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o-Quinodimethane Generation from α,α′-Dihalo-o-xylenes by Use of Sodium Benzenetellurolate

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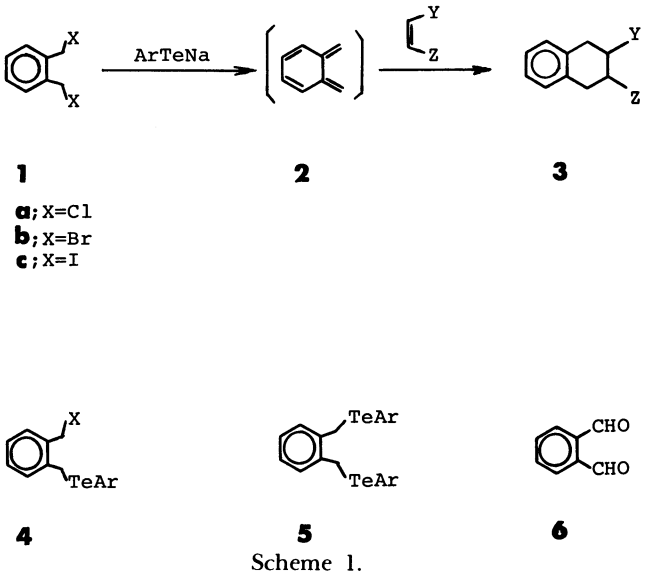
Treatment of α,α′-dihalo-o-xylenes with sodium benzenetellurolate gave o-quinodimethane which readily reacted with dienophiles leading to Diels–Alder adducts. The best yields were obtained when the reaction was carried out in refluxing ethanol using two molar equivalents of the benzenetellurolate to α,α′-dihalo-o-xylenes. This reaction competes with substitution of the halogen atoms with the benzenetellurolate anion to afford α,α′-bis(phenyltelluro)-o-xylene, which did not give o-quinodimethane under identical conditions. It is likely that the reaction proceeds through nucleophilic attack of benzenetellurolate anion at the tellurium atom of α-halo-α′-phenyltelluro-o-xylene which is formed in situ by the substitution of one of the halogen atoms of the starting α,α′-dihalo-o-xylene with the benzenetellurolate anion. When sodium benzeneselenolate was employed, no evidence of o-quinodimethane formation was observed under similar conditions.

Since Cava and his co-worker first recognized the intermediacy of α,α′-dibromo-o-quinodimethane in the reaction of α,α,α′,α′-tetrabromo-o-xylene with sodium iodide,[1] a variety of methods for the generation of o-quinodimethane intermediates have been developed and used for organic synthesis.[2–10] Recent advances in this methodology have enabled the facile generation of o-quinodimethanes under mild conditions[4m–r] with stereocontrol of the subsequent Diels–Alder reaction with a dienophile (intermolecularly or intramolecularly), leading to the successful preparation of polycyclic compounds such as steroids, alkaloids, terpenoids and some antibiotics.

For the syntheses of relatively simple compounds via Diels–Alder reaction of the unsubstituted o-quinodimethane, α,α′-dihalo-o-xylenes may be the first choice because of their ready availability as starting materials. The heterogeneous 1,4-dehalogenation of α,α′-dihalo-o-xylenes proceeds through reductions with Zn,[4d,e] Fe,[4f] or Cu[4g] metals. Only one homogeneous reduction[9] was reported using iodide anion.[4a–c] Dehalogenation of vic-dihalides[11] or α-halo carbonyls[12] with iodide ion is a well-known and versatile reaction, but dehalogenation of α,α′-dihalo-o-xylenes to o-quinodimethanes with iodide anion was restricted to activated systems having alkoxyl substituents on the aryl rings[4b,c] or halogens in the benzylic positions.[4a]

In this paper we report a new o-quinodimethane generation from nonactivated α,α′-dihalo-o-xylenes (**1**) promoted by sodium benzenetellurolate giving rise to Diels–Alder adducts in the presence of dienophiles (Scheme 1).

Dehalogenation with tellurolate anions has been successfully achieved in the cases of α-halo carbonyls,[13] vic-dihalides,[14] 1,4-dibromo-2-enes,[15] and 3,7-dibromo-5-cyclooctadiene,[16] but no precedence has been reported for the generation of o-quinodimethanes from α,α′-dihalo-o-xylenes.



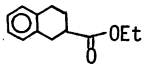
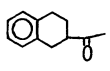
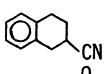
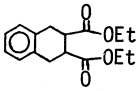
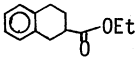
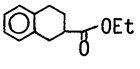
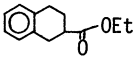
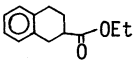
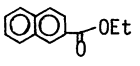
Scheme 1.

Results and Discussion

Dehalogenation of *vic*-dihalides[14] was reported using sodium hydrogen telluride (NaTeH), prepared from tellurium and sodium borohydride.[17] These successful results prompted us to investigate the dehalogenation of α,α′-dihalo-o-xylenes with NaTeH to generate o-quinodimethanes. The reaction in refluxing ethanol for 5 h in the presence of excess diethyl maleate gave diethyl 2,3-tetralindicarboxylate in 24% yield. In the cases of ethyl acrylate and other dienophiles, reduction of the C–C double bond of the dienophiles with NaTeH predominated, resulting in very poor yields of the desired adducts. In order to preclude this side reaction, we investigated the use of sodium benzenetellurolate (PhTeNa), as the nucleophile.

The reaction of α,α′-dihalo-o-xylenes with PhTeNa prepared from diphenyl ditelluride and sodium borohydride[18] was carried out in refluxing ethanol in the presence of an excess of a dienophile. Several dienophiles were examined using different arenetellurolate anions. The results are summarized in Table 1. Ethyl acrylate, methyl vinyl ketone, and acrylonitrile gave the corresponding Diels–Alder adducts in moderate yields. It should be noted that a similar reaction using sodium

Table 1. Generation of Quinodimethane[a)]

Haloxylene	Ar_2Te_2	Dienophile	Product	Yield/%
	Ph_2Te_2			45
	Ph_2Te_2			36
	Ph_2Te_2			30
	Ph_2Te_2			35
	$(p\text{-Me-}C_6H_4)_2Te_2$			31[b)]
	$(m\text{-Cl-}C_6H_4)_2Te_2$			20[b)]
	$(p\text{-MeO-}C_6H_4)_2Te_2$			31[b)]
	Ph_2Te_2			53[b)]
	Ph_2Te_2			<10

a) Reaction conditions: Ar_2Te_2 (5 mmol), α,α'-dihalo-*o*-xylene (5 mmol), dienophile (50 mmol), $NaBH_4$ (10.5 mmol, 400 mg), EtOH (30 mL), reflux, 2 h. b) GLC yield.

benzeneselenolate, PhSeNa, gave α,α'-bis(phenylseleno)-*o*-xylene in 75% yield together with the Michael adduct of benzeneselenolate to ethyl acrylate instead of the desired Diels–Alder adduct (see Experimental section).

When the reaction was carried out at room temperature, no apparent change was observed and no adduct was detected. After reaching reflux, the reaction mixture turned red, which may be due to the color of diaryl ditelluride, suggesting that reduction with arenetellurolate had occurred. Monitoring of the reaction by GLC showed that the reaction was complete within 1 h. When $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene was employed, the expected adduct,[19] ethyl 2-naphthoate, was formed in very poor yield. This is in marked contrast[20] to the iodide ion induced quinodimethane formation in which the corresponding adduct was formed in 65% yield from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene by the treatment with sodium iodide in the presence of *N*-phenylmaleimide.[4a)]

In all reactions in Table 1, the dialdehyde **6** was obtained as a by-product in about 30% yield based on the dihalide used. It is known that benzyl tellurolate is oxidized in air at room temperature to give benzaldehyde.[21] So the aldehyde is assumed to be formed by the oxidation of α,α'-bis(phenyltelluro)-*o*-xylene. In order to ensure this hypothesis, a control experiment was carried out. When a ethanol solution of PhTeNa and α,α'-dibromo-*o*-xylene was refluxed for 2 h, a new NMR singlet at δ 4.17 appeared, which was assigned to the methylene protons of α,α'-bis(phenyltelluro)-*o*-xylene (**5**). The mixture was then exposed to air and stirred at r.t. overnight, and the dialdehyde **6** was isolated in 60% yield. In a similar manner, α,α'-bis(phenyltelluro)-*o*-xylene (**5**) was isolated and conversion of **5** to **6** was monitored by NMR (see Experimental section).

The reaction of the α,α'-dibromo-*o*-xylene with sodium benzenetellurolate at room temperature or below resulted in substitution of bromide with $PhTe^-$ and no Diels–Alder adduct was detected by GLC. The reaction proceeds only when refluxed.

Another important factor was the molar ratio of PhTeNa to α,α'-dihalo-*o*-xylene. The yields of the desired adduct and the dialdehyde were plotted against the molar ratio of PhTeNa to α,α'-dibromo-*o*-xylene as shown in Fig. 1. The best yield of the adduct was obtained when the ratio was 2.0. As the ratio was increased the substitution predominated resulting in an increase of dialdehyde formation. An explanation for these results is that the excess of $PhTe^-$ displaces both halogen atoms of the dihalides before the reaction mixture reached reflux, and gave α,α'-bis(phenyltelluro)-*o*-xylene (**5**) which is not converted to the quinodimethane under these reaction conditions.

α,α'-Dichloro-*o*-xylene did not give the corresponding Diels–Alder adduct. When NaI was added to the reaction mixture of the α,α'-dichloro-*o*-xylene, the Diels–Alder adduct was obtained in a moderate yield,

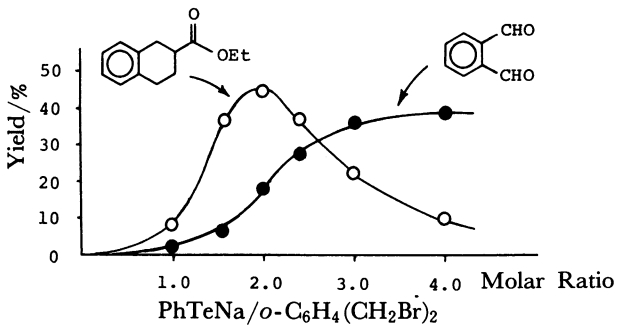


Fig. 1. Yields of the adducts at the different ratios of PhTeNa/*o*-$C_6H_4(CH_2Br)_2$.

probably due to the substitution of the chlorine atom with the iodine atom.

In order to elucidate the reaction path, some NMR studies were performed. When α,α'-dibromo-*o*-xylene was treated with two equivalents of PhTeNa in the presence of methyl acrylate at −20 °C in a mixed solvent of $CDCl_3$ and CD_3OD, the NMR indicated a mixture of the starting dibromide (benzylic protons of **1** at δ 4.64), α-bromo-α'-phenyltelluro-*o*-xylene (those of **4** at δ 4.43 and at δ 4.37), and α,α'-bis(phenyltelluro)-*o*-xylene (those of **5** at δ 4.17). Heating the mixtute to 60 °C, the first two compounds disappeared and the Diels–Alder adduct had formed. While the peak for **5** remained unchanged. This result indicated that substitution of one of the bromine atoms on the benzylic positions of **1b** with benzenetellurolate anion is a fast reaction even at low temperatures, and that substitution of the second bromine atom with $PhTe^-$ may compete with the quinodimethane formation giving rise to **5** which is not a precursor to **2** but to **6**. This conclusion is also supported by the evidence that when excess benzenetellurolate anion was used, formation of the dialdehyde **6** predominated and quinodimethane formation was suppressed as shown in Fig. 1. The fact that the yield of the Diels–Alder adduct was very low when a stoichiometric amount of benzenetellurolate anion was used may indicate that Path A in which quinodimethane was formed by direct attack of $PhTe^-$ at one of the bromine atoms of **1** can be ruled out, or if any, can not be the main path. So the next question is which does $PhTe^-$ attack the halogen atom or the tellurium atom of **4** in the subsequent step of the reaction.

There are some precedents on the reaction of alkyl halides with chalcogenolate anions. The direct attack at halogen atoms by tellurolate anions was suggested in the dehalogenation of *vic*-dihalides supported by the stereochemistry of the olefinic products formed from stereochemically pure *vic*-dihalides, i.e., anti elimination.[14c] In similar reactions using PhSeNa,[22] *vic*-dibromide, 2-iodoalkyl chloride, and 2-(phenylseleno)alkyl chloride undergo anti elimination by the direct attack of $PhSe^-$ at bromine, iodine, and selenium atoms, respectively. On the other hand the elimination of *vic*-dichloride proceeds in net syn fashion, indicating that the displacement of one of the chlorine atoms with $PhSe^-$ preceded the subsequent anti elimination which is caused by the nucleophilic attack of $PhSe^-$ on selenium of the in situ formed 2-(phenylseleno)alkyl chloride.

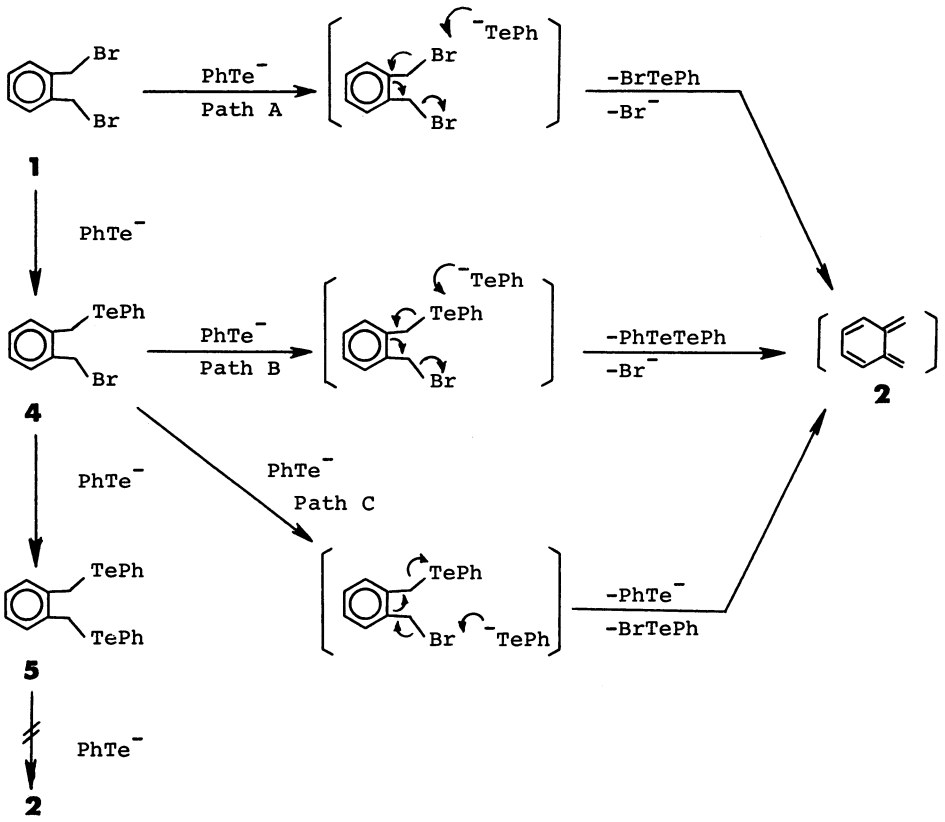
In the dehalogenation of α-halo ketones or α-halo amides to the parent ketones or amides by tellurolate anions, it has been proposed that the reduction is initiated by the displacement of the halide with $ArTe^-$ followed by the nucleophilic attack of a second molecule of tellurolate anion at the tellurium of the substituted intermediate.[13b] It has been previously reported that reactions of α-halo ketones[23] and benzyl halides[24] with thiolate and selenolate anions often give mixtures of reduction and substitution products depending on both the nature of the substrates and that of the reagents used as well as the reaction conditions. In the reaction with 3,7-dibromo-1,5-cyclooctadiene, thiolate and selenolate anions displaced bromide but tellurolate anion preferred the nucleophilic attack at one of the bromine atoms leading to the formation of a bicyclic compound.[16]

As described above, both examples of the nucleophilic attack of tellurolate anion at the halogen atoms and that at the chalcogen atoms are known, and both Path B and Path C seem probable. But we would like to propose that $PhTe^-$ attacks the tellurium atom of **4** than the halogen atom, since it is likely that bromide and iodide anions are expected to be better leaving groups than the benzenetellurolate anion from our knowledge obtained in the study about the tellurium chemistry in out laboratory. Contribution of iodide anion as the nucleophile to attack the tellurium or the iodine atoms of **4** or **5** can be ruled out by the fact that the presence of large excess of NaI in the reaction of **1c** with PhTeNa did not affect the yield of the adduct. The fact that **5** did not give the quinodimethane in the reaction with PhTeNa in the presence of NaI may also indicated that iodide anion does not substitute for the $PhTe^-$ group in the benzylic positions under these reaction conditions. So Path B seems to be the most probable, but the alternative pathways such as electron transfer[13c] in some stage of the reaction could not be ruled out.

In conclusion a new and facile homogeneous reaction for the generation of *o*-quinodimethane by use of benzenetellurolate anion has been discovered. The key step of this reaction is proposed to be the nucleophilic attack of benzenetellurolate anion at tellurium of intermediate **4**.

Experimental

General. Instruments used were as follows: melting points, Yanagimoto Micro Melting Point Apparatus; ^1H NMR, Hitachi R-24B or Japan Electron Optics JNM-PS-100; IR, Shimadzu IR-400; MS, Hitachi RMU-6A. Chemical shifts are expressed in parts per million using tetramethyl-



Scheme 2.

silane (TMS) as the internal standard.

Diaryl ditellurides and diphenyl diselenide were prepared as discribed in the literature[23b,25] or by similar procedures. α,α'-Dihalo-*o*-xylenes, dienophiles, solvent (tetrahydrofuran: THF), and other materials used were all purchased from commercial sources and used after purification by distillation or recrystallization.

Reaction of α,α'-Dibromo-*o*-xylene with NaTeH. Following the reported procedure,[17] NaTeH was prepared from Te (5 mmol, 650 mg) and $NaBH_4$ (19.8 mmol, 750 mg, added in three portions) in EtOH (20 ml) at the reflux, and to this solution was added diethyl maleate (10 mmol, 1.6 ml) under N_2. Deposition of tellerium was observed at this stage. α,α'-Dibromo-*o*-xylene (5 mmol, 1.32 g) was then added and the mixture was heated at reflux for 5 h. After the precipitates were filtered, the product was extracted into ether and dried over $MgSO_4$. The solvent and remaining diethyl maleate were removed in vacuo and the residue was chromatographed on silica gel (benzene/ether=9/1) to give 24% of diethyl 2,3-tetralindicarboxylate.[4n,8]

General Reaction, Reaction of α,α'-Dibromo-*o*-xylene with PhTeNa. To a solution of PhTeNa generated from Ph_2Te_2 (5 mmol, 2.05 g) and $NaBH_4$ (10.5 mmol, 400 mg) in EtOH (30 ml) at 25 °C, was added a THF (15 ml) solution of ethyl acrylate(50 mmol) and α,α'-dibromo-*o*-xylene (5 mmol, 1.32 g). The mixture was refluxed for 2 h with stirring. The resulting red solution was then stirred in contact with the air overnight at 25 °C. The red color faded and a white precipitate was formed. The precipitate was filtered, and the product was extracted into ether and dried over $MgSO_4$. The solvent was evaporated and the residue chromatographed on silica gel (benzene) to give a 45% yield of ethyl 2-tetralincarboxylate.[4n,9]

Reaction of α,α'-Dibromo-*o*-xylene with Sodium Benzeneselenolate. A THF solution (5 ml) of α,α'-dibromo-*o*-xylene (1 mmol, 264 mg) was added at 25 °C to an ethanol solution (10 ml) of ethyl acrylate (5 mmol, 0.53 ml) and PhSeNa (2 mmol) generated from diphenyl diselenide (1 mmol, 313 mg) and $NaBH_4$ (2.1 mmol, 80 mg). The reaction was continued at reflux for 2 h. The solution turned slightly yellow and white precipitates were observed. GLC analysis showed no formation of the Diels-Alder adduct. After the reaction was complete, 20 ml of benzene was added to the mixture. The precipitates were filtered and the solvent evaporated. The residue was chromatographed on silica gel (pentane/ether=95/5) to give 316 mg of α,α'-bis(phenylseleno)-*o*-xylene[26] (0.75 mmol, 75% based on α,α'-dibromo-*o*-xylene used) and 150 mg (0.58 mmol) of ethyl 3-(phenylseleno)propionate: IR (neat) 2980, 1732, 1583, 1220, 1025, 739, 694 cm^{-1}; ^1H NMR(TMS, CCl_4) δ=1.22 (t, 3H, J=7.2 Hz), 4.07 (q, 2H, J=7.2 Hz), 7.10—7.55 (m, 5H) and essentially two triplets (2H, each) centered at δ=2.60 and δ=3.03, each line shows further fine splitting due to partial conformational freezing; MS (*m/z*, ^{80}Se) 258 (M^+); Found: C, 51.12; H, 5.51%. Calcd for $C_{11}H_{14}O_2Se$: C, 51.37; H, 5.49%.

Formation of Phthalaldehyde 6 from 1b. To an ethanol solution of PhTeNa (10 mmol in 30 ml) formed as described above was added α,α'-dibromo-*o*-xylene (5 mmol, 1.32 g) in THF (15 ml) and the reaction was refluxed for 2 h. The resulting mixture was exposed to the air at 25 °C and stirred overnight. The product was extracted into ether and dried. Evaporation followed by column chromatography on silica gel (benzene) gave **6**[27] in 60% yield.

Intermediacy of 5 in the Formation of Phthalaldehyde 6. To an ethanol solution (20 ml) of PhTeNa formed from Ph_2Te_2 (4.5 mmol, 1.85 g) and $NaBH_4$ (9.5 mmol, 360 mg)

was added a THF (20 ml) solution of **1b** (4.5 mmol, 1.19 g). The solution turned yellow and a white precipitate formed immediately. The mixture was stirred at 25 °C for 2 h. The solvent was removed in vacuo and benzene (50 ml) was added to the residue. The precipitate was filtered under N_2 and the filtrate was evaporated to give 1.91 g of a red solid. The NMR spectrum showed two singlets at δ 4.17 and δ 6.87 with 1:1 ratio which was assigned to the methylene and the aromatic protons of **5**, respectively, together with the aromatic protons of the PhTe groups of **5** and Ph_2Te_2 as the impurity (δ=7.20—7.50, m and δ=7.70—8.00, m). By subtracting the integral due to Ph_2Te_2 in the ^1H NMR spectrum, the yield of **5** was estimated to be 66%. In the MASS spectrum of the mixture, a peak appeared at 311 (**5**, *m/z*, M^+—PhTe) together with the parent peak of Ph_2Te_2 (*m/z*=414), but the parent peak of **5** was not observed. Allowing the NMR sample to stand at r.t., the peaks at δ 4.17 and δ 6.87 gradually decreased and a new peak appeared at δ 10.45 which was assigned to aldehyde protons of **6**. An attempt for isolation and purification of **5** failed due to its instability toward oxygen and/or light.

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