Isotellurazoles: A New Heteroaromatic System

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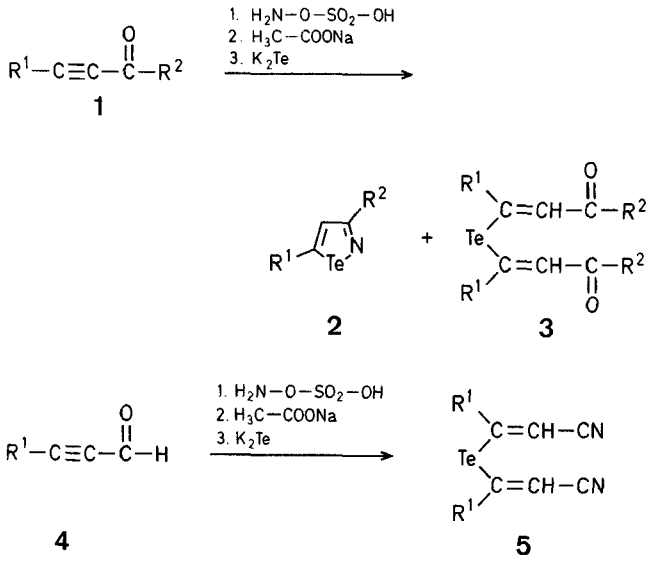
Recently[1], we described the synthesis of 1,2,5-telluradiazole, the first pentaatomic uncondensed heterocyclic system containing nitrogen-tellurium bonds, and some of its derivatives. Now we report the synthesis of another pentaatomic uncondensed heterocyclic system containing nitrogen-tellurium bonds, isotellurazole **(2)**.

The isotellurazole derivatives **2** are obtained in low yields by reacting α-acetylenic ketones **1** with hydroxylamine-*O*-sulphonic acid in buffered aqueous sodium acetate medium in the presence of potassium telluride by a one-pot procedure (Table). Water may be replaced by methanol as reaction me-

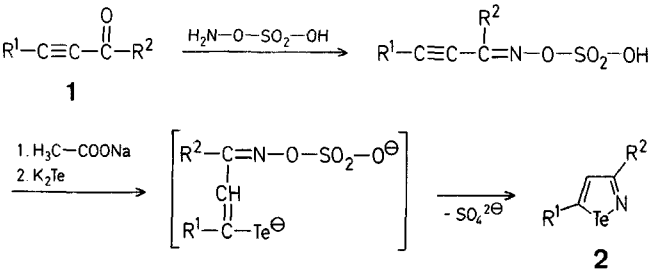
dium with the same results. In place of potassium telluride, lithium telluride may be used with similar results, but the use of the former allows a better work-up.

Isotellurazoles **2** are accompanied by the corresponding tellurobis[alkenyl ketones] **3** and, in the case of 4-phenyl-3-butyn-2-one **(1e)**, also by the reduction product, 4-phenyl-3-buten-2-one. Moreover, the addition of telluride always causes redox reactions as shown by the blackening of the mixture, consequent upon the formation of elemental tellurium.

The use of acetylenic aldehydes **4** in place of the ketones **1** does not give 3-unsubstituted isotellurazoles, but yields the tellurobis[alkenenitriles] **5** (Table).



A reasonable mechanism for the formation of isotellurazoles **2** involves the initial transformation of the carbonyl group into an oxime-*O*-sulphonic acid, followed by nucleophilic addition of the telluride anion to the triple bond according to known reactions[2] and the cyclization by nucleophilic displacement of the sulphate anion.



The oxime-*O*-sulphonic acids and their analogues react with reducing agents to give imines or carbonyl compounds after hydrolysis[3], while those of aldehydes are unstable, forming nitriles[4]. This fact, combined with the presence of strong reducing agents like tellurides in the reaction mixture, account for the formation of side product **3** as well as for the failure to obtain 3-unsubstituted isotellurazoles from acetylenic aldehydes **4**. The cyclization is prevented when the side reaction dominates by the interaction of telluride with the acetylenic bond of two molecules of the starting material.

The prepared isotellurazoles are characterized by rather high melting points combined, at least for the alkyl derivatives, with ease of sublimation, and tendency to escape when organic solutions are evaporated in open air. Under electron impact, they undergo a fragmentation analogous to that of isothiazoles[5] with loss of R^1—C≡CH and R^2—CN; nevertheless, the 3-propyl derivative undergoes the McLafferty rearrangement[6] with loss of ethene.

The ^{1}H-N.M.R. spectra show signals at about $\delta = 10.3$ and 8.0 ppm for protons in position 5 and 4 respectively. Both of such signals have satellites due to the coupling with ^{125}Te.

3-Butyn-2-one **(1a)**[7], 1-pentyn-3-one **(1b)**[8], 1-hexyn-3-one **(1c)**[9], 3-pentyn-2-one **(1d)**[10], 4-phenyl-3-butyn-2-one **(1e)**[11], propynal **(4a)**[12], phenylpropynal **(4b)**[13], potassium telluride[14], and lithium telluride[14] were prepared according to known procedures.

Isotellurazoles 2 and Tellurobis[alkenyl Ketones] 3; General Procedure:

The reaction components are used in the molar ratio ketone : hydroxylamine-*O*-sulphonic acid : sodium acetate : potassium telluride = 1 : 1 : 2 : 1.

The α-acetylenic ketone **1** (Table) is added to a solution of hydroxylamine-*O*-sulphonic acid in water (5 ml) at 0°C under nitrogen and vigorously stirred for 20–35 min till a clear solution is obtained. Sodium acetate is then added and the stirred solution is treated with a 0.6 molar aqueous solution of potassium telluride in about 20 min. The stirring is continued for 4 h at room temperature and worked up as follows.

Work-up A for **2a, 2b,** and **2c:** The reaction mixture is extracted with ether (5 × 30 ml), the ether phase is dried with sodium sulphate and concentrated to a volume of 10 ml. The solid separated on cooling at −30 °C is treated with ether (10 ml), filtered, and the ether solution is cooled to −30°C to obtain more of the solid product (see below). The ether fractions are combined, evaporated to dryness, and the residue is taken up in dichloromethane (3 ml). The dichloromethane phase is extracted with 1 normal hydrochloric acid (1 × 1 ml) and water (2 × 2 ml). The acid extracts are filtered, treated with 15 normal ammonia until pH > 10, extracted with dichloromethane (10 × 5 ml), the extract is dried with sodium sulphate, and evaporated to dryness. Sublimation of the residue at 70°C/0.01 torr gives the corresponding isotellurazole **2a–c.** Products **2a–c** are further purified by crystallization (Table).

Work-up A for **3a, 3b,** and **3c:** The dichloromethane phase from the acid extraction is combined with the solid product obtained (see above), evaporated to dryness, and sublimed at 70°C/0.001 torr to give the corresponding tellurobis[alkenyl ketones] **3a–c.**

Work-up B for **2d:** The reaction mixture is extracted with ethyl acetate (4 × 20 ml), dried with anhydrous sodium sulphate, evaporated to dryness, and the residue sublimed at 70°C/0.01 torr to give 3,5-dimethylisotellurazole **(2d)** (Table).

Work-up B for **3d:** The mother liquor from the extraction with ethyl acetate is evaporated to dryness and the residue is purified by preparative thin layer chromatography on silica gel [Merck $PF_{254/366}$, thickness: 1 mm, eluent: benzene/acetone (98 : 2)]. The product **3d** is obtained only in traces and is identified spectroscopically.

Work-up C for **2e:** The reaction mixture is extracted with ethyl acetate (7 × 15 ml) and concentrated to a volume of 5 ml. To avoid loss connected with the relevant solubility of 3-methyl-5-phenylisotellurazole hydrochloride in the organic phase, the ethyl acetate solution is extracted with 0.5 normal hydrochloric acid (1 × 3 ml) and water (4 × 3 ml), then such a series of extractions is repeated until **2e** is present (9 times). The combined acidic extracts are treated with 15 normal ammonia until pH is > 10, extracted with dichloromethane (4 × 5 ml), dried with sodium sulphate and evaporated to dryness to yield **2e** (Table).

Work-up C for **3e:** The tarry residue left after extraction with ethyl acetate containing the reduction product 4-phenyl-3-buten-2-one and 4,4′-tellurobis[4-phenyl-3-buten-2-one] **(3e)** is purified by preparative thin layer chromatography on silica gel [Merck $PF_{254/366}$, thickness: 1 mm, eluent: benzene/acetone (95 : 5)].

Tellurobis[alkenenitriles] 5; General Procedure:

The reaction is carried out as for the preparation of isotellurazoles **2** using α-acetylenic aldehydes **4** in place of α-acetylenic ketones **1,** but reducing the reaction time to avoid the complete conversion of the oxime intermediate into nitrile. The formation of oxime derivative needs about 2 min. The addition of sodium acetate and then of potassium telluride is carried out without delay.

Table. Isotellurazoles **2** and other Organotellurides **3** and **5**

Product No.	R^1	R^2	Starting material No.	Starting material [mmol]	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a]	Mol weight in $CHCl_3$[b]	M.S.[c], m/e M^+ (rel. int. %)	I.R. (KBr)[d] ν [cm^{-1}]	U.V. (CH_3CN)[e] λ_{max} [nm] (ε)	^{1}H-N.M.R. [δ [ppm][f] (**2**: acetone-d_6; **3, 5**: $CDCl_3$/TMS)
2a	H	CH_3	**1a**	12.35	6	94–96° (acetone)	C_4H_5NTe (194.7)	205	197 (96)	1530, 1303 690, 369[g]	218 (5400) 235 sh (4100) 306 (5200)	2.42 (s, 3H); 8.09 (d, 1H, J=6.6 Hz); 10.22 (d, 1H, J=6.6 Hz)
3a	H	CH_3	**1a**	12.35	11	190–192° (acetone)	$C_8H_{10}O_2Te$ (265.8)	—	—	1640 (C=O) 703 (CH)	—	2.32 (s, 3H); 7.52 (d, 1H, J=9.6 Hz); 8.76 (d, 1H, J=9.6 Hz)
2b	H	C_2H_5	**1b**	10.64	5	75–77° (ether)	C_5H_7NTe (208.7)	—	211 (69)	1533, 1298, 683, 370[g]	217 (5700) 236 (4300) 305 (5400)	1.26 (t, 3H, J=7.6 Hz); 2.81 (q, 2H, J=7.6 Hz); 8.14 (d, 1H, J=6.5 Hz); 10.23 (d, 1H, J=6.5 Hz)
3b	H	C_2H_5	**1b**	10.64	6	153–155° (acetone)	$C_{10}H_{14}O_2Te$ (293.8)	—	—	1650 (C=O) 708 (CH)	—	1.16 (t, 3H, J=7.3 Hz); 2.59 (q, 2H, J=7.3 Hz); 7.53 (d, 1H, J=9.5 Hz); 8.69 (d, 1H, J=9.5 Hz)
2c	H	n-C_3H_7	**1c**	10.76	4	67–69° (ether)	C_6H_9NTe (222.7)	—	225 (5)	1527, 1302, 684, 371[g]	217 (5900) 237 (4500) 305 (5400)	0.92 (t, 3H, J=7.3 Hz); 1.76 (sext, 2H, J=7.3 Hz); 2.78 (t, 2H, J=7.3 Hz); 8.13 (d, 1H, J=6.4 Hz); 10.24 (d, 1H, J=6.4 Hz)
3c	H	n-C_3H_7	**1c**	10.76	3	97–98° (ether)	$C_{12}H_{18}O_2Te$ (321.9)	—	—	1653 (C=O) 708 (CH)	—	0.94 (t, 3H, J=7.2 Hz); 1.7 (sext, 2H, J=7.2 Hz); 2.55 (t, 2H, J=7.2 Hz); 7.53 (d, 1H, J=9.5 Hz); 8.69 (d, 1H, J=9.5 Hz)
2d	CH_3	CH_3	**1d**	14.92	10	110–111° (acetone)	C_5H_7NTe (208.7)	210	211 (96)	1559, 1311, 687, 358[g]	221 (6700) 239 sh (4500) 304 (5300)	2.28 (s, 3H); 2.59 (d, 3H, J=1.5 Hz); 7.55 (q, 1H, J=1.5 Hz)
3d	CH_3	CH_3	**1d**	14.92	traces[h]	—	—	—	—	—	—	—
2e	C_6H_5	CH_3	**1e**	9.71	7	149–150° (ethyl acetate)	$C_{10}H_9NTe$ (270.8)	272	273 (15)	1544, 1302, 681, 358[g]	294 (10600) 306 sh (8400) 331 sh (3600)	2.5 (s, 3H); 7.09–7.35 (m, 5H); 8.01 (s, 1H)
3e[i]	C_6H_5	CH_3	**1e**	9.71	3	185–187° (ether)	$C_{20}H_{18}O_2Te$ (418.0)	—	—	1649 (C=O) 756, 689 (C_6H_5)	—	2.34 (s, 3H); 6.73—7.05 (m, 6H)
5a	H	—	**4a**	10.88	20	87–89° (ethyl acetate)	$C_6H_4N_2Te$ (231.8)	—	—	2198 (C≡N) 703 (CH)	—	6.66 (d, 1H, J=10.8 Hz); 8.23 (d, 1H, J=10.8 Hz)
5b	C_6H_5	—	**4b**	11.14	14	132–135° (cyclohexane)	$C_{18}H_{12}N_2Te$ (383.9)	—	—	2198 (C≡N) 750, 688 (C_6H_5)	—	6.02 (s, 1H); 7.02–7.40 (m, 5H)

[a] Satisfactory microanalyses obtained: C ±0.23, H ±0.13, N ±0.30.
[b] The molecular weights were determined with a Knauer vapor pressure osmometer at 37°C.
[c] The mass spectra were determined with a Varian MAT CH 7 mass spectrometer operating at 70 eV; the values are referred to the tellurium isotope 130.
[d] The I.R. spectra were recorded on a Perkin Elmer 283 spectrophotometer.
[e] The U.V. spectra were run on a Cary 118C spectrophotometer.
[f] The ^{1}H-N.M.R. spectra were measured on a Varian XL 100 spectrometer.
[g] The absorption bands are tentatively assigned to the ring on empirical basis.
[h] See experimental.
[i] 4-Phenyl-3-buten-2-one is also formed in 4% yield.

Work-up D for **5a**: The reaction mixture is extracted with ether (5 × 30 ml), the ether phase dried with sodium sulphate, evaporated to dryness, and the residue is crystallized from ethyl acetate to yield 3,3′-tellurobis[2-propenenitrile] **(5a)**.

Work-up E for **5b**: The reaction mixture is extracted with ethyl acetate (5 × 40 ml), the extract dried with sodium sulphate, and evaporated. The residue obtained is submitted to preparative T.L.C. on silica gel [Merck $PF_{254/366}$, thickness: 1 mm, eluent: benzene/methanol (99 : 1)] to yield 3,3′-tellurobis[3-phenyl-2-propenenitrile] **(5b)**.

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