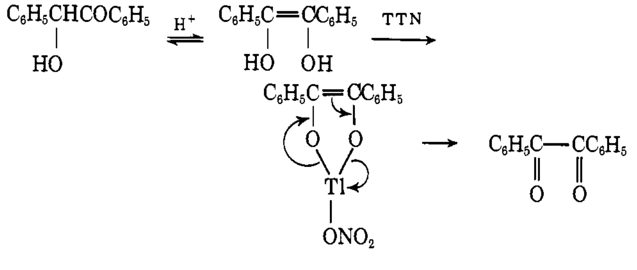
Table III. Oxidation of Benzoins to Benzils with TTN–H_3O^+

$$Ar\overset{OH}{\overset{|}{C}}HCOAr' \longrightarrow ArCOCOAr'$$

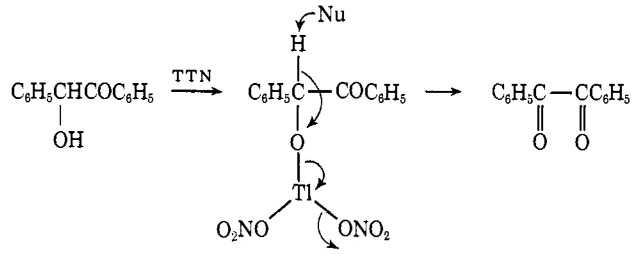
Ar	Ar′	Yield, %[a]	Mp, °C	Lit. mp, °C
C_6H_5	C_6H_5	95	94–95	94–95[b]
$2\text{-}ClC_6H_4$	$4\text{-}CH_3OC_6H_4$	88	103–104	104[c]
$2\text{-}ClC_6H_4$	$2\text{-}ClC_6H_4$	79	134–135	128[d]
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	78	102–103	104[e]
C_6H_5	$4\text{-}CH_3OC_6H_4$	85	61–62	62–63[f]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	80	131–132	133[g]

[a] Calculated on pure, recrystallized material. [b] Footnote *b*, Table I. [c] Footnote *e*, Table II. [d] H. H. Hodgson and W. Rosenburg, *J. Chem. Soc.*, 14 (1930). [e] Footnote *e*, Table II. [f] Footnote *b*, Table I. [g] W. Bolsler, *Chem. Ber.*, **14**, 327 (1881).

Scheme IV



Scheme V



Oxidation of benzoin to benzil most probably proceeds *via* one, or both, of the pathways shown in Schemes IV and V. The mechanism outlined in Scheme IV is particularly attractive in that enolization has been shown to be the rate-determining step in the analogous oxidations of benzoins to benzils with both mercury(II) and lead(IV) salts,[12] and the importance of enediol formation is emphasized by the almost total suppression of oxidation observed when this step is not possible, as with benzoin methyl ether (*vide supra*).

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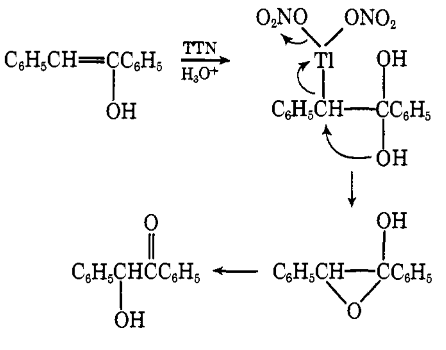
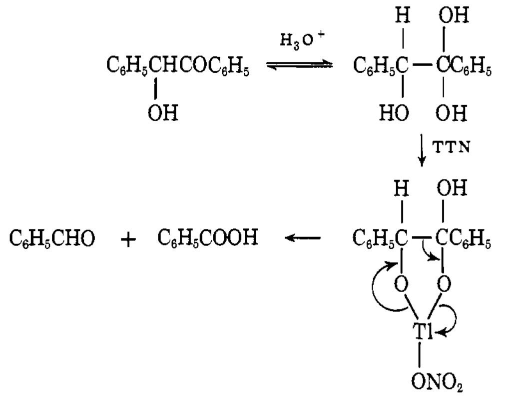
(11) A number of plausible alternate pathways can be envisioned for this conversion; the following finds its analogy in the conversion of cyclohexanone to adipoin with TTN–HOAc (A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Org. Chem.*, 37, 3381 (1972)).



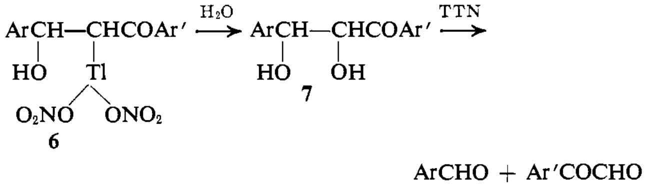
(12) (a) S. Patai and I. Shenfield, *J. Chem. Soc. B*, 366 (1966); (b) K. Ichikawa and Y. Takeuchi, *Nippon Kagaku Zasshi*, 79, 1060 (1958).

Aryl aldehydes and carboxylic acids (or esters) were observed as minor reaction products in all of the oxidations carried out with chalcones, deoxybenzoins, and benzoins, and may be formed by cleavage of benzoins, as shown in Scheme VI. Similar reactions have been recorded in the lead(IV) acetate oxidation of benzoin,[13a] and TTN is known to be an efficient oxidant for 1,2-diaryl-1,2-dihydroxyethanes.[13b] Alternatively, cleavage to aldehydes and acids may occur at an earlier stage in the oxidation. Thus, the initial oxythallation adduct **6** can either undergo oxidative rearrangement as shown in Scheme I, or direct solvolysis of the thallium substituent to give the glycol **7**, as shown in Scheme VII. Cleavage of this latter species with TTN would yield an aryl aldehyde and a glyoxal; these latter compounds are known to hydrate readily,[14] and a second cleavage reaction of the hydrate would yield an aryl carboxylic acid. Evidence in support of these fragmentation reactions was obtained from the following control experiments. Firstly, 1,2,3-triphenylprop-1-en-3-one (**8**) was oxidized with TTN under the standard reaction conditions (Scheme VIII). In this case, oxidative rearrangement of the intermediate oxythallation adduct **9** is less favorable sterically than with simple chalcones, and this solvolysis of the thallium substituent to give the glycol **10** becomes the predominant reaction. Hence the product of oxidative rearrangement (**11**) was only formed in minor amounts; the major products were benzaldehyde (60%) and benzil (75%). Secondly, phenylglyoxal was oxidized to a mixture of benzoic acid and benzaldehyde by TTN in aqueous acidic glyme.

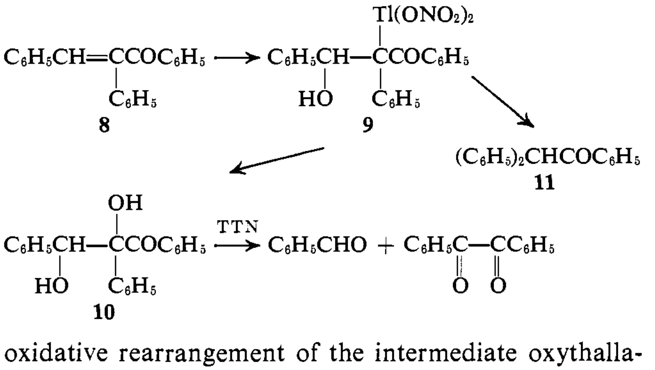
Scheme VI



Scheme VII



Scheme VIII



Summary

TTN oxidation of chalcones to benzils, with loss of one carbon atom, has been shown to take place by means of a discrete series of three independent oxidations involving the intermediacy of deoxybenzoins and then benzoins. This reaction constitutes a simple and convenient method for the synthesis of unsymmetrical benzils from the readily accessible chalcones.

Experimental Section[15]

Starting Materials. All of the chalcones, deoxybenzoins, and benzoins were prepared by standard literature procedures.

General Procedure for the Oxidation of Chalcones to Benzils with TTN–Glyme–Perchloric Acid. The chalcone (0.01 mol) was added to a solution of 0.03 mol of TTN in 20 ml of glyme and 10 ml of water containing 5 ml of 70% perchloric acid, and the mixture was stirred and heated under reflux for 2–7 hr (see Table I; optimum reaction times were determined by standard glc sampling techniques). Thallium(I) nitrate was removed from the cooled reaction mixture by filtration, and the filtrate was diluted with water and extracted with chloroform (2 × 25 ml). The organic extracts were washed with water, dried (Na_2SO_4), concentrated, and chromatographed on acid-washed alumina (2 × 12 cm) using benzene as eluent. Evaporation of the eluate gave the crude benzil which was purified by recrystallization or distillation.

General Procedure for the Oxidation of Deoxybenzoins to Benzils with TTN–Glyme–Perchloric Acid. The deoxybenzoin (0.01 mol) was added to a solution of 0.02 mol of TTN in 20 ml of glyme and 10 ml of water containing 10 ml of 70% perchloric acid, and the mixture was stirred and heated under reflux for 0.5–1 hr. Isolation and purification of the benzil were then carried out as described above.

General Procedure for the Oxidation of Benzoins to Benzils with TTN–Glyme–Perchloric Acid. These oxidations were performed in exactly the same manner as described above for deoxybenzoins.

Oxidation of Chalcone to 3,3-Dimethoxy-1,2-diphenylpropan-1-one (2, Ar = Ar′ = C_6H_5). A solution of chalcone (2.08 g, 0.01 mol) in 40 ml of methanol was added to a solution of 4.44 g (0.01 mol) of TTN in 5 ml of 70% perchloric acid, and the resulting mixture was stirred overnight at room temperature. Thallium(I) nitrate (2.4 g, 93%) was removed by filtration, and the filtrate was diluted with water and extracted with chloroform (2 × 20 ml). The extracts were washed with aqueous sodium bicarbonate solution, dried (Na_2SO_4), and evaporated to give a pale yellow oil which partially solidified on standing. Crystallization of the solid from ethanol gave 0.69 g (26%) of 3,3-dimethoxy-1,2-diphenylpropan-1-one as colorless needles: mp 94–95°; nmr δ 3.14 (s, 3 H), 3.38 (s, 3 H), 4.73 (d, 1 H), 5.01 (d, 1 H) (J = 9 Hz), 7.2–8.1 (m, 10 H).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.55; H, 6.67. Found: C, 75.69; H, 6.87.

When 10 ml of boron trifluoride–methanol complex in 20 ml of anhydrous methanol was employed as solvent system, and the reaction allowed to proceed for 11 hr at room temperature, 2 (Ar =

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(13) (a) E. Baer, *J. Amer. Chem. Soc.*, **62**, 1597 (1940); (b) A. McKillop, R. A. Raphael, and E. C. Taylor, *J. Org. Chem.*, **37**, 4204 (1972).

(14) E. H. Rodd, "The Chemistry of Carbon Compounds," Vol. III B, Elsevier, Amsterdam, 1956, p 895.

(15) Melting points were determined on a Kofler hot-stage melting point apparatus and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders of the University of East Anglia. Where appropriate, identity of compounds was confirmed by comparison of ir spectra, determined by the normal Nujol mull and liquid film techniques on a Perkin-Elmer Model 257 grating infrared spectrometer, and nmr spectra, determined as solutions in carbon tetrachloride on a Perkin-Elmer R12 60-MHz spectrometer, using TMS as internal standard. Glpc analyses were performed using Perkin-Elmer Models PE 452 and F11 gas chromatographs equipped with 1-m Apiezon L and 50-m capillary columns, respectively. Quantitative analyses of chromatograms were performed using a Vitatron UR 400 digital readout integrator.

Ar′ = C_6H_5) was obtained in 44% yield after an identical isolation technique to that described above.

Hydrolysis of 3,3-Dimethoxy-1,2-diphenylpropan-1-one (2, Ar = Ar′ = C_6H_5) to Deoxybenzoin. A solution of the acetal **2** (Ar = Ar′ = C_6H_5, 200 mg) in a mixture of 2 ml of 70% perchloric acid and 15 ml of methanol was heated under reflux for 4 hr. Most of the methanol was then evaporated under reduced pressure and the residue cooled to 0°. Filtration and recrystallization of the solid which had precipitated gave 80 mg (55%) of deoxybenzoin as colorless needles, mp 54–55°; ir and nmr spectra were superimposable on those of a genuine sample.

Oxidation of Benzoin Methyl Ether by TTN in Acidic Methanol. A mixture of benzoin methyl ether (2.26 g, 0.01 mol) and TTN (4.44 g, 0.01 mol) in 40 ml of methanol containing 5 ml of 70% aqueous perchloric acid was heated under reflux for 2 hr. The reaction mixture was then cooled and filtered to remove thallium(I) nitrate (1.61 g, 60%), and the filtrate was diluted with water and extracted with chloroform. The chloroform extract was dried ($MgSO_4$) and evaporated to give 2.20 g of a pale yellow-green liquid which was found to consist (glc) of benzoin methyl ether (88%), benzil (7%), benzaldehyde (2%), and methyl benzoate (3%).

Oxidation of Deoxybenzoin by TTN in Acidic Methanol. A mixture of deoxybenzoin (1.96 g, 0.01 mol) and TTN (9.1 g, 0.0205 mol) in 30 ml of methanol containing 5 ml of 70% aqueous perchloric acid was heated under reflux for 2 hr. The reaction mixture was then cooled and filtered to remove thallium(I) nitrate (5.6 g, 97%), and the filtrate was diluted with water and extracted with chloroform (2 × 25 ml). The chloroform extract was dried ($MgSO_4$) and analyzed by glc, which showed that the following compounds were present: benzoin methyl ether (40%), benzil (39%), benzaldehyde (10%), and methyl benzoate (10%).

Preparation of Benzoin Nitrate Ester (5). (a) From Deoxybenzoin and TTN. Deoxybenzoin (3.92 g, 0.02 mol) was added with stirring to a solution of TTN (8.88 g, 0.02 mol) in a mixture of glyme (40 ml), water (20 ml), and 60% aqueous perchloric acid (8 ml). The mixture was stirred at room temperature for 56 hr, during which time a finely divided precipitate of thallium(I) nitrate formed. The precipitate was removed by filtration, and standard work-up (chromatography on alumina, benzene elution) yielded 3.6 g (73%) of a yellow solid. Careful chromatography on silica gel (benzene elution) yielded 1.91 g (53% of the crude product) of benzoin nitrate ester as a pale yellow solid: mp 70–72°; nmr δ 7.03 (s, 1 H), 7.43 (s, 8 H), 7.85–8.05 (m, 2 H); ir 1295, 870–820, 690 cm^{-1} (these bands are characteristic of nitrate esters).

Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.29; N, 5.45. Found: C, 64.96; H, 4.25; N, 4.99.

(b) From Desyl Bromide and Silver Nitrate. Desyl bromide (4.13 g, 0.015 mol) was added to a solution of silver nitrate (3.82 g, 0.022 mol) in 30 ml of anhydrous acetonitrile, and the reaction mixture was stirred for 12 hr at room temperature in a flask wrapped in tin foil. The reaction mixture was filtered and the filtrate partitioned between benzene and saturated aqueous sodium chloride solution. The benzene layer was separated, washed with saturated aqueous sodium chloride solution, dried ($MgSO_4$), and evaporated to give 3.8 g (99%) of nitrate ester **5**, mp 71–73°, the ir and nmr spectra of which were superimposable on those of the product obtained as described under (a) above.

Conversion of the Nitrate Ester 5 into Benzil. The results obtained from control experiments on the conversion of ester **5** into benzil under various conditions are summarized in Table IV. The following standard conditions were employed: a mixture of 1.3 g (0.005 mol) of the ester **5** and 0.005 mol of the appropriate thallium salt (see Table IV) in 20 ml of glyme, 10 ml of water, and 10 ml of 70% aqueous perchloric acid was heated under reflux for 1 hr. The cooled reaction mixture was diluted with water and extracted with benzene, and the extract was dried ($MgSO_4$) and evaporated. The composition of the resulting product was estimated by nmr.[16]

Table IV. Product Composition (%)

Thallium salt added (mol)	Benzil	Benzoin	Ester **5**
$Tl(NO_3)_3$ (0.005) + $TlNO_3$ (0.005)	>95	<5	Trace
$Tl(NO_3)_3$ (0.005)	84	2–5	12–16
$TlNO_3$ (0.005)	63	14	23
None	78–83	*a*	17–22

[a] Not detectable by nmr.

Oxidation of 1,2,3-Triphenylprop-1-en-3-one (8). A mixture of 1.42 g (0.005 mol) of 1,2,3-triphenylprop-1-en-3-one[17] and 4.44 g (0.01 mol) of TTN in 20 ml of glyme and 10 ml of water containing 5 ml of 70% perchloric acid was stirred and heated under reflux for 6 hr. The mixture was then cooled, diluted with 100 ml of water, and extracted with chloroform (2 × 25 ml). The extracts were dried (Na_2SO_4) and evaporated to give 1.75 g of an orange-yellow oil which was chromatographed on acid-washed alumina. Glpc examination of the evaporated eluate showed the presence of benzaldehyde (60%), benzil (75%), and a small amount of benzophenone formed by further oxidation of 2,2-diphenylacetophenone. The latter compound was not sufficiently volatile to be determined by glpc, but it was identified in the eluate by tlc comparison with a genuine sample.

Oxidation of Phenylglyoxal by TTN. A solution of TTN (4.44 g, 0.01 mol) in a mixture of 20 ml of water and 5 ml of 70% aqueous perchloric acid was added to a solution of freshly distilled phenylglyoxal (1.35 g, 0.01 mol) in 15 ml of glyme, and the resulting mixture was heated under reflux for 2 hr. The cooled mixture was partitioned between benzene and saturated sodium chloride solution, and the benzene layer was separated and washed with saturated aqueous sodium bicarbonate solution. The benzene layer was dried ($MgSO_4$) and the solvent evaporated to leave 300 mg of a pale yellow oil, homogeneous on glc, which was readily identified (ir, nmr) as benzaldehyde. Acidification of the bicarbonate washings from the above extraction with concentrated hydrochloric acid resulted in precipitation of a colorless solid. This was collected by filtration to give 100 mg of a solid, mp 118–120°, which was identified (ir, melting point) as benzoic acid.

Acknowledgment. We are grateful for partial financial support provided by grants from Eli Lilly and Co. and from G. D. Searle and Co. B. P. S. acknowledges the award of an S. R. C. Scholarship, and M. E. F. the award of a Marshall Scholarship.

(16) The ester **5** decomposes to benzil under glc conditions. Similarly, benzoin cannot be estimated by glc techniques, as it is known to undergo disproportionation during glc to give a mixture of about 80% benzil and 20% deoxybenzoin: D. L. Bunbury and M. S. Osyany, *J. Chromatogr.*, **14**, 98 (1964).

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