

CONVERSION OF α -HALOESTERS AND ALKYNES INTO CORRESPONDING CINNAMATES AND KETONES DERIVATIVES RESPECTIVELY BY USING SOME ORGANOTELLURIUM COMPOUNDS AS REAGENTS

Abdel-Amir M. Fenjan

Department of Chemistry, College of Science for Women, University of Baghdad.

E-mail : fenjanamir@yahoo.com.

Abstract

Telluroxidation of di-n-propyl telluride **1** guides to obtain trans - cinnamate derivatives from condensation of substituted aldehydes and α -haloesters in one – pot reaction. p-Diphenetyl tellurinic acid anhydride **3** converts terminal alkynes into corresponding ketones through hydration process to oxidize triplet bond into carbonyl group. Infrared spectra have assisted all organochemical conversions and their identification strongly. The possible reactions mechanisms were proposed.

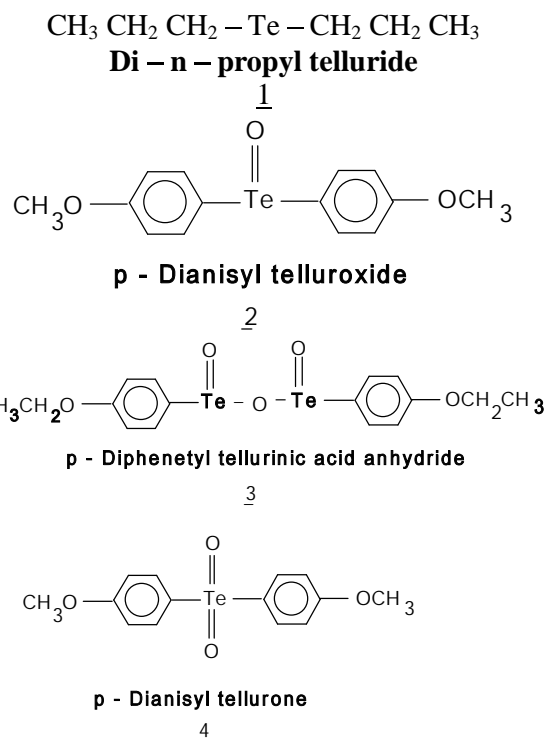
Introduction

With the development of organotellurium chemistry, some attention has been paid on the use of tellurium ylides in organic synthesis [1]. A wide range of organotellurium compounds were prepared and described as heterogeneous compounds and investigated for many purposes [2-7]. Organotellurinic acids anhydrides have been little investigated [2, 8]. Dianisyltelluroxide **2** oxidizes thiols into disulphides and hydroquinones, catechols into quinones even in the presence of phenols, amines or such functional groups. Many thiones are converted smoothly into ketones and sulphur with formation of diaryltelluride [9].

Experimental

Physical Measurements:

All chemicals were of high purity and used from the products of BDH, Aldrich, Fluka and Merck companies except of p-diphenetyl tellurinic acid anhydride **3** was prepared as described in the literatures [2, 5]. All products were fitted by their melting points, boiling points and I.R spectra. Infrared spectra were recorded in the range 4000 – 400 cm^{-1} using a Bruker IFS-113, KBr disc. Microanalysis for (C, H) were carried out using a CHN Corder-MT3 Uanac instrument. Melting points were determined on a Gallenkamp melting point apparatus and uncorrected.



Typical Experimental Procedure:

1. Conversion of α -haloesters into cinnamate derivatives

Synthesis of methyl-m-nitrocinnamate

A mixture of m-nitrobenzaldehyde (7.5 mmole, 1.14 gm), methyl chloroacetate (7.5 mmole, 0.82 gm) and di-n-propyl telluride (7.5 mmole, 1.60 gm) in 40 ml of dry THF were stirred and refluxed for 7 hrs in a N_2 atmosphere. Set aside a solution for 0.5 hr, then stir it further 0.5 hr at R. T. After the solvent was separated under a reduced

pressure, the residue wash with water and brine solution, then extract with ethyl acetate (2×50 ml). Dry the organic layer over anhydrous MgSO₄ and filter off. After concentration of the solution under a reduced pressure, the crude product was separated on cooling at (-10 °C) with yield (1.11 gm, 72%). Recrystallization from ethanol, gave yellowish – white powder, m.p = 183 – 185 °C decompose, while standard sample of Merck company, m.p = 184 – 186 °C decompose.

2. Conversion of alkynes into ketone derivatives

Synthesis of acetophenone

Phenylacetylene (4.5 mmole, 0.46 gm) was mixed with p-diphenetyl tellurinic acid anhydride (0.45 mmole, 0.25 gm) in 20 ml of acetic acid and 30 ml of ether were stirred at reflux for 24 hrs in a N₂ atmosphere. After the solvent was evaporated under a reduced pressure, the ether layer was washed with 5% aq. NaHCO₃ and dried on anhydrous MgSO₄. After concentration of the solution, column chromatography of the residue on silica gel using benzene as an eluant gave a product with yield (0.41 gm, 77%), b.p = 204 °C, while standard sample of Fluka company, b.p = 202 °C.

3. Synthesis of p-phenetyl tellurinic acid anhydride **3**

A 100 ml solution of 10% aqueous NaOH was slowly added to a vigorously stirred solution of p-phenetyl tellurium trichloride (0.014 mole, 5gm) dry THF 50 ml. The mixture was stirred at R.T for 12 hrs, then solvent was distilled off. The cooled colourless mixture was acidified with acetic acid. The precipitate filtered and dried to afford (2.75 gm, 36 %) yield, as a white crystalline material, m.p. 232-234 °C. C₁₆ H₁₈ O₅ Te₂ (M.Wt = 545), C.H.N. elemental analysis, Calculate, (Found): %C = 35.23 (35.76), %H = 3.30 (3.58).

Discussion

The present work describes the preparation of some important organic compounds by using organotellurium compounds as reagents in chemical transformations of organic synthesis. Organotellurium compounds which

were used, starting materials, conditions and products are shown in (Tables (1-2)) and (schemes 1- 4). When an equimolar mixture of p-nitro- benzaldehyde (run 1) or meta-isomer (run 2), di-n-propyl telluride **1** and methylchloroacetate were refluxed in dry THF for 7hrs in N₂ atmosphere gave the products of methyl-p-nitrocinnamate (run 1) or meta-isomer (run 2) in 75% or 72% yields respectively (Table (1)). Also, we have got the products phenyl-p-nitrocinnamone (run 3) or meta-isomer (run 4) at the same conditions in 79% or 77% yields respectively. Because the telluronium salts can be prepared easily from di-n-propyl telluride **1** and α-haloester, the formation of the (di-n-propyl)Te⁺CH₂YX⁻ and their condensation with carbonyl compounds can be carried out as one-pot reaction.

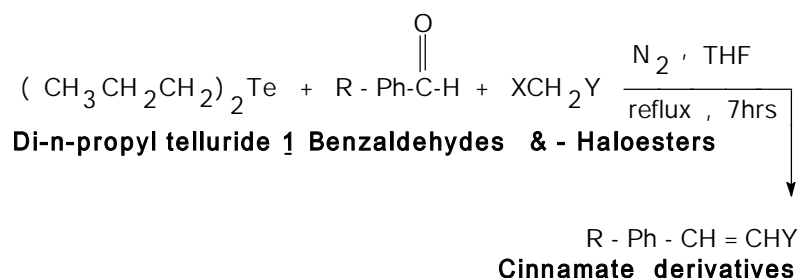
In view of the lower energy and higher polarity of (C-Te) bond in organotellurium compounds, it can be condensed the telluronium salt with the carbonyl derivatives in neutral medium. Apparently the outcome of the reaction is highly dependent on the stability of the telluronium ylide.

It is likely to proceed through a 6-membered cyclic form and it should be suitable the synthesis of cinnamate derivatives with base - sensitive functional groups.

Future research in this area will hopefully serve to define the full synthetic potential of these reactions. Infrared spectrum (KBr disc) of cinnamate derivatives showed stretching vibration with strong sharp band due to carbonyl group (C = O) in the regions (1730 cm⁻¹, run 1), (1720 cm⁻¹, run 2) for esters and (1690 cm⁻¹, run 3), (1675 cm⁻¹, run 4) for ketones respectively. The disubstituted trans (C-H) olefinic showed stretching vibration with medium sharp band at (3010-3050 cm⁻¹). The double bond (C = C) showed stretching vibration with sharp medium band in the region (1650-1665 cm⁻¹). All the products were found to be the trans - isomer by their infrared spectra and melting point according to standard samples. The infrared spectra of starting material- methylchloroacetate (Cl - CH₂COOCH₃), (0.001M, in ether solvent) showed stretching vibration with strong sharp band belongs to (C - Cl) bond in the region (710 cm⁻¹). The band assigned to (C - Cl) bond was absent in

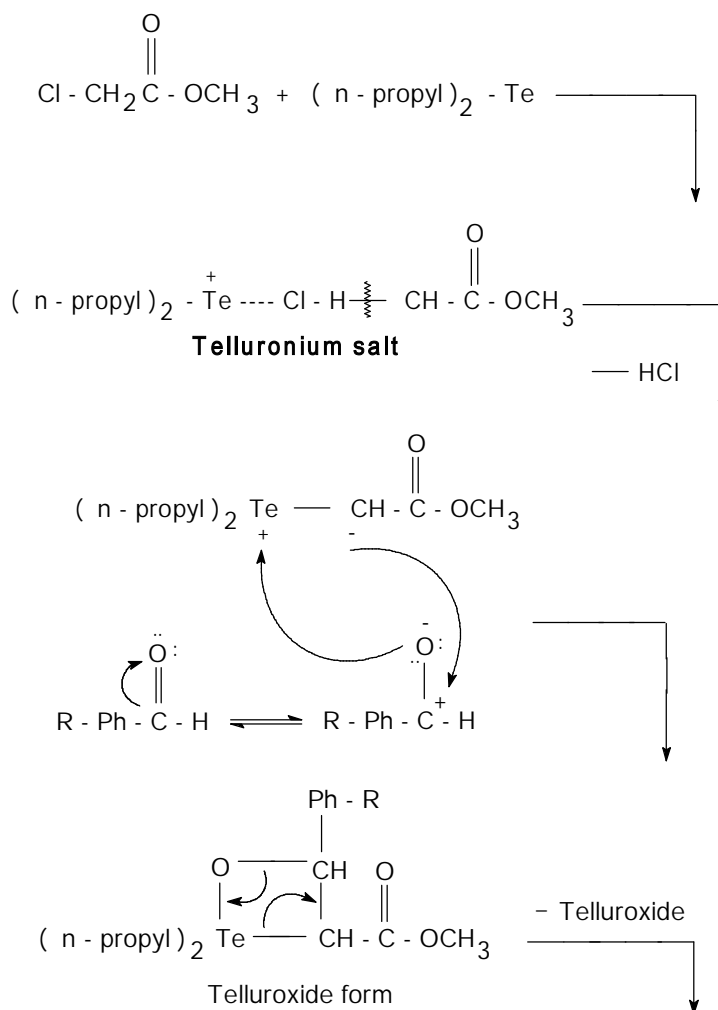
the spectra of the corresponding cinnamate derivatives. This is an evidence that α -haloester converts into cinnamate derivatives certainly as well as the infrared

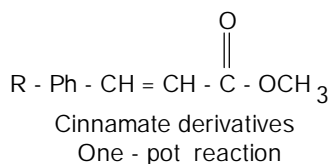
spectra of the standard samples for (methyl-m-nitrocinnamate, run 2) and (phenyl-m-nitrocinnamone, run 4) are the similar comparison with the corresponding prepared cinnamate derivatives.



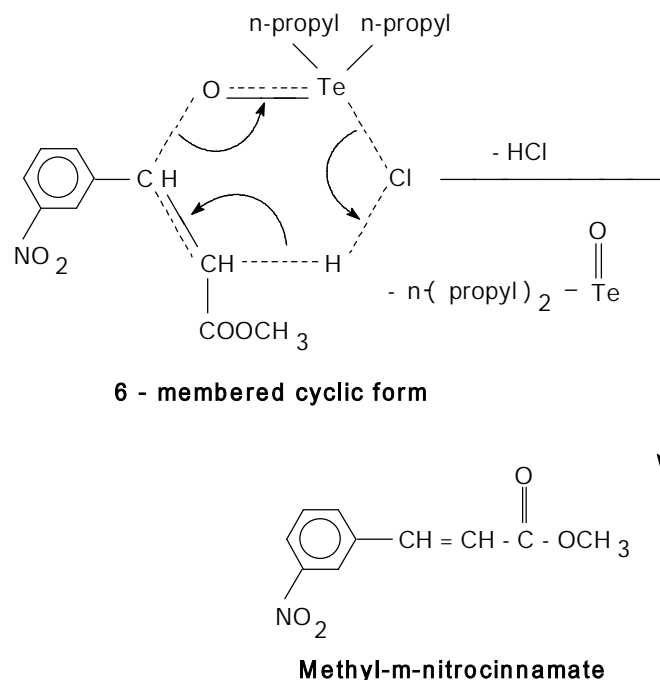
Where R = p, m - NO₂, X = Cl, Y = COOCH₃, COPh, Ph = Phenyl

Scheme (1) : The condensation reaction of aldehyde derivatives and α -haloesters with telluride **1**.





Thus, the cyclic form is:



Scheme (2): Mechanism's formation of cinnamate derivatives.

Table (1)
Conversion of α -haloesters into cinnamate derivatives.

Run	R	X	Y	Cinnamate	% Yield
1	P-NO ₂	Cl	COOCH ₃	p- NO ₂ PhCH=CHCOOCH ₃	75
2	m-NO ₂	Cl	COOCH ₃	^{b1} m-NO ₂ PhCH=CHCOOCH ₃	72
3	P-NO ₂	Cl	COPh	P-NO ₂ PhCH=CHCOPh	79
4	m-NO ₂	Cl	COPh	m-NO ₂ PhCH=CHCOPh ^{b2}	77

^{b1, b2} = The products were fitted with the standard samples.

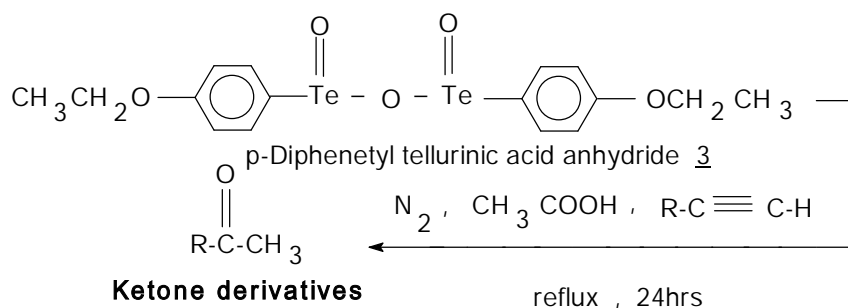
The p-diphenetyl tellurinic acid anhydrides **3** was prepared by reaction of phenetyl with tellurium tetrachloride to give p-phenetyl tellurium trichloride [5]. Treatment of the latter with aqueous NaOH afforded the corresponding aryl tellurinic acid which spontaneously lose water to give the anhydride **3**. We found that compound **3** was usually inert to non-terminal alkynes. It catalyzed the hydration of terminal alkynes in acetic acid at reflux (Table (2), Scheme (3)). It is expected to have a potential oxidizing ability like

p-dianisyl telluroxide **2** and p-dianisyl tellurone **4** due to their similar labile (Te-O) bonds [10]. Sonoda presented that benzene tellurinic acid anhydride induced acetoxylation of olefins and ketones with acetic acid [11]. During the reaction, acetic acid plays as a hydrogen donor to the carbon atom of double bond which holds tellurium group by hydration process (Scheme (4)). So, phenylacetylene transfers into a acetophenone (run 1) and 1-octyne into n-hexylmethylketone (run 2) in 77% and 80% yields respectively.

The reactions did not go according to non-terminal alkynes (run 3 and run 4).

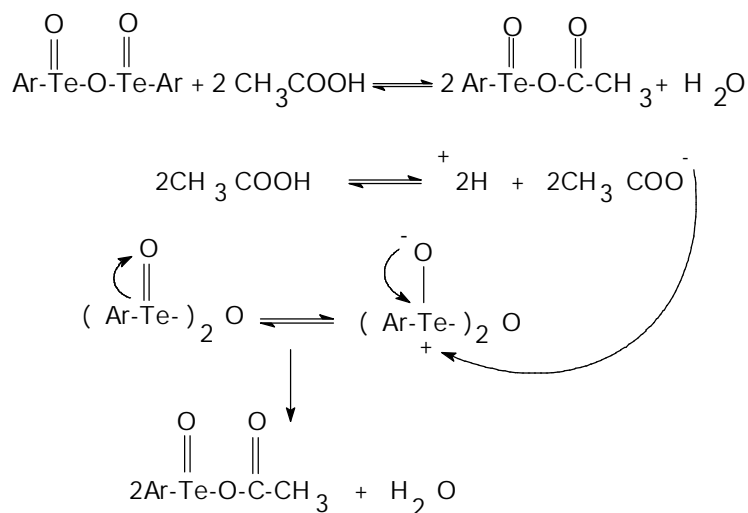
The infrared spectra (0.001M, in CCl_4 solvent) of ketone derivatives showed stretching vibration with strong sharp band due to carbonyl group ($\text{C}=\text{O}$) at (1685 cm^{-1} , run 1), (1725 cm^{-1} , run 2). The band assigned to triplet bond ($\text{C}::\text{C}$), (normally stretching vibration at 2120 cm^{-1} , run 1; 2140 cm^{-1} , run 2, both medium sharp bands) and alkyne (C-H), (normally stretching vibration at 3280 cm^{-1} , run 1; 3300 cm^{-1} , run 2, both

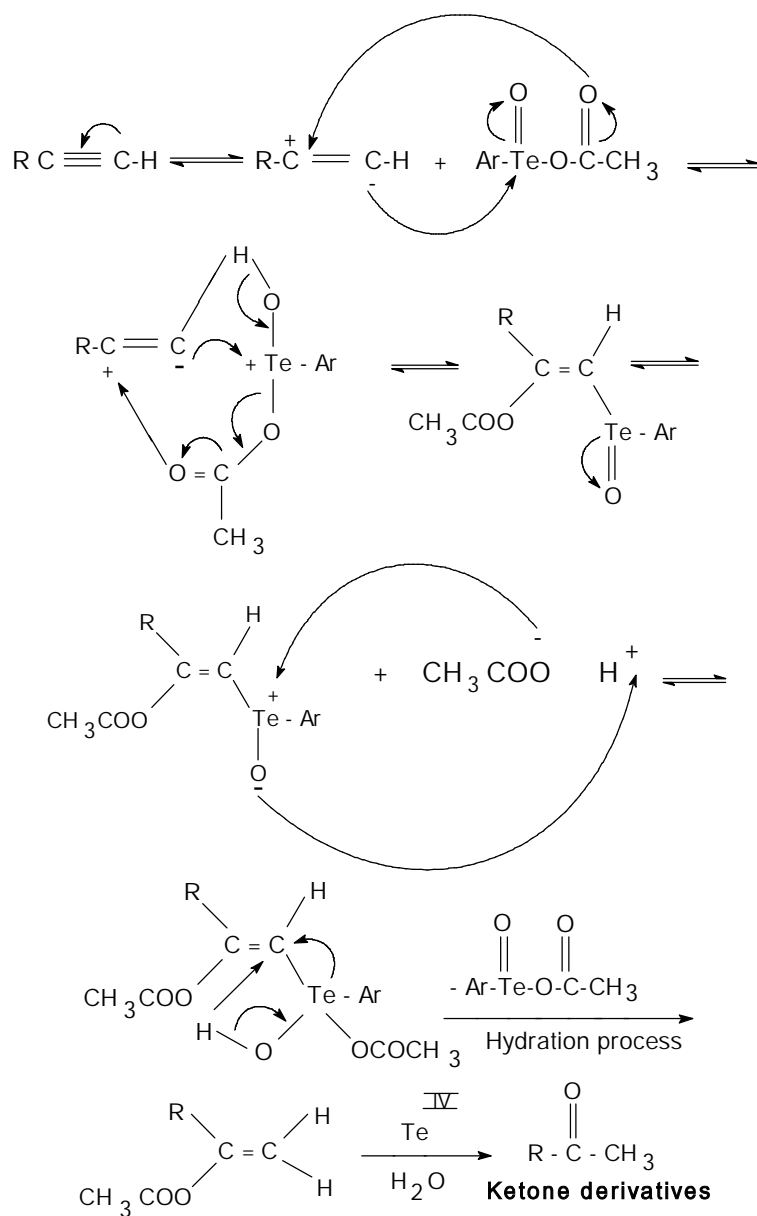
medium sharp bands) were absent in the infrared spectra of the corresponding ketone derivatives. These are evidences that triplet bond converts into carbonyl group certainly besides the infrared spectra of the standard samples for (acetophenone, run 1) and (n-hexylmethylketone, run 2) are the similar comparison with the corresponding prepared ketone derivatives.



Where $\text{R} = \text{Ph}, \text{n-C}_6\text{H}_{13}$

Scheme (3): Conversion's reaction of alkynes into ketone derivatives.





Scheme (4): Mechanism's formation of ketone derivatives.

Table (2)
Conversion of alkynes into ketone derivatives.

Run	Alkyne	Ketone	% Yield
1	$C_6H_5 - C \equiv C - H$	$C_6H_5 - C(O) - CH_3$ ^{b3}	77
2	$n-C_6H_{13} - C \equiv C - H$	$n-C_6H_{13} - C(O) - CH_3$ ^{b4}	80
3	$n-C_6H_{13} - C \equiv C - CH_3$	No reaction	—
4	$C_6H_5 - C \equiv C - CH_3$	No reaction	—

^{b3, b4} = The products were fitted with the standard samples.

Conclusions

The present work furnished new routes for synthesis some organic compounds in selective yields by using di-n-propyl telluride **1** and p-diphenetyl tellurinic acid anhydride **3** as reagents in organic synthesis. Thus, telluride **1** transfers α -haloesters into cinnamate derivatives due to 6-membered cyclic form mechanism in one pot reaction. Tellurinic acid anhydride **3** have found to transfer only terminal alkyne into ketone derivatives according to the hydration process mechanism

References

- [1] A. Osuka, J.Tetrahedron Letts., 24, 1983, 2599.
- [2] K. J. Irgolic, the textbook (The organic chemistry of tellurium), 1974, Gordon and Beach London.
- [3] Michael R. Detty (Oxidation of selenides and tellurides with positive halogenating species), J. Org. Chem., 45, 1980, 274-279.
- [4] S. Uemura and S. Fukuzawa (α -Elimination of organic halides from organotellurium halides), J. Organomet. Chem., 268, 1984, 223-234.
- [5] Ali Z. Al-Rubaie, A-Amir M. Fenjan, Najih I. Al-Salim and Shakeer A. N. Al-Jadaan (Synthesis and characterization of some new organotellurium compounds containing an orth-acetamido group), J. Polyhedron, 14, 1995, 2575-2579.
- [6] A-Amir M. Fenjan and Jalil R. Ugal (A thermal analysis study of some disubstituted aryltellurium trihalides), J. Thermochem. Acta, 306, 1997, 167-170.
- [7] M. Al-Luaib and W. Al-Fyad, J. Science (Iraq), 22, 2004, 1.
- [8] N. Petragnani and G. Vicentini, J. Bol. Quim, 5, 1959, 75.
- [9] D. H. R. Barton, S. V. Ley and C. A. Meerholz, J. Tetrahedron Letts., 21, 1980, 1785.
- [10] L. Engmann and M. P. Cava, J. Chem. Soc. Chem. Commun., 164, 1982.
- [11] N. Sonoda, Abstracts, 18th Symposim on (Organic sulfur and phosphorus chemistry), Hiroshima, January-1985, p. 57.

الخلاصة

يمكن تكثيف المركب ثنائي بروبايل التلورايد **1** مع الالديهيدات الاروماتية، وألفا-هالواسترات بسهولة للحصول على مشتقات السيانامات المقابلة في خطوة واحدة. يستطيع المركب بارا- إيثوكسي بنزين حامض التيلورينيك اللامائي **3** تحويل الاصرة الثلاثية الطرفية في الالكينات الى الكيتونات المقابلة. أكدت أطياف الاشعة تحت الحمراء صحة كافة التحويلات الكيميائية العضوية المنجزة وتشخيص مركباتها النهائية بدقة مقارنة مع النماذج القياسية. لقد تم إقتراح الميكانيكيات المناسبة لهذه التفاعلات.