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A new synthetic method for diphenacyl telluride Synthesis of some new organotellurium compounds containing Ar–COCH(R) groups via α-tellurocynatoketones

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Abstract

A new series of organotellurocyanate containing Ar–COCH(R) groups (i.e., $C_6H_5COCH_2TeCN$ (**1**), 4-$BrC_6H_4COCH_2TeCN$ (**2**), 4-$PhC_6H_4COCH_2TeCN$ (**3**) and $C_6H_5COCH(CH_3)TeCN$ (**4**)) were prepared by reacting KTeCN with the appropriate α-bromoketone in dry DMSO solution. Treatment of **1**, **2**, **3** and **4** with 10% NaOH afforded ditellurides **5**, **6**, **7** and **8** in high yields. Refluxing the ditelluride with activated copper powder in dry dioxane gave the corresponding tellurides (**9**, **10**, **11** and **12**) in good yields. Treatment of tellurides with thionyl chloride, bromine and iodine gave the dichloride (**13**–**16**), dibromide (**17**–**20**) and diiodide (**21**–**24**), respectively, in high yields. Both, tellurocyanate (**1**–**4**) and ditelluride (**5**–**8**) gave the trichloride (**25**–**28**), tribromide (**29**–**32**) and triiodide (**33**–**36**) when reacted with $SOCl_2$, Br_2 and I_2, respectively. Treatment of **9**–**16** with *m*-chloroperbenzoic acid (MCPBA) afforded the corresponding alkyl aryl ketones in fair to good yields. All the compounds were characterized by elemental analysis and spectroscopic data.

Keywords: Potassium tellurocyanate; Telluride; Ditelluride; Phenacyl group

1. Introduction

A few publications [1–3] have reported unsuccessful attempts for the preparation of diphenacyl telluride via reduction of diphenacyltellurium dichloride, which in turn was prepared from the reaction of $TeCl_4$ with acetophenone, with a variety of mild reducing agents. Photodecomposition of diphenacyltellurium dichloride did not afford the corresponding telluride [4], although diphenacyl telluride is regarded as an unstable intermediate in a non-silver implication process upon physical development of photography [5]. Engman [6] reported for the first time a successful method for the synthesis of diphenacyl telluride by a mild $Na_2S_2O_5$ reduction of diphenacyltellurium dichloride in a two-phase system.

We are currently interested in potassium tellurocyanate as tellurating agent for preparing some organotellurium compounds [7–9]. We now report a novel preparative method for diphenacyl telluride and related substances using α-tellurocyanatoalkyl aryl ketones as starting materials.

2. Experimental

2.1. Physical measurements

^1H- and ^{13}C-NMR spectra were obtained with a JEOL EX-90FT NMR spectrometer instrument and were recorded in $CDCl_3$ solutions containing TMS as internal standard. Infrared (IR) spectra were recorded for KBr discs with a Pye-Unicam SP3-300s instrument. Elemental analyses (C, H and N) were obtained for all compounds on a Carlo-Ebra EA-1108B Elemental Analyzer. Conductivities were measured with WTW

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conductivity meter LBR, using a cell constant of 0.80 cm^{-1}. Melting points for all solid compounds were determined by Gallenkamp melting point apparatus and are uncorrected. Molecular weight was measured in benzene using Kanure Cryscopic meter and benzene was used as a standard reference. Mass spectra were determined on a Finnigan MAT-321 spectrometer at 70 eV and measurements were carried out on ^{130}Te isotope. Tellurium analyses were carried out by the use of a Shimadzu-AA 630-3z atomic absorption spectrophotometer as described previously [10].

2.2. Synthesis

Phenacyl bromide, 4-bromophenacyl bromide, 4-phenylphenacyl bromide and α-bromopropiophenone were commercial products.

*2.2.1. Phenacyl tellurocyanate, $C_6H_5COCH_2TeCN$ (**1**)*

A mixture of freshly crushed and finely ground tellurium powder (1.02 g; 8 mmol) and dry powdered potassium cyanide (0.53 g; 8 mmol) in dry DMSO (15 cm^3) was refluxed under nitrogen atmosphere with stirring for 1 h. The resulting solution was cooled to room temperature (r.t.) and to it added a solution of phenacyl bromide (1.59 g; 8 mmol) in 15 cm^3 of dry DMSO dropwise over a period of 30 min. After stirring for 2 h at r.t., the yellow solution was filtered, poured into water (300 cm^3) and left for 12 h. Extraction with benzene (4×100 cm^3) gave a pale yellow solution, which was dried ($MgSO_4$) and filtered. The filtrate was evaporated to give a yellow precipitate. Recrystallization from a mixture of ethanol and chloroform (3:2) gave compound **1** as a yellow solid in 35% yield, m.p. 71–72 °C.

IR (cm^{-1}, KBr): ν_{CO} 1650s; ν_{CN} 2210s.

^{1}H-NMR (δ, $CDCl_3$): 4.65 (s, CH_2, 2H; $J_{^{125}Te-^{1}H} =$ 29.1 Hz); 7.30–8.10 (m, $Ar-H$, 5H).

^{13}C-NMR (δ, $CDCl_3$): 49.5, 116.5, 128.4, 129.1, 132.5, 137.6, 198.3.

Anal. Calc. for C_9H_7ONTe: C, 39.63; H, 2.58; N, 5.13; Te, 46.8. Found: C, 39.46; H, 2.98; N, 5.15; Te, 46.4%.

The following compounds were prepared similarly using the appropriate α-bromoketone.

*2.2.2. 4-Bromophenacyl tellurocyanate, 4-$BrC_6H_4COCH_2TeCN$ (**2**)*

Yellow solid, 57% yield, m.p. 106 °C.

IR (cm^{-1}, KBr): ν_{CO} 1650s; ν_{CN} 2210s.

^{1}H-NMR (δ, $CDCl_3$): 4.40 (s, CH_2, 2H; $J_{^{125}Te-^{1}H} =$ 34.4 Hz); 7.65 (q, $Ar-H$, 4H).

^{13}C-NMR (δ, $CDCl_3$): 42.8, 117.7, 126.5, 130.0, 132.2, 133.0, 196.5.

Anal. Calc. for $C_9H_6NOBrTe$: C, 30.74; H, 1.72; N, 3.98; Te, 36.29%.

Found: C, 30.62; H, 1.70; N, 3.76; Te, 36.42%.

*2.2.3. 4-Phenylphenacyl tellurocyanate, 4-$PhC_6H_4COCH_2TeCN$ (**3**)*

Yellow solid, 59% yield, m.p. 121–123 °C.

IR (cm^{-1}, KBr): ν_{CO} 1655s; ν_{CN} 2170s.

^{1}H-NMR (δ, $CDCl_3$): 4.50 (s, CH_2, 2H; $J_{^{125}Te-^{1}H} =$ 26.8 Hz); 7.12–8.40 (m, $Ar-H$, 9H).

^{13}C-NMR (δ, $CDCl_3$): 40.2, 118.4, 127.5, 128.0, 134, 6, 136.0, 141.5, 145.2, 198.1.

Anal. Calc. for $C_{15}H_{11}NOTe$: C, 51.64; H, 3.17; N, 4.01; Te, 36.58%.

Found: C, 52.12; H, 3.96; N, 3.36; Te, 36.44%.

*2.2.4. Propiophenon-2-yl tellurocyanate, $C_6H_5COCH(CH_3)TeCN$ (**4**)*

Yellow solid, 39% yield, m.p. 89–90 °C.

IR (cm^{-1}, KBr): ν_{CO} 1630s; ν_{CN} 2160s.

^{1}H-NMR (δ, $CDCl_3$): 2.10 (d, CH_3, 3H; $J_{HH} = 14.1$ Hz); 5.50 (q, CH, 1H); 7.41–8.25 (m, $Ar-H$, 5H).

^{13}C-NMR (δ, $CDCl_3$): 28.3, 53.2, 116.8, 128.5, 129.0, 133.2, 137.5, 200.5.

Anal. Calc. for $C_{10}H_9NOTe$: C, 41.88; H, 3.16; N, 4.88; Te, 44.49%.

Found: C, 42.01; H, 3.30; N, 5.00; Te, 44.14%.

*2.2.5. Diphenacyl ditelluride, $(C_6H_5COCH_2)_2Te_2$ (**5**)*

To a solution of **1** (0.28 g; 1.02 mmol) in dry ethanol (25 cm^3) was added a solution of sodium hydroxide (0.16 g; 2.45 mmol) in 15 cm^3 of dry ethanol. The resulting mixture was stirred for 50 min at 40 °C under oxygen atmosphere. The solution was then refluxed for 1 h, cooled to r.t. and filtered. The filtrate was acidified with 10% hydrochloric acid. A red semisolid compound was formed, washed with a small amount of benzene and dried. Recrystallization from a mixture of methanol and dichloromethane (1:4) gave a red semisolid compound in 39% yield.

IR (cm^{-1}, KBr): ν_{CO} 1695m; ν_{Te-C} 475w, 530w.

^{1}H-NMR (δ, $CDCl_3$): 4.41 (s, CH_2, 4H; $J_{^{125}Te-^{1}H} =$ 26.8 Hz); 7.20–8.00 (m, $Ar-H$, 10H).

^{13}C-NMR (δ, $CDCl_3$): 37.4, 128.5, 129.2, 132.2, 137.3, 198.1.

Anal. Calc. for $C_{16}H_{14}O_2Te_2$: C, 38.94; H, 2.85; Te, 51.71%.

Found: C, 39.20; H, 2.64; Te, 52.11%.

*2.2.6. Bis(4-bromophenacyl) ditelluride, $(4\text{-}BrC_6H_4COCH_2)_2Te_2$ (**6**)*

Red solid in 67% yield, m.p. 97–99 °C.

IR (cm^{-1}, KBr): ν_{CO} 1685s; ν_{Te-C} 480w, 530w.

^{1}H-NMR (δ, $CDCl_3$): 4.34 (s, CH_2, 4H; $J_{^{125}Te-^{1}H} =$ 35.8 Hz); 7.62 (q, $Ar-H$, 8H).

^{13}C-NMR (δ, $CDCl_3$): 36.5, 126.1, 130.0, 132.2, 133.2, 198.5.

Anal. Calc. for $C_{16}H_{12}O_2Br_2Te_2$: C, 29.51; H, 1.86; Te, 39.18%.

Found: C, 29.38; H, 1.85; Te, 38.82%.

*2.2.7. Bis(4-phenylphenacyl) ditelluride, $(4\text{-}PhC_6H_4COCH_2)_2Te_2$ (**7**)*

Red solid, 76% yield, m.p. 107 °C.

IR (cm^{-1}, KBr): ν_{CO} 1650s; ν_{Te-C} 480w, 510w.

^{1}H-NMR (δ, $CDCl_3$): 4.47 (s, CH_2, 4H; $J_{^{125}Te-^{1}H}$ = 34.0 Hz); 7.20–8.35 (m, $Ar-H$, 18H).

^{13}C-NMR (δ, $CDCl_3$): 30.9, 127.3, 127.4, 128.5, 129.0, 129.5, 132.6, 139.5, 146.5, 195.5.

Anal. Calc. for $C_{28}H_{22}O_2Te_2$: C, 52.08; H, 3.43; Te, 39.52%.

Found: C, 52.10; H, 3.42; Te, 39.26%.

*2.2.8. Bis(propiophenon-2-yl) ditelluride, $(C_6H_5COCH(CH_3))_2Te_2$ (**8**)*

Red solid, 60% yield, m.p. 60–62 °C.

IR (cm^{-1}, KBr): ν_{CO} 1665s; ν_{Te-C} 495w, 535w.

^{1}H-NMR (δ, $CDCl_3$): 1.71 (d, CH_3, 6H; $J_{HH} = 12.1$ Hz); 5.25 (q, CH, 2H); 7.20–8.10 (m, $Ar-H$, 10H).

^{13}C-NMR (δ, $CDCl_3$): 35.0, 49.1, 128.0, 129.0, 130.2, 133.6, 135.4, 197.2.

Anal. Calc. for $C_{18}H_{18}O_2Te_2$: C, 41.45; H, 3.47; Te, 48.93%.

Found: C, 42.10; H, 3.42; Te, 49.14%.

*2.2.9. Diphenacyl telluride, $(C_6H_5COCH_2)_2Te$ (**9**)*

A solution of diphenacyl ditelluride (0.98 g; 2 mmol) and activated copper (0.38 g; 6 mmol) in dry dioxane (20 cm^3) was refluxed for 3 h. The reaction mixture was filtered hot. The filtrate was allowed to cool to r.t. and the solution was evaporated to dryness. The resulting yellow solid was recrystallized from petroleum ether (60–80 °C) to give yellow crystals in 67% yield, m.p. 78–80 °C (Lit. [6], 78–79 °C).

IR (cm^{-1}, KBr): ν_{CO} 1730m, 1650s; ν_{Te-C} 475w, 530w.

^{1}H-NMR (δ, $CDCl_3$): 4.55 (s, CH_2, 4H; $J_{^{125}Te-^{1}H}$ = 25.1 Hz); 7.20–8.05 (m, $Ar-H$, 10H).

^{13}C-NMR (δ, $CDCl_3$): 35.8, 128.7, 129.9, 132.7, 137.5, 197.8.

Anal. Calc. for $C_{16}H_{14}O_2Te$: C, 52.52; H, 3.85; Te, 34.87%.

Found: C, 52.37; H, 3.94; Te, 35.14%.

*2.2.10. Bis(4-bromophenacyl) telluride, $(4\text{-}BrC_6H_4COCH_2)_2Te$ (**10**)*

Yellow crystals, 77% yield, m.p. 130–132 °C (Lit. [6], 131–132 °C).

IR (cm^{-1}, KBr): ν_{CO} 1700s, 1640s; ν_{Te-C} 485w, 525w.

^{1}H-NMR (δ, $CDCl_3$): 4.35 (s, CH_2, 4H; $J_{^{125}Te-^{1}H}$ = 34.9 Hz); 7.75 (q, $Ar-H$, 8H).

^{13}C-NMR (δ, $CDCl_3$): 36.4, 126.1, 129.8, 132.2, 133.0, 197.6.

Anal. Calc. for $C_{16}H_{12}O_2Br_2Te$: C, 36.69; H, 2.31; Te, 24.37%.

Found: C, 36.38; H, 2.28; Te, 23.92%.

*2.2.11. Bis(4-phenylphenacyl) telluride, $(4\text{-}PhC_6H_4COCH_2)_2Te$ (**11**)*

Yellow crystals, 74% yield, m.p. 138–139 °C.

IR (cm^{-1}, KBr): ν_{CO} 1730s, 1620s; ν_{Te-C} 485w, 510w.

^{1}H-NMR (δ, $CDCl_3$): 4.45 (s, CH_2, 4H; $J_{^{125}Te-^{1}H}$ = 32.2 Hz); 7.10–8.37 (m, $Ar-H$, 18H).

^{13}C-NMR (δ, $CDCl_3$): 37.4, 127.1, 127.6, 128.0, 128.5, 136.2, 141.4, 145.5, 197.5.

Anal. Calc. for $C_{28}H_{22}O_2Te$: C, 64.91; H, 4.27; Te, 24.63%.

Found: C, 64.65; H, 4.28; Te, 24.37%.

*2.2.12. Bis(propiophenon-2-yl) telluride, $(C_6H_5COCH(CH_3))_2Te$ (**12**)*

Yellow crystals, 56% yield, m.p. 70–71 °C.

IR (cm^{-1}, KBr): ν_{CO} 1700m, 1665m; ν_{Te-C} 470w, 530w.

^{1}H-NMR (δ, $CDCl_3$): 2.01 (d, CH_3, 6H; $J_{HH} = 13.7$); 5.30 (q, CH, 2H); 7.15–8.10 (m, $Ar-H$, 10H).

^{13}C-NMR (δ, $CDCl_3$): 37.0, 48.0, 130.5, 129.0, 130.2, 131.3, 132.4, 135.2, 199.6.

Anal. Calc. for $C_{18}H_{18}O_2Te$: C, 54.88; H, 4.60; Te, 32.39%.

Found: C, 54.95; H, 4.49; Te, 32.17%.

*2.2.13. Synthesis of diorganyltellurium dichloride (**13**, **14**, **15**, **16**)*

Compounds **13**, **14**, **15** and **16** were prepared by the following method:

To a solution of the corresponding telluride (1.5 mmol) in dry diethyl ether (10 cm^3) was added slowly with stirring a solution of thionyl chloride (1.5 mmol) in 20 cm^3 of dry diethyl ether. A pale yellow precipitate was formed during the addition. Evaporation of the solvent gave a pale yellow solid. Recrystallization from ethanol/chloroform (1/3) gave a white crystal of the corresponding dichloride (Table 1).

*2.2.14. Synthesis of diorganyltellurium dibromide (**17**, **18**, **19**, **20**)*

Compounds **17**, **18**, **19** and **20** were prepared according to the following method:

To a solution of the corresponding telluride (2 mmol) in 20 cm^3 of dry diethyl ether was added drop by drop a solution of bromine (1.28 g; 8 mmol) in 40 cm^3 of dry diethyl ether. A fine yellow precipitate was formed immediately and soon became almost colourless. Bromine was added until a permanent colour of bromine resulted when an additional drop of bromine was added. The solvent was allowed to evaporate at r.t. and a yellow precipitate of the corresponding dibromide was obtained. The product was recrystallized from ethanol

Table 1
Physical and analytical data for compounds **13**–**36**

Compounds	Colour	Melting point (°C)	Yield (%) [a]	Analysis (%) [b]			Molar conductivity (Λ_M) [c]
				C	H	Te	
$(C_6H_5COCH_2)_2TeCl_2$ (**13**)	White	192–193	87(89)	44.01(43.99)	3.30(3.23)	29.32(29.21)	18.1
$(4\text{-}BrC_6H_4COCH_2)_2TeCl_2$ (**14**)	White	202–203	83(87)	32.57(32.32)	2.37(2.03)	21.25(21.46)	18.2
$(4\text{-}PhC_6H_4COCH_2)_2TeCl_2$ (**15**)	White	154–155	80(87)	57.01(57.10)	3.80(3.76)	21.45(21.66)	21.1
$(C_6H_5COCH(CH_3))_2TeCl_2$ (**16**)	White	152–154	60(76)	46.88(46.50)	4.12(3.90)	27.21(27.45)	18.0
$(C_6H_5COCH_2)_2TeBr_2$ (**17**)	Orange	201–203	80(82)	36.72(36.56)	2.56(2.68)	23.96(24.27)	24.9
$(4\text{-}BrC_6H_4COCH_2)_2TeBr_2$ (**18**)	Yellow	210–212	82(88)	27.88(28.11)	1.68(1.76)	18.53(18.67)	20.0
$(4\text{-}PhC_6H_4COCH_2)_2TeBr_2$ (**19**)	Yellow	210–212	82(91)	49.42(49.61)	3.23(3.27)	18.65(18.82)	24.9
$(C_6H_5COCH(CH_3))_2TeBr_2$ (**20**)	Yellow	200–201	71(84)	39.23(39.04)	3.23(3.27)	23.32(23.04)	19.5
$(C_6H_5COCH_2)_2TeI_2$ (**21**)	Red	253–254	88(83)	31.78(31.01)	2.30(2.27)	40.75(40.96)	28.5
$(4\text{-}BrC_6H_4COCH_2)_2TeI_2$ (**22**)	Orange	257–259	89(93)	24.63(24.71)	1.52(1.55)	16.21(16.40)	32.3
$(4\text{-}PhC_6H_4COCH_2)_2TeI_2$ (**23**)	Red	160–161	76(79)	37.38(37.53)	2.52(2.49)	16.52(16.53)	38.0
$(C_6H_5COCH(CH_3))_2TeI_2$ (**24**)	Red	220–224	62(87)	32.88(33.37)	2.86(2.80)	19.43(19.70)	30.0
$C_6H_5COCH_2TeCl_3$ (**25**)	White	242–243	90(88)	26.95(27.21)	2.02(1.99)	35.82(36.14)	13.2
$4\text{-}BrC_6H_4COCH_2TeCl_3$ (**26**)	White	150–152	92(95)	22.42(22.24)	1.37(1.39)	29.62(29.54)	24.0
$4\text{-}PhC_6H_4COCH_2TeCl_3$ (**27**)	White	140–142	80(86)	38.86(39.17)	2.63(2.58)	29.50(29.75)	22.4
$C_6H_5COCH(CH_3)TeCl_3$ (**28**)	White	145–147	52(73)	29.48(29.41)	2.81(2.47)	35.11(34.76)	20.1
$C_6H_5COCH_2TeBr_3$ (**29**)	Yellow	202–204	83(85)	19.99(19.75)	1.38(1.45)	25.78(26.23)	28.0
$4\text{-}BrC_6H_4COCH_2TeBr_3$ (**30**)	Yellow	135–137	83(88)	17.27(17.26)	1.40(1.07)	22.45(22.57)	27.9
$4\text{-}PhC_6H_4COCH_2TeBr_3$ (**31**)	Yellow	131–133	85(87)	30.38(29.89)	2.23(1.97)	22.75(22.68)	24.1
$C_6H_5COCH(CH_3)TeBr_3$ (**32**)	Yellow	130–131	54(65)	21.46(21.59)	1.72(1.81)	25.32(25.50)	29.1
$C_6H_5COCH_2TeI_3$ (**33**)	Red	155–156	84(80)	14.99(15.31)	1.38(1.12)	20.03(20.34)	30.0
$4\text{-}BrC_6H_4COCH_2TeI_3$ (**34**)	Red	129–130	87(79)	13.20(13.60)	1.12(0.85)	18.23(18.06)	40.0
$4\text{-}PhC_6H_4COCH_2TeI_3$ (**35**)	Red	135–137	89(89)	23.72(23.90)	1.29(1.57)	17.65(18.14)	51.0
$C_6H_5COCH(CH_3)TeI_3$ (**36**)	Red	171–173	59(55)	16.73(16.85)	1.21(1.41)	19.72(19.89)	30.1

[a] Yields by using diorganyl ditellurides as starting materials are in parentheses.

[b] Calculated values are in parentheses.

[c] 10^{-3} M solutions: Et_4NCl Λ_M (DMSO): 30 Ω^{-1} cm^2 mol^{-1}.

and chloroform (1:1) to give yellow crystals in good yield. Physical and analytical data are presented in Table 1.

2.2.15. *Synthesis of diorganyltellurium diiodide (**21**, **22**, **23**, **24**)*

Compounds **21**, **22**, **23** and **24** were prepared as follows:

Iodine (0.39 g; 1.5 mmol) in dry diethyl ether (15 cm^3) was added to a well stirred solution of the corresponding telluride (1.5 mmol) in 30 cm^3 of dry diethyl ether at r.t. An orange-red precipitate was formed immediately. The product was washed with ethanol then dried in vaccuo. Recrystallization from ethanol and chloroform (1:2) gave an orange crystal of the diiodide (Table 1).

2.2.16. *Synthesis of organyltellurium trichloride (**25**, **26**, **27**, **28**)*

25, **26**, **27** and **28** were prepared by treating ArTeCN (1.5 mmol) with thionyl chloride (1.5 mmol) by the same method for the preparation of the dichloride. Recrystallization of the product from ethanol and chloroform (1:1) gave a white solid of the corresponding trichloride (Table 1).

2.2.17. *Synthesis of organyltellurium tribromide (**29**, **30**, **31**, **32**)*

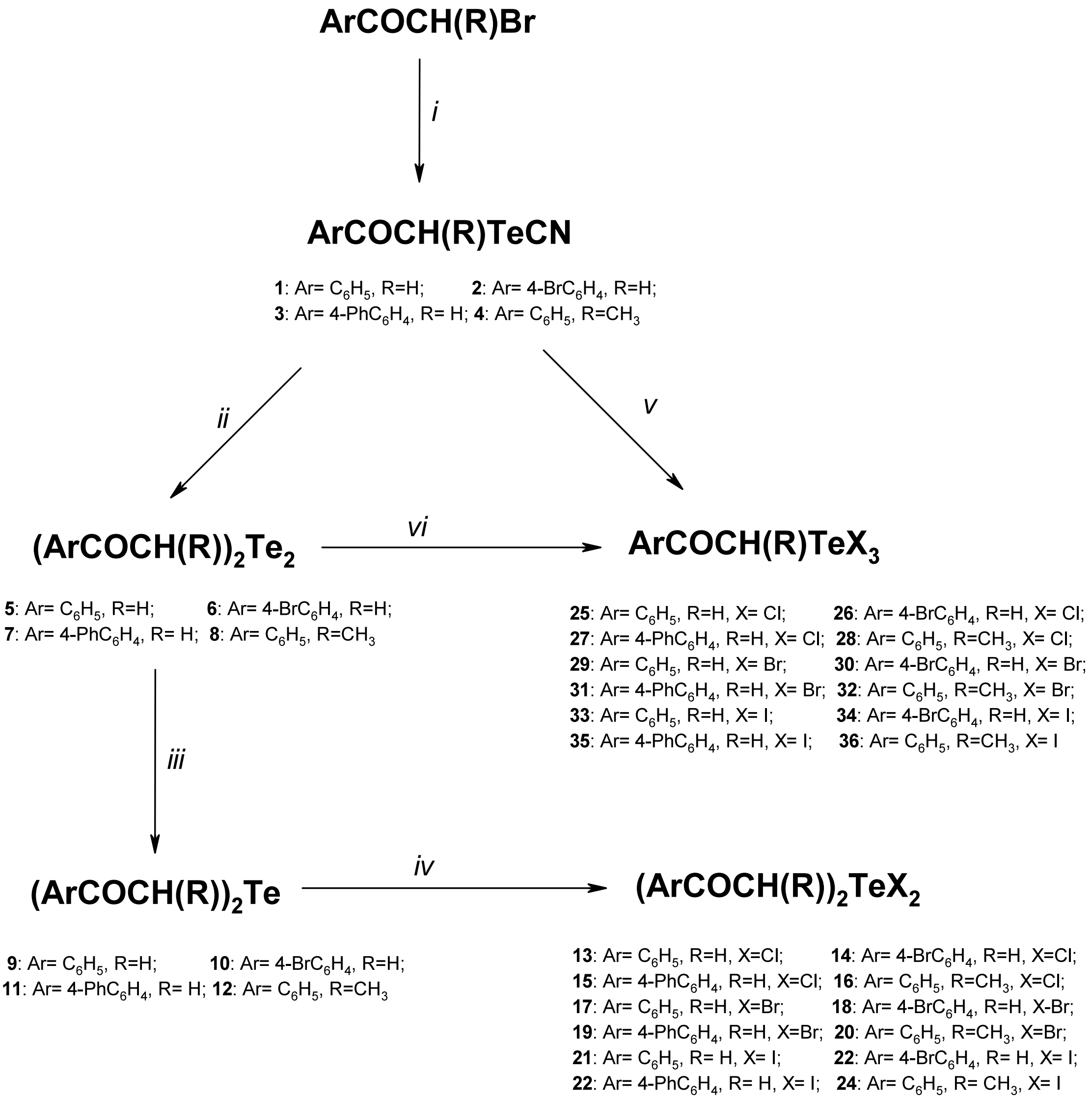
Compounds **29**, **30**, **31** and **32** were prepared by the treatment of aryltellurocyanate (1.5 mmol) with bromine (1.5 mmol) as described for the preparation of the dibromide to give a yellow product. Recrystallization from ethanol and chloroform (1:1) gave a yellow solid in good yield (Table 1).

2.2.18. *Synthesis of organyltellurium triiodide (**33**, **34**, **35**, **36**)*

The same procedure as for the diiodide was applied to prepare compounds **33**, **34**, **35** and **36**, but ArTeCN was used as starting material. All compounds obtained as orange-red crystals after recrystallization from a mixture of ethanol and dichloromethane (2:3).

Compounds **25**–**36** were also prepared by adding thionyl chloride, bromine and iodine to the corresponding ditelluride (i.e., **5**, **6**, **7** and **8**) to afford the trichloride, tribromide and triiodide in good yields (see Table 1 for comparison).

Physical and analytical data for compounds **13**–**36** are presented in Table 1.



Scheme 1. Preparative method for compounds **1**–**36**. Reagents: (i) KTeCN/DMSO (ii) 10% NaOH (iii) Cu/dioxane (iv) $SOCl_2$, Br_2 and I_2 (v) $SOCl_2$, Br_2 and I_2 (vi) $SOCl_2$, Br_2 and I_2.

2.3. Oxidation of diorganyl tellurides with MCPBA

A typical experimental procedure is as follows. To a dry CH_2Cl_2 (5 cm^3) solution of diphenacyl telluride (1.46 mg; 0.40 mmol) was added dropwise a dry CH_2Cl_2 (3 cm^3) solution of *m*-chloroperbenzoic acid (MCPBA; 70% purity, 1.04 mg, 0.60 mmol) at 0 °C under N_2, and the resulting mixture was stirred for 2 h at 0 °C. The mixture was poured into saturated aqueous Na_2CO_3 solution (60 cm^3) and extracted with CH_2Cl_2 (30×4 cm^3). The extracts dried over $MgSO_4$ and evaporated to leave an oily residue which was purified by column chromatography to afford acetophenone in 64% yield as the only product.

4-Bromoacetophenone, 4-phenylacetophenone and propiophenone were obtained in 58, 62 and 59% yields, respectively.

2.4. Oxidation of diorganyltellurium dichlorides with MCPBA

Similar method described in Section 2.3 was applied to diorganyltellurium dichlorides (0.40 mmol). Acetophenone, 4-bromoacetophenone, 4-phenylacetophenone and propiophenone were obtained in 56, 61, 59 and 48% yields, respectively.

3. Results and discussion

Four new organotellurocyanates (i.e., $C_6H_5COCH_2$-TeCN (**1**), 4-$BrC_6H_4COCH_2TeCN$ (**2**), 4-$PhC_6H_4COCH_2TeCN$ (**3**) and $C_6H_5COCH(CH_3)TeCN$ (**4**)) were prepared from the reaction of potassium tellurocyanate [11] with the appropriate α-bromoketone

Table 2
Some representative IR, ^{1}H-NMR and ^{13}C-NMR data

Compounds	IR (cm^{-1})	^{1}H-NMR (δ, $CDCl_3$)	^{13}C-NMR (δ, $CDCl_3$)
13	1650s, 530w, 470w, 325m	4.75 (s, 4H, CH_2); 7.30–8.20 (m, 10H, $Ar-H$)	40.4, 128.2, 129.5, 131.8, 136.9, 196.5
16	1665s, 520w, 470w, 315m	2.10 (d, 6H, CH_3); 5.43 (q, 2H, CH); 7.40–8.40 (m, 10H, $Ar-H$)	10.2, 46.1, 127.0, 127.6, 128.1, 128.7, 136.0, 141.5, 197.6
18	1690s, 510w, 470w	4.35 (s, 4H, CH_2); 7.80 (q, 8H, $Ar-H$)	40.0, 128.0, 129.5, 131.0, 132.5, 139.5, 146.5, 188.5
20	1660s, 505w, 480w	2.05 (d, 6H, CH_3); 5.40 (q, 2H, CH); 7.30–8.21 (m, 10H, $Ar-H$)	10.3, 42.1, 128.1, 129.3, 132.2, 137.5, 196.5
22	1660s, 505w, 470w	4.31 (s, 4H, CH_2); 7.65 (q, 8H, $Ar-H$)	41.4, 126.0, 130.2, 132.0, 133.2, 197.5
24	1685m, 530w, 490w	2.05 (d, 6H, CH_3); 5.40 (q, 2H, CH); 7.30–8.20 (m, 10H, $Ar-H$)	10.2, 47.4, 128.5, 129.2, 132.0, 137.5, 196.4
25	1690s, 480w, 325m	4.80 (s, 2H, CH_2); 7.35–8.20 (m, 5H, $Ar-H$)	41.6, 127.6, 128.5, 131.6, 137.8, 196.5
26	1680s, 475w	4.50 (s, 2H, CH_2); 7.85 (q, 4H, $Ar-H$)	47.6, 128.3, 129.1, 132.5, 137.5, 196.7
28	1660s, 460w	2.15 (d, 3H, CH_3); 5.35 (q, 1H, CH); 7.30–8.15 (m, 5H, $Ar-H$)	9.89, 40.9, 127.8, 129.1, 131.8, 137.0, 198.8
30	1655s, 465w	4.45 (s, 2H, CH_2); 7.65 (q, 4H, $Ar-H$)	40.2, 127.1, 128.5, 129.0, 129.6, 130.5, 132.7, 139.5, 146.5, 196.8
31	1690s, 465w	4.50 (s, 2H, CH_2); 7.10–8.40 (m, 9H, $Ar-H$)	45.5, 126.8, 127.5, 128.1, 128.5, 136.2, 140.8, 145.5, 197.8
35	1665s, 485w	4.46 (s, 2H, CH_2); 7.21–8.40 (m, 9H, $Ar-H$)	40.2, 127.3, 127.8, 128.6, 136.1, 141.2, 145.5, 198.3

in dry DMSO solution. Pure compounds were obtained after one recrystallization as yellow solids in fair yields (35–59%). The IR spectra of these compounds showed low carbonyl absorption, which appeared around 1650 cm^{-1} as a strong band. Furthermore, compounds **1**, **2**, **3** and **4** show strong bands at 2210, 2210, 2170 and 2160 cm^{-1}, respectively, which are attributed to ν(Te–CN) [12,13]. In the ^{1}H-NMR spectra, the expected ratio of aliphatic to aromatic protons was observed. The methylene protons (COCH_2TeCN) appeared as singlet at around 4.40 ppm for **1**, **2** and **3**, while for compound **4** the COCH(CH_3)–TeCN proton appeared as quartet (see Section 2). ^{13}C-NMR spectra of compounds **1**, **2**, **3** and **4** revealed the presence of Te–CN around 118.0 ppm and CO at around 197.0 ppm. These agree well with literature values [14]. In general, compounds **1**–**4** are moderately stable at room temperature and are to handle at room temperature.

Treatment of compounds **1**, **2**, **3** and **4** with ethanolic sodium hydroxide (10%) is the most obvious way to prepare the ditellurides **5**, **6**, **7** and **8**, respectively, as many ditellurides have been prepared by this method [13b,14]. Compounds **6**, **7** and **8** were obtained as red solids while **5** was obtained as a red semisolid compound. Attempts to solidify **5** were unsuccessful. These new compounds were obtained in good yields and quite stable to handle them at room temperature (Scheme 1). IR and NMR data together with elemental analyses support the formation of these new compounds.

IR spectra indicate the presence of ν_{CO} between 1650 and 1695 cm^{-1} as a strong band. ^{13}C-NMR spectra showed the presence of CO signal between 197.2 and 198.5 ppm.

It has been known that the tellurides containing –$COCH_2$– groups were prepared for the first time by a mild $Na_2S_2O_5$ reduction of diorganyltellurium dichlorides in a two-phase system [6]. Refluxing compounds **5**, **6**, **7** and **8** in dry dioxane for 1 h in presence of a threefold molar excess of activated copper gave compounds **9**, **10**, **11** and **12** as yellow solids in 67, 77, 74 and 54% yields, respectively. It is worth noting that compounds **9** and **10** have been prepared in 55 and 76% yields, respectively, by reducing the diphenacyltellurium dichloride and bis(4-bromophenacyl)tellurium dichloride in the two-phase system [6]. Thus, we developed a new route to prepare these tellurides in good yields.

The tellurides **9**–**12** readily reacted with thionyl chloride, bromine and iodine to afford dichloride (**13**–**16**), dibromide (**17**–**20**) and diiodide (**21**–**24**) derivatives, respectively in good yields (Scheme 1). Isolated yields, melting points, colours and analytical data for compounds **13**–**24** are shown in Table 1. The molar conductance of each compound (**13**–**24**) was examined over a range of concentration in DMSO solution. In each case, a non-linear plot of molar conductivity (Λ_M) against (concentration)$^{1/2}$ was found to be typical of a weak electrolyte. All compounds gave appreciable conducting solution at a concentration of 10^{-3} M (Table 1). IR and NMR data for all compounds are presented in Table 2.

Compounds **1**, **2**, **3** and **4** and compounds **5**, **6**, **7** and **8** can be easily converted to the trichloride (**25**–**28**), the tribromide (**29**–**32**) and the triiodide (**33**–**36**) with thionyl chloride, bromine and iodine, respectively. Conductivity measurements in DMSO solution indicated that compounds **25**–**36** are weak electrolytes, and the values of Λ_M approach 1:1 electrolytes (Table 1).

Table 3
Oxidation of compounds **9**–**16** with MCPBA [a]

Compounds	Products (GLC yield (%))
9	Acetophenone (64)
10	4-Bromoacetophenone (58)
11	4-Phenylacetophenone (62)
12	Propiophenone (59)
13	Acetophenone (56)
14	4-Bromoacetophenone (61)
15	4-Phenylacetophenone (59)
16	Propiophenone (48)

[a] At 0 °C for 2 h.

Table 4
Molecular weight determination for selected compounds

Compounds	Molecular weight (Calc.)	Molecular weight (Found)
2	351.65	349.93
8	521.54	523.62
10	523.68	523.04
11	518.08	519.95
17	525.69	527.00
22	777.49	774.03
19	677.89	672.69
23	553.75	557.84
25	353.10	358.66
26	434.99	437.85
27	429.20	432.46
32	500.50	500.99

These observations agree well with those of the previous work [15].

IR spectra of compounds **1**–**24** showed two bands in the range of 460–580 cm^{-1} due to ν_{as}(Te–C) and ν_{s}(Te–C), which agree well with previous works [8,15]. On the other hand, IR spectra of compounds **25**–**36** showed only one ν(Te–C) in the range 485–460 cm^{-1}. IR spectra of all compounds showed a remarkably low carbonyl absorption in comparison with their chalcogen analogues and their α-bromoketones. Thus, IR spectrum of **5** showed a low carbonyl absorption at 1650 cm^{-1}. This effect is less pronounced for its chalcogen analogues diphenacyl selenide (1670 cm^{-1}) and diphenacyl sulphide (1690 cm^{-1}) [6]. The lowering of ν(C=O) frequency may be due to the coordination of the carbonyl oxygen to the tellurium atom in which the –COCH(R)– group is acting as unsymmetrical bidentate ligand [15]. IR spectra of compounds **9**–**12** showed two bands for ν(C=O). Thus, we believe that only one C=O is coordinated to the Te atom through its oxygen atom, and that the other is free (see Section 2 and Table 2). These observations agree well with Singh and co-workers' work [16]. ^{1}H- and ^{13}C-NMR data are in good agreement with the formulation of these compounds (Table 2).

When tellurides **9**–**12** and diorganyltellurium dichlorides **13**–**16** were oxidized with MCPBA in dichloromethane [17], the corresponding methyl aryl ketones were obtained in good yields as the only product (Table 3).

Molecular weight determination for selected compounds indicated that these compounds are monomeric in benzene solution (Table 4).

In conclusion, we have shown that tellurides containing –COCH(R)– group can be synthesized indirectly by using this efficient synthetic route. Many types of new acetylated organotellurium compounds were also prepared by using the corresponding tellurocyante as a starting material. These new compounds could be used in organic synthesis as they contain a weak tellurium–carbon bond.

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