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Reaction of Acetophenone Hydrazones with $TeCl_4$: Novel Formation of 2,5-Diaryltellurophenes and Benzotellurophenes

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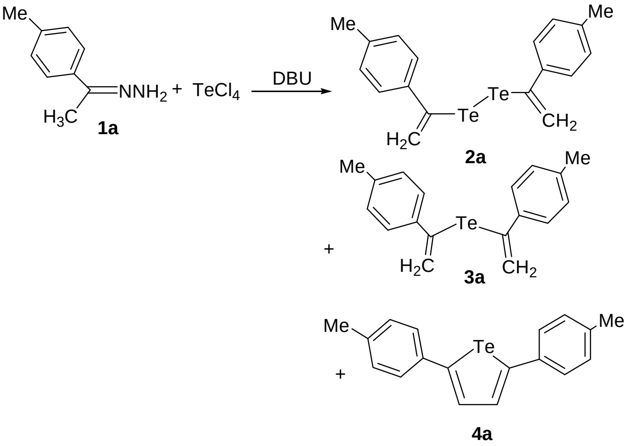
Reaction of acetophenone hydrazones with $TeCl_4$ in the presence of DBU in CH_2Cl_2 at rt gave vinyl ditellurides and tellurides, whereas 2,5-diaryltellurophenes were obtained in refluxing DMF. Interestingly, when 1,2-diphenylethanone hydrazone was used as a substrate, 3-phenylbenzotellurophene was obtained in 45% yield. The reaction would proceed through telluroketone intermediates.

Thiophenes, selenophenes, and tellurophenes are interesting compounds because of their installation of a group 16 element within a ring framework.[1] Tellurophene, the heaviest known group 16 heterocycle, should prove even more useful for optoelectronic applications. The presence of Te (Tellurophenes) can promote phosphorescence in some cases and afford lower optical band gaps compared to thiophenes and selenophenes, which provide novel electronic properties for application of organic light-emitting diode technologies and anion recognition property.[2] Because of synthetic challenges, their development lags behind that of their lighter counterparts. Synthesis of these compounds includes reaction of $TeCl_4$ with dilithio-1,3-butadienes,[3] reaction of Na_2Te with 1,3-butadiynes,[4] reaction of 1,4-bis(butyltelluro)-1,3-butadiene with butyllithium,[5] or reaction of Negishi's reagent "Cp_2Zr" with acetylenes and $TeCl_2$.[6] However, these methods have some difficulties to get the substrates. Thus, new type of synthesis for tellurophenes and benzotellurophenes would be required. Recently, we have demonstrated the synthesis of camphor derived ditellurides by the reaction of camphor hydrazones with $TeCl_4$ in the presence of bases.[7] In the course of further application of this methodology, we have found an unexpected result for the formation of 2,5-diaryltellurophenes and benzotellurophenes. In this communication, we would like to show a completely new methodology of tellurophenes from acetophenone hydrazones, $TeCl_4$ and DBU.

We first tried the reaction of 4'-methylacetophenone hydrazone (**1a**) with $TeCl_4$ in the presence of DBU under several reaction conditions. Treatment of hydrazone **1a** with 1.2 eq of $TeCl_4$ and 2.4 eq of DBU in CH_2Cl_2 resulted in the formation of a mixture of bis(1-*p*-tolylvinyl)ditelluride (**2a**) and telluride (**3a**) (2:3) in 8% and 12% yields, respectively (Table 1, Entry 1). By using toluene as a solvent, the result was similar even in refluxing conditions (Entry 3). When the reaction was carried out in refluxing DMF for 12h, 2,5-di(*p*-tolyl)tellurophene was obtained in 48% yield (Entry 5). Finally, yield of **4a** was improved to 58% when excess amounts of $TeCl_4$ (3.0 eq) and DBU (9.0 eq) were used (Entry 6). The structures of tellurophene **4a**, ditelluride **2a**, and telluride **3a** were determined by spectroscopic and elemental analyses.

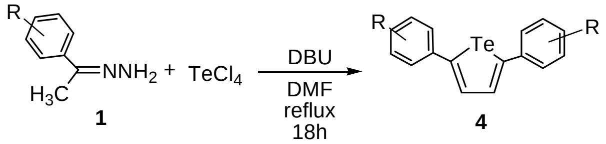
Table 1. Reaction of acetophenone hydrazone 1a with $TeCl_4$

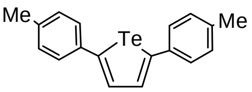


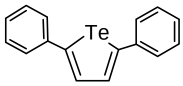
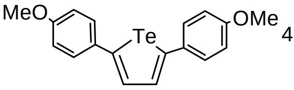
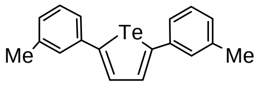
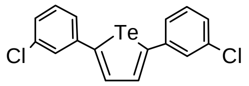
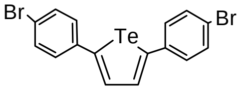
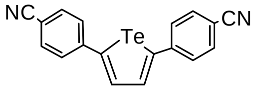
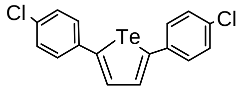
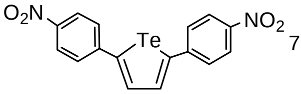
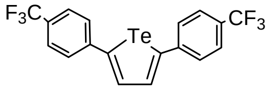
Entry	$TeCl_4$ / eq.	Solvent	DBU /eq.	Temp. /°C	**2a** /%	**3a** /%	**4a** /%
1	1.2	CH_2Cl_2	2.4	rt	8	12	0
2	2.2	CH_2Cl_2	6.0	rt	23	24	0
3	2.2	toluene	6.0	reflux	25	30	0
4	2.2	DMF	6.0	rt	10	35	0
5	2.2	DMF	6.0	reflux	0	18	48
6	3.0	DMF	9.0	reflux	0	18	58

With the optimized reaction conditions in hand (3 eq of $TeCl_4$, 9 eq of DBU in DMF refluxed for 12 h), we investigated the substrate scope with various acetophenone hydrazones (Table 2). Replacement of aryl group with meta- and para-substituted aromatic groups gave the desired products in good yields (Entries 1-5). Generally, hydrazones having electron-withdrawing groups gave better yields of products than those of electron-donating groups (Entries 7-10).

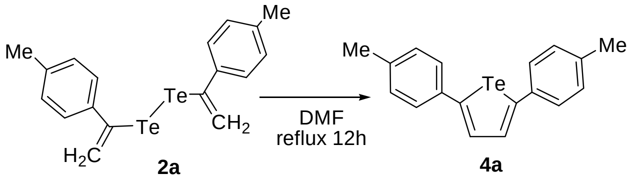
Table 2. Synthesis of 2,5-diaryltellurophenes from acetophenone hydrazones and $TeCl_4$



Entry	**1**	R	**4**		Yield/ %
1	**1a**	*p*-Me	**4a**		58%

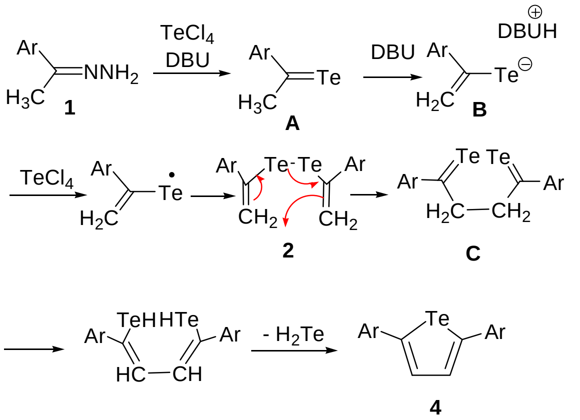
2	**1b**	H	**4b**		61%
3	**1c**	*p*-OMe	**4c**		42%
4	**1d**	*m*-Me	**4d**		57%
5	**1e**	*m*-Cl	**4e**		68%
6	**1f**	*p*-Br	**4f**		51%
7	**1g**	*p*-CN	**4g**		69%
8	**1h**	*p*-Cl	**4h**		68%
9	**1i**	*p*-NO_2	**4i**		73%
10	**1j**	*p*-CF_3	**4j**		69%

The next interest is the reaction mechanism of this reaction. We thought that the intermediate of the reaction would be the ditelluride **2** derived from initially formed telluroketone. When isolated ditelluride **2a** was refluxed in DMF for 12 h, ditelluride **2a** was changed to tellurophene **4a** in almost quantitative yield, whereas monotelluride **3a** was remained unchanged under similar conditions (Scheme 1).



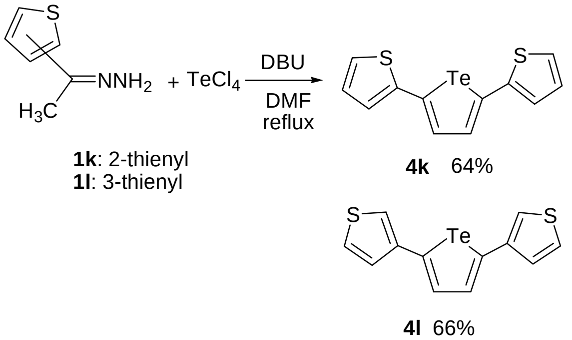
Scheme 1. Thermolysis of ditelluride 2a

Thus, the reaction might proceed as follows: Hydrazone **1** reacted $TeCl_4$ under basic conditions to give telluroketone **A**, which enolyzed to give enetellurolate **B**, oxidation of which gave ditelluride **2** via radical intermediate. At elevated temperature, 3,3-sigmatropic reaction of **2** proceeded to give bis-telluroketone **C**, which easily enolyzed, cylized, and oxidized to give tellurophene **4** (Scheme 2). Formation of radical intermediate would be similar to that of the synthesis of ditelluride derived from camphor hydrazone and $TeCl_4$.[7]



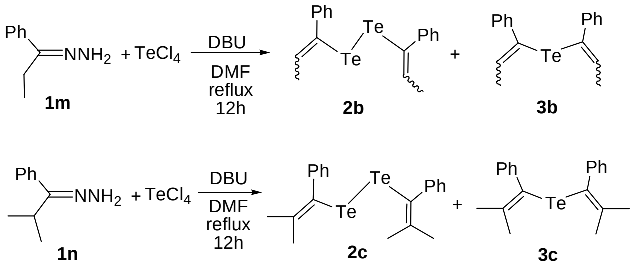
Scheme 2. Reaction mechanism

Heteroaromatic compound such as 2-acetylthiophene hydrazone **1k** and 3-acetylthiophene hydrazone **1l** also reacted with $TeCl_4$ to afford the corresponding tellurophenes **4k** and **4l** in 64% and 66% yields, respectively (Scheme 3). 2,5-Bis(2-thienyl)tellurophene **4k** was previously synthesized by the reaction of 1,4-dithienyl-1,3-butadiyne with Li_2Te,[8] while 2,5-bis(3-thienyl)tellurophene **4l** was not synthesized by this procedure due to the difficulty of the synthesis of starting 1,3-butadiyne.



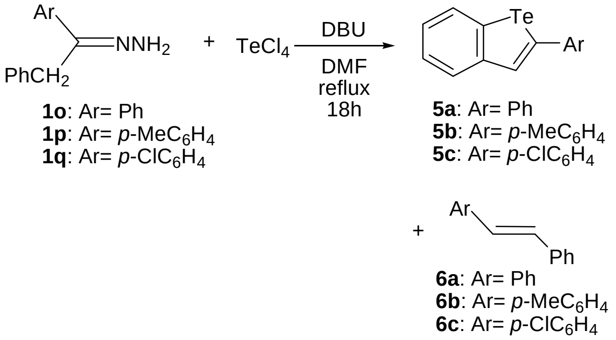
Scheme 3. Reaction of acetylthiophene hydrazones with $TeCl_4$

Since the driving force of the reaction would be the formation of ditelluride, we then tried the other alkyl substituted ketone hydrazones to investigate the possibility of synthesis of 2,3,4,5-tetra-substituted tellurophene. However, propiophenone hydrazone **1m** reacted with $TeCl_4$ gave the corresponding isomeric mixtures of vinyl ditelluride **2b** in 44% yield along with telluride **3b** (20%), no tetra-substituted tellurophene was observed. Additionally, reaction of isobutyrophenone hydrazone **1n** with $TeCl_4$ in the presence of DBU gave ditelluride **2c** and monotelluride **3c** in 21% and 23% yields, respectively (Scheme 4).



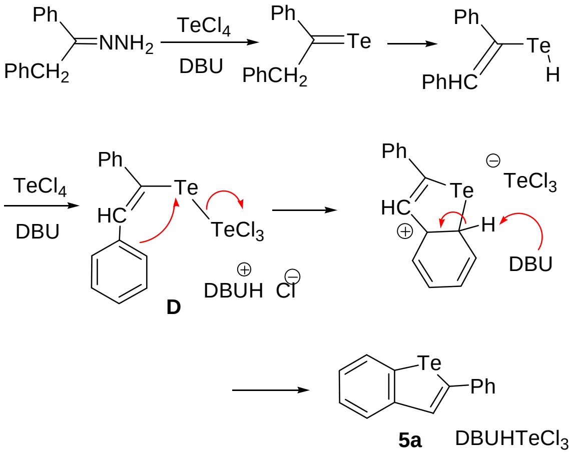
Scheme 4. Reaction of propiophenone or isobutyrophenone with $TeCl_4$

Interestingly, 1,2-diphenylethanone (dihydrobenzoin) hydrazone **1o** reacted with $TeCl_4$ to afford benzotellurophene **5a** in 45% yield along with *trans*-stilbene (25%). Similarly, substituted benzotellurophenes **5b** and **5c** were obtained in 39% and 43% yields along with stilbene **6b** (5%) and **6c** (15%), respectively (Scheme 5).



Scheme 5. Synthesis of benzotellurophenes

Initially formed telluroketone reacted with $TeCl_4$ to afford tellurium ion **D**, intramolecular aromatic substitution gave benzotellurophene **5** (Scheme 6). It is well known that diazoalkanes were formed as intermediates for this type of reaction,[9] thus, *trans*-stilbene might be formed via diazoalkane intermediate.



Scheme 6. The mechanism of formation of benzotellurophene 5

Previously, benzotellurophenes are generally synthesized via four-step procedure from *o*-(methyltelluro)benzaldehyde or *o*-bromethylbenzene and *t*-BuLi and tellurium.[10] The present method requires only two-steps starting from commercially available 1,2-diphenylethanones.

In summary, we have synthesized 2,5-disubstituted tellurophenes from easily available ketone hydrazones and $TeCl_4$. Benzotellurophenes are also formed by the reaction of 1,2-diphenylethanone hydrazones with $TeCl_4$ in the presence of DBU. By applying intramolecular sigmatropic reaction followed by oxidation, a novel type of tellurophene synthesis was provided. Further application of this methodology is currently under investigation.

Supporting information is available on http://dx.doi.org/ .

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