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$$\delta = \rho_F F + \rho_R R + \delta o$$

δo is the intercept of the equation, and ρ_F and ρ_R are the regression coefficients. F and R are contributions arising from field and inductive effects, taken together, and resonance effects, respectively.[9]

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Notes

Thallium in Organic Synthesis. 51. Oxidation of Enolizable Ketones to α-Nitrato Ketones by Thallium(III) Nitrate in Acetonitrile[1]

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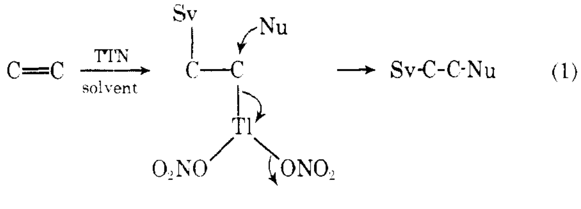
Thallium(III) nitrate (TTN) is a versatile reagent for the oxidation of a wide variety of olefinic and enolic groups, and in almost all cases the exclusive or predominant reaction pathway is oxidative rearrangement.[2] Occasionally, however, nucleophilic displacement of the thallium substituent in the intermediate oxythallation adduct leads to unrearranged products (eq 1). This latter type of reaction appears to occur most frequently when water or methanol is used as solvent (i.e., Nu = H_2O or CH_3OH), but we[3] and others[4-7] have noted instances where nitrate ion participates as the nucleophile to give nitrate esters, usually in low yield. Recently, however, Ouellette and Bertsch have shown that certain olefins and cyclopropanes can be converted into diol dinitrates in moderate to excellent yield by treatment with TTN in pentane,[8] and this report prompts us to describe some related studies.

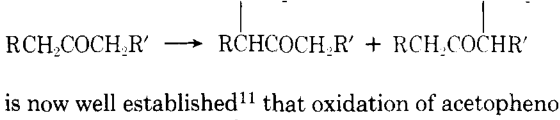


(1)

In the course of our systematic study of the utility of TTN as an oxidant, we have examined the reactions of various types of functional groups with TTN in aprotic, poorly or nonnucleophilic solvents. We describe now one aspect of these studies, namely the smooth conversion of enolizable ketones into the corresponding α-nitrato ketones[9] by treatment with TTN in either dimethyl or diethyl carbonate or, preferably, acetonitrile.

Addition of TTN to an equimolar amount of acetophenone dissolved in dimethyl or diethyl carbonate resulted in the immediate formation of a dark brown color as the TTN dissolved. When the mixture was heated to 60–80 °C, however, the brown color rapidly discharged and thallium(I) nitrate precipitated. NMR spectroscopic examination of the product obtained after workup showed that it consisted of approximately equal amounts of unreacted acetophenone and its α-nitrato derivative, $C_6H_5COCH_2ONO_2$. Similar results were obtained with a variety of substituted acetophenones and with propiophenone. When 2 equiv of TTN[10] were used, however, acetophenone was converted into the α-nitrato ketone in 84–87% yield; propiophenone was similarly converted into $C_6H_5COCH(ONO_2)CH_3$ in 86–89% yield.

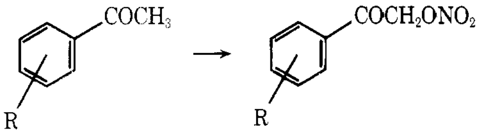
Use of dimethyl and diethyl carbonate for the oxidation of substituted acetophenones was not entirely satisfactory. In certain cases, most notably with 3-methoxyacetophenone, the α-nitrato ketone was obtained in poor yield (10–15%); in other cases the reactions proceeded exothermically, and NMR examination of the crude products revealed the presence of variable amounts of decomposition products. Fortunately, these problems were readily eliminated by the use of acetonitrile as solvent; 2 equiv of TTN were again necessary.[10] Oxidations were carried out at 60–80 °C for 12 h and led to excellent yields of the α-nitrato ketones. Yield data for the various conversions are listed in Table I. Unsymmetrical dialkyl ketones of the type $RCH_2COCH_2R^1$ (butan-2-one, pentan-2-one) were also smoothly oxidized in high yield, but as anticipated, approximately equal amounts of isomeric α-nitrato ketones were obtained (eq 2).



$$\mathrm{RCH_2COCH_2R'} \longrightarrow \mathrm{R\overset{ONO_2}{\overset{|}{C}}HCOCH_2R'} + \mathrm{RCH_2CO\overset{ONO_2}{\overset{|}{C}}HR'} \qquad (2)$$

It is now well established[11] that oxidation of acetophenones by TTN in methanol results in initial methoxythallation of the enol C=C bond and that a subsequent 1,2-aryl migration

Table I. Oxidation of Ketones to α-Nitrato Ketones with TTN/CH_3CN



R	registry no.	mp, °C	yield, %[a]	registry no.
H	98-86-2	b	97	66702-75-8
4-CH_3	122-00-9	60	89	66702-76-9
3-CH_3O	586-37-8	b	90	66702-77-0
4-CH_3O	100-06-1	97	89	66702-78-1
4-Cl	99-91-2	82	91	66702-79-2
4-Br	99-90-1	79 (dec)	90	66702-80-5
4-NO_2	100-19-6	100	84	66702-81-6

$RCH_2COCH_2R \rightarrow RCH(ONO_2)COCH_2R$

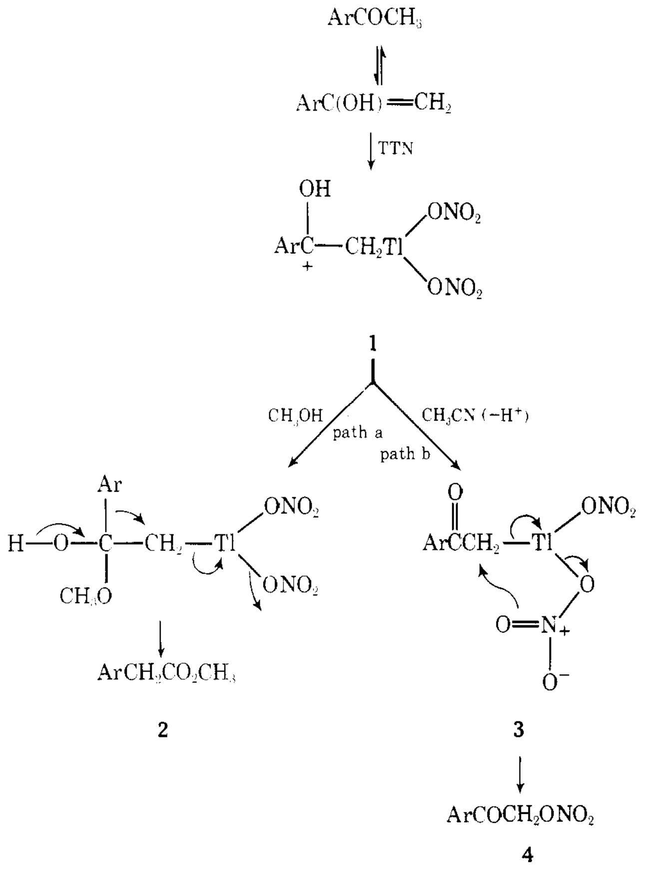
R	registry no.	mp, °C	yield, %[a]	registry no.
H	67-64-1	b	78	6745-71-7
CH_3CH_2	123-19-3	b	85	66702-82-7
$CH_3(CH_2)_2$	502-56-7	b	88	66702-83-8
C_6H_5	102-04-5	b	90	66702-84-9

$RCOCH_2R' \rightarrow RCOCH(ONO_2)R'$

R	registry no.	R′	mp, °C	yield, %[a]	registry no.
t-C_4H_9	75-97-8	H	b	87	66702-85-0
C_6H_5	93-55-0	CH_3	b	90	60434-74-4
2-$C_{10}H_7$	93-08-3	H	89	81	66702-86-1

[a] Estimated by NMR. [b] Liquid; no attempt was made to purify liquid α-nitrato ketones, as these are known to be thermally unstable.[12,13] The spectroscopic data (IR, NMR) for all products were consistent with the assigned structures.

Scheme I



gives methyl arylacetates (**2**) (Scheme I, path a). In a nonnucleophilic solvent such as diethyl carbonate or acetonitrile, however, reaction of the electrophilic Tl(III) salt with the enol C=C bond can proceed only as far as **1**, which would be expected to undergo rapid deprotonation to **3**. Reductive displacement of the weak C–Tl bond by nitrate anion (an intramolecular route is shown in Scheme I, path b) then leads to the α-nitrato ketone (**4**).

Experimental Section[14]

General Procedure for the Preparation of α-Nitrato Ketones. A solution of the ketone (10 mmol) in acetonitrile (5 mL) was added in one portion to a solution of TTN (20 mmol) in acetonitrile (25 mL) and the mixture was heated at 60–80 °C for 12 h. It was then cooled and the precipitated thallium(I) nitrate was collected by filtration and washed well with ether (3 × 100 mL). The filtrate was washed with water (2 × 150 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude α-nitrato ketone; yields were determined by NMR.

No attempt was made to purify liquid α-nitrato ketones as these are known to be thermally unstable. Solid products (Table I) were recrystallized from aqueous methanol for microanalysis.

4-$CH_3C_6H_4COCH_2ONO_2$. Anal. Calcd for $C_9H_9NO_4$: C, 55.39; H, 4.65; N, 7.18. Found: C, 54.95; H, 4.73; N, 6.97.

4-$CH_3OC_6H_4COCH_2ONO_2$. Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30; N, 6.63. Found: C, 50.93; H, 4.31; N, 6.66.

4-$ClC_6H_4COCH_2ONO_2$. Anal. Calcd for $C_8H_6ClNO_4$: C, 44.57; H, 2.80; Cl, 16.44; N, 6.49. Found: C, 45.71; H, 3.10; Cl, 16.81; N, 5.95.

4-$BrC_6H_4COCH_2ONO_2$. Anal. Calcd for $C_8H_6BrNO_4$: C, 36.95; H, 2.33; Br, 30.73; N, 5.38. Found: C, 37.01; H, 2.18; Br, 31.15; N, 5.15.

4-$O_2NC_6H_4COCH_2ONO_2$. Anal. Calcd for $C_8H_6N_2O_6$: C, 42.11; H, 3.53; N, 12.28. Found; c, 42.34; H, 2.69; N, 12.46.

2-$C_{10}H_7COCH_2ONO_2$. Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.42; H, 4.21; N, 6.27.

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Registry No.—TTN, 13746-98-0; acetonitrile, 75-05-8.

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