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$TeCl_4$-Mediated Reaction of β-Keto Nitroalkanes with Activated Olefins. Formation of 3-Acyl-2-isoxazolines

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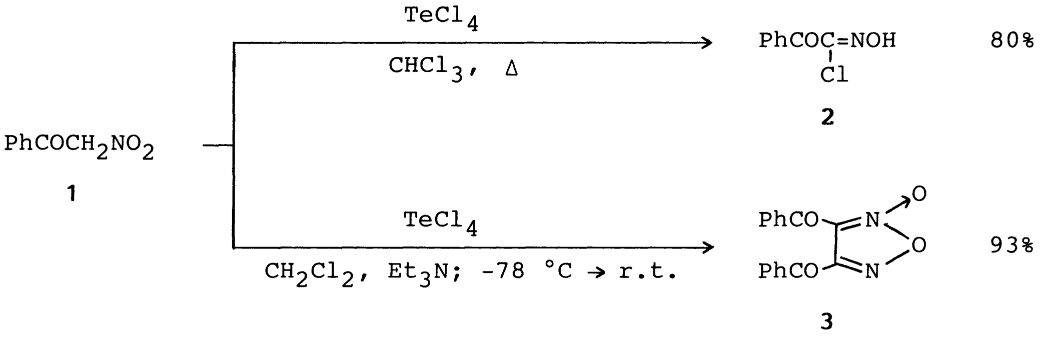
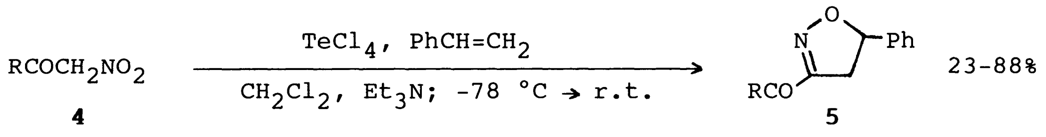
Treatment of β-keto nitroalkanes with tellurium tetrachloride followed by triethylamine in the presence of activated olefins leads to 3-acyl-2-isoxazolines in good to modest yields.

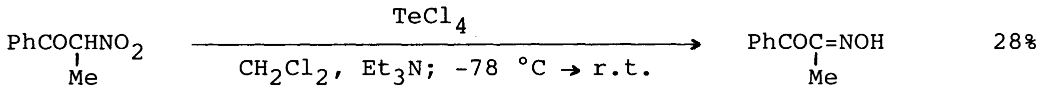
Reaction of nitromethane with tellurium tetrachloride ($TeCl_4$) was earlier reported to afford nitromethyltellurium trichloride as a pale yellow, high-melting solid.[1] We have observed, however, that benzoylnitromethane (**1**), when heated with $TeCl_4$ in chloroform, underwent both chlorination of active methylene carbon and partial deoxygenation of nitro group to form α-(hydroxyimino)-α-chloroacetophenone (**2**) together with small amounts of furoxane **3**. When the reaction was carried out in dichloromethane in the presence of triethylamine at low temperatures, **3** was the only product.



These findings have led us to exploit it into a new one-pot preparation of 3-acyl-2-isoxazolines **5** from readily available β-keto nitoalkanes **4**[2)] and activated olefins. Thus, to a stirred mixture of **4**, $TeCl_4$ and dichloromethane as solvent was added styrene followed by triethylamine at -78 °C, and the resulting yellow mixture was allowed to stand at room temperature for 5 h. and then worked up as usual to give isoxazoline **5** in yields shown in Table. In the absence of olefin, furoxane **3** was the major product.



A similar reaction of **4** with stilbene was quite slow under the same conditions, but when the reaction was carried out under reflux in benzene, 3-acyl-4,5-diphenyl-2-isoxazolines were obtained in good yields. Formation of isoxazolines presumably takes place through the intermediacy of nitrile oxide which is derived from the initially formed α-chloro oxime. Thus, a β-keto nitroalkane of branched structure **6**, being unable to form nitrile oxide, underwent a slow reaction with $TeCl_4$ to afford 1,2-diketone monooxime **7** in a low yield. No chlorination product was detected in the product mixture. Simple nitroalkanes such as nitromethane and phenylnitromethane did not form any isoxazolines under similar conditions.



6 **7**

$$\underset{\text{Me}}{\text{PhCOCHNO}_2} \xrightarrow[\text{CH}_2\text{Cl}_2,\ \text{Et}_3\text{N};\ -78\ ^\circ\text{C} \rightarrow \text{r.t.}]{\text{TeCl}_4} \underset{\text{Me}}{\text{PhCOC=NOH}} \quad 28\%$$

Reaction of $TeCl_4$ with methyl ketones to form bis(acylmethyl)tellurium dichlorides has been well documented,[3)] and some applications of this type of reaction have recently been presented.[4,5)] Our results provide herein an additional mode of reaction with $TeCl_4$, where the tellurium(IV) species acts as an chlorinating and deoxygenating agent.

A representative procedure is as follows: To a mixture of α-nitroacetophenone (1 mmol), $TeCl_4$ (1 mmol) and dichloromethane (5 ml) cooled down to -78 °C was added dropwise styrene (8 mmol) followed by triethylamine (4 mmol) in the same solvent (5 ml) under nitrogen, and the resulting yellow clear solution was allowed gradually to come to room temperature and stood for 5 h, during which time tellurium dioxide was formed as a pale yellow precipitate. The reaction was quenched by the addition of water and the insolubles were removed by filtration over Celite. The organic layer was

Table 1. 2-Acyl-5-phenyl-2-isoxazolines (**5**) from β-keto nitoroalkanes (**4**) and styrene

Nitroalkane(**4**)			2-Isoxazoline (**5**)	
R	Yield/%a)	Mp/°C	IR/cm^{-1}	^{1}H-NMR/δ, ppm
C_6H_5-	82	oil6)		
4-MeC_6H_4-	88	88-89b)	1640 1595 1565 1250	2.42(3H, s), 3.38(1H, dd, J=17.7 and 8.9 Hz), 3.77(1H, dd, J=17.7 and 11.6 Hz), 5.76(1H, dd, J=11.6 and 8.9 Hz), 7.25-7.34(2H, m), 7.35-7.42(5H, m), 8.15-8.16(2H, m)
4-MeOC_6H_4-	86	68-70b)	1640 1595 1570 1245	3.39(1H, dd, J=17.7 and 8.9 Hz), 3.78(1H, dd, J=17.7 and 11.6 Hz), 3.87(3H, s), 5.75(1H, dd, J=11.6 and 8.9), 6.93-6.99(2H, m), 7.31-7.42(5H, m), 8.26-8.32(2H, m)
4-ClC_6H_4-	88	104-105b)	1630 1675 1250 1090	3.38(1H, dd, J=17.7 and 8.9 Hz), 3.77(1H, dd, J=17.7 and 11.6Hz), 5.78(1H, dd, J=11.6 and 8.9 Hz), 7.31-7.41(5H, m), 7.43-7.48(2H, m), 8.20-8.24(2H, m)
C_2H_5-	23	oilb)	1680 1575 1220 920	1.17(3H, t, J=7.3 Hz), 2.98(2H, q, J=7.3 Hz), 3.15(1H, dd, J=17.7 and 8.9 Hz), 3.56(1H, dd, J=17.7 and 11.6 Hz), 5.74(1H, dd, J=11.6 and 8.9 Hz), 7.26-7.42(5H, m)
C_2H_5O-	67	oil7)		

a) Yields are not optimized.

b) New compounds; identified by analyses and mass, IR, ^{1}H- and ^{13}C-NMR spectra.

separated and the aqueous layer was extracted with three portions of dichloromethane (10 ml). The combined organic phases were dried and evaporated under reduced pressure to leave an oily residue, which was chromatographed over silica gel to give 3-benzoyl-5-phenyl-2-isoxazoline, bp 160-165 °C (0.6 Torr) (lit.6) 140-145 °C (0.25 Torr)). Yield, 0.27 g (82%).

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