consistent with space group *Pna*2. A total of 1171 reflections were collected with the ω scan mode, yielding 704 reflections with $I \geq 2\sigma(I)$. The intensities were reduced to structure factor amplitudes in the usual fashion and phased with direct methods (MULTAN)[7] to yield the structure. With μ = 1.919 cm^{-1} no absorption correction was necessary. After preliminary least-squares refinement, the hydrogen atoms were located and included in the final full-matrix anisotropic series with the hydrogen atoms allowed isotropic thermal freedom. Refinement converged with R = 0.049 and R_w = 0.045, with the largest peaks on the final difference map of 0.2e/Å^3 near the fluorine atoms. Effects of anomalous dispersion were excluded from the refinement as these could not establish the absolute configuration of the molecule.

Registry No. 2, 92818-41-2; 3, 92818-42-3; 4, 92818-43-4; 5, 92818-44-5; 7, 92818-45-6; $Cl_3SiCH{=}CH_2$, 75-94-5; $MeCl_2SiCH{=}CH_2$, 124-70-9; $Me_3SiCH{=}CH_2$, 754-05-2; $(EtO)_3SiCH{=}CH_2$, 78-08-0; $(MeO)_3SiCH{=}CH_2$, 2768-02-7; $CF_2{=}CF_2$, 116-14-3; (2,2,3,3-tetrafluorocyclobutyl)trichlorosilane, 33664-06-1; (2,2,3,3-tetrafluorocyclobutyl)methyldichlorosilane, 383-74-4; (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane, 312-81-2; (2,2,3,3-tetrafluorocyclobutyl)triethoxysilane, 92818-39-8; (2,2,3,3-tetrafluorocyclobutyl)trimethoxysilane, 92818-40-1; 2,3,3-trifluoro-1-cyclobutene, 3932-66-9.

Supplementary Material Available: X-ray data: Table I-a (atomic coordinates), Table I-b (thermal parameters, Table II-a (bond distances), and Table II-b (bond angles) (2 pages). Ordering information is given on any current masthead page.

Organotellurium Chemistry. 9. Structural Parameters in the Telluroxide-Catalyzed Aldol Condensation

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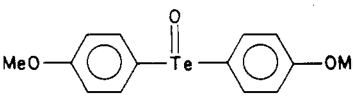
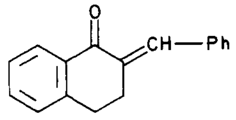
A number of aromatic telluroxides have been prepared and their relative activity as aldol catalysts has been determined. High catalytic activity is associated with electron-donating substituents on the aromatic ring which can increase the basicity of the telluroxide function by a resonance effect.

Several years ago, it was found in our laboratories that bis(*p*-methoxyphenyl) telluroxide (1) functioned as a selective aldol catalyst in boiling toluene.[1] This reaction appeared to be particularly promising for the condensation of aromatic aldehydes with active methylene compounds under aprotic conditions to give products such as 2.



1

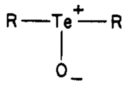


2

We now report more detailed studies of this reaction aimed at improving its efficiency by ascertaining (a) the effects of structural variations of the telluroxide catalyst and (b) solvent and concentration effects in the promotion of aldol-type condensations.

Results and Discussion

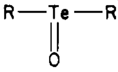
Telluroxides should exhibit a certain degree of basic character by virtue of the polar nature of the tellurium–oxygen bond in telluroxide monomers. Indeed, in 1977



$$R-\underset{\underset{\displaystyle O_-}{|}}{\overset{+}{Te}}-R$$

a pK_a of ~14.9 in acetonitrile was reported for telluroxide 1,[2] although comparative values for other telluroxides are not known. Apparently, the inherent basic nature of 1 as a dipole is responsible for the promotion of the aldol-type reactions which we observed.

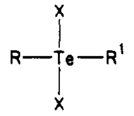
In the present study, we have synthesized a number of structurally varied telluroxides (3–8) with the aim of assessing, albeit qualitatively, their relative propensity to promote aldol-type reactions. For the purposes of this investigation the condensation of benzaldehyde with α-tetralone to give the readily isolated benzylidene derivative 2 was chosen as the standard reaction.



$$R-\underset{\underset{\displaystyle O}{\|}}{Te}-R^{1}$$

3, R = R^1 = Ph
4, R = Ph; R^1 = Me
5, R = *p*-methoxyphenyl; R^1 = *p*-(dimethylamino)phenyl
6, R = R^1 = *p*-(dimethylamino)phenyl
7, R = R^1 = *m*-methoxyphenyl
8, R = R^1 = mesityl

Synthesis of Telluroxides. Telluroxides 3–7 were made by the base treatment of the Te dichloro or dibromo derivatives 9–13. The dibromo derivative 9, 10, and 13 were made from the corresponding monotellurides 14–16 by the action of bromine. The known dichloro derivatives 11 and 12 were prepared by reported procedures.[3,4] Telluroxide 8 was made by periodate oxidation of telluride 17.



$$R-\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle X}{|}}{Te}}-R^{1}$$

9, R = R^1 = Ph; X = Br
10, R = Ph; R^1 = Me; X = Br
11, R = *p*-methoxyphenyl;
R^1 = *p*-(dimethylamino)phenyl;
X = Cl
12, R = R^1 = *p*-(dimethylamino)phenyl;
X = Cl
13, R = R^1 = *m*-methoxyphenyl; X = Br

R—Te—R^1

14, R = R^1 = Ph
15, R = Ph; R^1 = Me
16, R = *m*-methoxyphenyl
17, R = R^1 = mesityl

R—Te—Te—R

18, R = Ph
19, R = R^1 = *m*-methoxyphenyl
20, R = R^1 = mesityl

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(1) Engman, L.; Cava, M. P. *Tetrahedron Lett.* 1981, *22*, 5251.

(2) Naddaka, V. I.; Garkin, V. P.; Sadekov, I. D.; Minkin, V. I. *Zh. Org. Khim.* 1977, *13*, 220.

0022-3263/84/1949-4819$01.50/0

Table I. Effect of Solvent and Temperature on the Condensation of Benzaldehyde and α-Tetralone

catalyst	solvent	temp, °C	time, h	isolated yield of 2, %
1 (4 mol %)	toluene	80	1	41
	Me_2SO	80	1	52
	MeCN	80	1	19
5 (4 mol %)	toluene	80	3	75
	Me_2SO	80	3	93
	MeCN	80	4	65

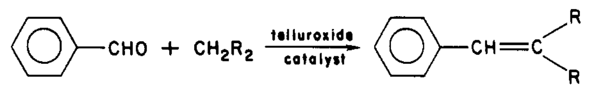
Table II. Effect of Catalyst Structure on the Benzaldehyde–Tetralone Condensation

no.	catalyst	solvent	time, h	temp, °C	yield of 2, %
1	3	Me_2SO	1.0	100	0
2	4	Me_2SO	1.0	100	2
3	7	Me_2SO	1.0	100	0
4	8	Me_2SO	1.0	100	6
5	1	Me_2SO	0.5	100	14
6	5	Me_2SO	0.5	100	37
7	6	Me_2SO	0.5	100	54

Table III. Effect of Telluroxide 5 Concentration on the Benzaldehyde–Tetralone Condensation

concn, mol %	conditn	time, h	yield of 2, %
8	toluene (reflux)	1	94
4	toluene (reflux)	1	91
2	toluene (reflux)	1	72

Table IV



no.	cat. (mol %)	R	solvent	temp, °C, time, h	product (R)	yield, %
1	1 (8)	COOMe	toluene	110, 2	COOMe	27
2	5 (2)	COOMe	benzene	80, overnight	COOMe	72
3	5 (2)	COOMe	Me_2SO	100, 1	COOMe	68
4	6 (2)	COOMe	Me_2SO	100, 1	COOMe	73
5	1 (8)	CN	toluene	110, 2	CN	50
6	5 (2)	CN	toluene	110, 1.5	CN	96
7	5 (2)	CN	CH_2Cl_2	RT,[a] 3	CN	97

[a] RT = room temperature.

Synthesis of Precursors. Tellurides 14, 16, and 17 were prepared by the copper-promoted detelluration of the corresponding ditellurides 18–20;[5] telluride 15 was made by the methylation of the readily prepared phenyltellurolate ion.[6] Whereas the known ditelluride 18 was readily prepared,[7] the preparation of ditelluride 20 appeared not to be described previously. We found that lithium–halogen exchange of 2-bromomesitylene with *t*-BuLi, followed by telluration and subsequent oxidation of the resulting tellurolate ion led to ditelluride 20 in excellent yield.

Ditelluride 19 was not known. Attempts to prepare it from 3-bromoanisole in an analogous manner by lithium–halogen exchange, telluration, and oxidation gave an impure product in 25% yield which could not be purified. NMR analysis of the crude product indicated the presence of bis(*o*-methoxyphenyl) telluride, arising out of a lithium-ortho proton exchange prior to telluration. This difficulty was surmounted by the use of the Grignard reagent from 3-bromoanisole, which upon telluration and subsequent oxidation led to a 63% yield of the oily ditelluride 19, free from ortho isomers. It was found best to detellurize the crude oily ditelluride to the oily monotelluride 16, followed by conversion to the crystalline telluroxide by oxidation with $NaIO_4$ or preferably via the base treatment of the intermediate dibromide 13.

It was observed that hydrolysis of the dichlorides 11 and 12 to 5 and 6 proceeded especially rapidly and in good yield with aqueous ammonia at room temperature, as compared to the preparation of telluroxides 3, 4, and 7.

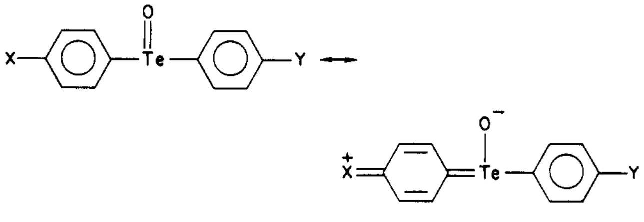
Solvent Effect. Telluroxides 1 and 5 were chosen as catalysts in the standard reaction of benzaldehyde and α-tetralone. Toluene, Me_2SO, and acetonitrile were used as solvents at 80 °C for 1–4 h, and the product (2) was isolated by using standard procedures. The results of these experiments are presented in Table I. Although the more polar Me_2SO was superior to toluene, acetonitrile gave somewhat lower yields.

Structural Effects. The efficiency of telluroxides 1–7 in the promotion of benzaldehyde–tetralone condensation was next investigated. The standard reaction was run only to partial completion in Me_2SO as solvent as 100 °C for 0.5 h, 1.0 h in some cases, and by using 4 mole % of catalyst. At the end of the reaction period, the reaction was quenched, and following routine workup the product (2) was isolated by column chromatography.

The results are summarized in Table II.

It is evident that the efficacy of an aryl telluroxide as an aldol catalyst is very much dependent upon substituent effects. Diphenyl telluroxide (entry 1) is totally ineffective; replacement of one phenyl by an alkyl group (entry 2) gives rise to a barely detectable activity. Dimesityl telluroxide (entry 4) has weak but definite catalytic activity; this may be attributed to the electron-releasing inductive effect of the methyl groups.

The *p*-methoxy substituents of our original telluroxide 1 are now clearly revealed as having been essential for its catalytic function. A comparison with the *m*-methoxy-substituted isomer 7 (entry 3), which has *no* catalytic activity, leads to the conclusion that the *p*-methoxy effect must be an electron-donating *resonance effect through the tellurium atom of the telluroxide*, as shown below.[8] Such an effect would result in (a) an increased basicity of the telluroxide oxygen and (b) a decreased tendency of the telluroxide function to exist in a nonpolar hydrated or polymeric form.[9] In accord with this interpretation, replacement of one and then both methoxyls of 1 by the more basic dimethylamino group leads to increasingly improved catalytic activity (entries 5, 6, and 7).



From the preparative point of view, the mono(dimethylamino) telluroxide 5 is a more practical reagent than

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(3) Petragnani, N. *Tetrahedron* **1961**, *12*, 219.

(4) Morgan, G. T.; Burgess, H. *J. Chem. Soc.* **1929**, 1103.

(5) For other examples of copper-promoted detellurations see: (a) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97. (b) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron Suppl.* **1981**, *37*, 213.

(6) H. Rheinboldt In "Methoden der Organischen Chemie (Houben-Weyl)"; Muller, E., Ed.; George Thieme Verlag: Stuttgart, 1955; p 1047.

(7) Günther, W. H. H.; Nepywoda, J.; Chu, J. Y. C. *J. Organomet. Chem.* **1974**, *74*, 79.

(8) Electronic interactions between the substituents on an aromatic ring and the tellurium in diaryl tellurides have been observed: Sadekov, I. D.; Bushkov, A. Ya; Minkin, V. I. *Russ. Chem. Rev.* **1979**, *48*, 343. A referee has pointed out that the resonance effects which we have observed may be electromeric in nature, such that direct π-overlap of the aryl system and the tellurium atom does not occur. Further studies are required to clarify this possibility.

(9) Hydrated forms of telluroxides have been observed, i.e.: Rust, E. *Chem. Ber.* **1897**, *30*, 2828.

its bis(dimethylamino)analogue **6**. As shown in Table III, it has considerable catalytic activity even at a concentration of 2 mol %.

The superiority of catalysts **5** and **6** over the dimethoxy analogue **1** is especially evident in the condensation of benzaldehyde with dimethyl malonate or malononitrile, as shown in Table IV.

Further studies of the use of telluroxides **5** and **6** as novel base catalysts appear to be warranted. Such studies are being pursued in our laboratories.

Experimental Section

General Methods. Melting points were recorded on a Thomas-Hoover melting point apparatus and are uncorrected. NMR and mass spectra were recorded on a Bruker WM-250 FT and a Hitachi-Perkin-Elmer RMH 2 spectrometers. Chemical shifts are reported in δ units downfield from Me_4Si in $CDCl_3$ solution. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Tellurium-containing mass peaks are reported for Te 130. The aryltellurium compounds described below required no special protection against air or light.

Dimesityl Ditelluride (20). To a stirred solution of 2-bromomesitylene[10] (5.97 g) in dry THF (90 mL) cooled in dry ice–acetone, under nitrogen, was added *t*-BuLi (26.1 mL of a 2.3 molar solution). After 3 h at −78 °C well-ground elemental tellurium (3.83 g) was added rapidly in one portion. The mixture was allowed to warm slowly to room temperature. Within $^1/_2$ h all the metal had virtually dissolved. The reaction mixture containing lithium mesityl tellurolate was poured with stirring into a solution of $K_3Fe(CN)_6$ (12 g in 600 mL of water). After an hour of stirring the product was extracted with CH_2Cl_2 (3 × 200 mL). The dried extract (anhydrous $CaCl_2$) was evaporated and the residue was filtered through a short silica column with benzene–hexane (1:4) as eluant to give ditelluride **20**: mp 125–127 °C (6.10 g, 82% yield); NMR 6.87 (s, 4 H, Ar), 2.36 (s, 12 H, 4 *o*-Me), and 2.32 (s, 6 H, 2 *p*-Me). This material was used without further purification, in the subsequent step.

Bis(*m*-methoxyphenyl) Ditelluride (19). To a stirred solution of *m*-bromoanisole (3.74 g) in dry THF (30 mL) under nitrogen was added magnesium turnings (0.49 g) at room temperature. The mixture was heated under reflux until most of the magnesium dissolved. The Grignard reagent solution was cooled to room temperature and well-powdered tellurium metal was added. After $^1/_2$ h most of the metal dissolved. The reaction mixture was saturated with dry air at room temperature. The *m*-methoxyphenyl ditelluride (**19**) was obtained after routine workup as a red oil (2.96 g, 63.0% yield): NMR 7.38–7.34 (m, 4 H, Ar), 7.07 (m, 2 H, Are, 6.77–6.73 (m, 2 H, Ar) and 3.75 ns, 6 H, OMe); mass spectrum, *m/e* 474 (M^+). It was used in the subsequent step without further purification.

Dimesityl Telluride (17). A solution of ditelluride **20** (4.94 g) in dry toluene (150 mL) was refluxed overnight after the addition of electrolytic copper (1.40 g). The reaction mixture was filtered free of the inorganic material and evaporated to dryness. The residue was practically pure telluride **17**: mp 123–125 °C (lit.[10] mp 129 °C); NMR 6.85 (s, 4 H, Ar), 2.34 (s, 12 H, 4 Me), 2.24 (s, 6 H, 2 Me).

Diphenyl Telluride (14). Detelluration of ditelluride **18**[7] (4.1 g) with copper (1.40 g) in toluene (150 mL) yielded monotelluride **14**[6] (2.70 g, 95.9%) as an oil: NMR 7.70–7.67 (m, 4 H), 7.27–7.17 (m, 6 H).

Bis(*m*-methoxyphenyl) Telluride (16). The oily ditelluride **19** (0.5 g) was detellurized with copper (0.14 g) in toluene to yield the monotelluride **16** (0.37 g, 97.3%) as an oil: NMR 7.29–7.23 (m, 4 H), 7.12 (t, 2 H, Ar), 6.83–6.79 (m, 2 H, Ar), 3.75 (s, 6 H, OMe); mass spectrum, *m/e* 344 (M^+).

Phenyl Methyl Telluroxide (4). To a stirred solution of telluride **15**[6] (3 g) in CCl_4 (20 mL) was added dropwise at room temperature a solution of Br_2 (2.3 g) in CCl_4 (10 mL). After evaporation of the solvent, the resulting pale yellow solid (**10**) was stirred with ammonia (40 mL) at 40 °C for 1 h. The resulting curdy white precipitate of telluroxide **4** was filtered, washed, and dried for several days at 50 °C (vacuum): mp 128–130 °C; NMR 8.01–7.99 (m, 2 H, ar), 7.39–7.26 (m, 3 H, Ar), 2.87 (s, 3 H, Me). Telluroxide **4** analyzed as a hemihydrate. Anal. Calcd for $C_7H_8TeO{\cdot}1.5H_2O$: C, 31.75; H, 3.40; Te, 48.22. Found: C, 31.8; H, 3.05; Te, 47.96.

Bis(*m*-methoxyphenyl) Telluroxide (17). (a) Periodate Oxidation of Telluride (16). A mixture of telluride **16** (0.80 g) and $NaIO_4$ (0.50 g) in MeCN–MeOH–H_iO (30 mL, 1:1:1) was refluxed for 2 h. The cooled mixture was diluted with water (100 mL) and extracted with $CHCl_3$ (3 × 30 mL). The residue from the chloroform extract was chromatographed on a silica column, the telluroxide **7** being eluted by $CHCl_3$–MeOH (9:1). It was crystallized from benzene as a hydrate benzene solvate (0.26 g): mp 189–191 °C; NMR (unsolvated) 7.50–7.20 (m, 6 H, Ar), 7.04–7.01 (m, 2 H, Ar), 3.74 (s, 6 H, OMe). Anal. Calcd for $C_{14}H_{14}TeO_3{\cdot}2H_2O{\cdot}1.5C_6H_6$: C, 54.05; H, 5.33; Te, 24.97. Found: C, 53.87; H, 4.68; Te 25.71.

(b) Via Telluronium Bromide 13. Telluride **16** (0.365 g) in CCl_4 (15 mL) was treated with a solution of Br_2 (0.2 g) in CCl_4 (5 mL). The solvent was evaporated and the residue was telluronium dibromide **13** (0.48 g): mp 186–187; mass spectrum, *m/e* 423 (M − Br, 7%), 344 (M − 2Br, 43%), 214 (M − $TeBr_2$, 100%). The dibromide was stirred with concentrated ammonia (30 mL) at room temperature for 1 h. The product was extracted into chloroform and the residue upon evaporation was crystallized from benzene to yield telluroxide **7** (0.29 g, 58%).

***p*-(Dimethylamino)phenyl *p*-Methoxyphenyl Telluroxide (5).** Well-ground [*p*-(dimethylamino)phenyl] [*p*-methoxyphenyl]tellurium dichloride (**11**, 5.5 g) was stirred at room temperature with concentrated ammonia (50 mL) for $^1/_2$ h. The resulting white precipitate was filtered and washed with water and dried (3.4 g). It was then crystallized from CH_2Cl_2–hexane to give pure **5** (2.8 g): mp 202–204 °C (lit.[5b] mp 209–210.5 °C); NMR 7.62 (d, 2 H, J = 7.5 Hz), 7.50 d, 2 H, J = 7.5 Hz, Ar), 6.97 (d, 2 H, J = 7.5 Hz, Ar), 6.71 (d, J = 7.5 Hz, Ar), 6.71 (d, J = 7.5 Hz), 3.81 (s, 3 H, OMe), 2.98 (s, 6 H, NMe_2). Anal. Calcd for $C_{15}H_{17}NO_2Te$: C, 48.57; H, 4.62; N, 3.77; Te, 34.40. Found: C, 48.55; H, 4.81; N, 3.76; Te, 34.57.

Bis[*p*-(dimethylamino)phenyl] Telluroxide (6).[12] Bis[(dimethylamino)phenyl]tellurium dichloride[4] (**12**, 1.6 g) was converted by treatment with concentrated ammonia to telluroxide **6**[11] (1.4 g, 100%): mp 227–230 °C (after crystallization from CH_2Cl_2–hexane); NMR 7.51 (d, 4 H, J = 7.5 Hz, Ar), 6.72 (d, 4 H, J = 7.5 Hz), 2.98 (s, 6 H). Anal. Calcd for $C_{16}H_{20}N_2OTe$: C, 50.05; H, 5.25; N, 7.29; Te, 33.20. Found: C, 49.67; H, 5.32; N, 7.24; Te, 32.74.

Dimesityl Telluroxide (8). Dimesityl telluride (**17**, 3.66 g) was oxidized with $NaIO_4$ (2.14 g) in MeCN–MeOH–H_2O (300 mL, 1:1:1) to give after workup, as described earlier, telluroxide **8** (3.65 g, 95%): mp 179–180 °C (lit[11] mp 204 °C); NMR 6.84 (s, 4 H, Ar), 2.54 (s, 12 H, 4 Me), 2.26 ns, 6 H, 2 Me).

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 83-03897). It was presented in preliminary form at the International Selenium, Tellurium Conference held in Birmingham, U.K. in Aug, 1983. One of us (M.A.) thanks the Chemicals Inspection and Testing Institute, Osaka, Japan, for a leave of absence.

Registry No. **1**, 57857-70-2; **2**, 6261-32-1; **3**, 51786-98-2; **4**, 75117-88-3; **5**, 80246-39-5; **6**, 65683-57-0; **7**, 92720-44-0; **8**, 92720-45-1; **11**, 63971-78-8; **12**, 62846-44-0; **13**, 92720-50-8; **14**, 1202-36-4; **15**, 872-89-9; **16**, 92720-49-5; **17**, 70165-32-1; **18**, 32294-60-3; **19**, 92720-48-4; **20**, 92720-46-2; PhCH=C$(COOMe)_2$, 6626-84-2; PhCH=C$(CN)_2$, 2700-22-3; benzaldehyde, 100-52-7; tetralone, 29059-07-2; dimethyl malonate, 108-59-8; malononitrile, 109-77-3; 2-bromomesitylene, 576-83-0; tellurium, 13494-80-9; lithium mesityl tellurolate, 92720-47-3; *m*-bromoanisole, 2398-37-0; copper, 7440-50-8.

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(10) Smith, L. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II., p 95.

(11) Lederer, K. *Chem. Ber.* **1916**, *49*, 345.

(12) Telluroxide 6 has been generated in situ as a selective oxidant (ref 5b).