

(10 mL). the combined organic layers are dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The oil obtained is purified by preparative TLC to give an oil assigned as the *E,E* diene.

**6a:** yield, 60.0 mg (43.8%); pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.30 (m, 5 H), 6.80 (ddd,  $J = 15.5, 8.3, 1.0$  Hz, 1 H), 6.55 (d,  $J = 15.5$  Hz, 1 H), 6.33 (dd,  $J = 15.5, 8.3$  Hz, 1 H), 6.24 (broad d,  $J = 15.5$  Hz, 1 H), 3.75 (s, 6 H), 1.62 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  171.07 s, 136.75 s, 133.28 d, 131.18 d, 130.74 d, 128.38 d, 127.94 d, 127.49 d, 126.23 d, 55.76 s, 52.78 q, 20.44 q; IR ( $\text{CHCl}_3$ ) 3020, 2960, 1750, 1735, 1605, 1500, 1465, 1455, 1440, 1385, 1270, 1210, 1120, 1100, 990; *M*, 274.1200, found 274.1205. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_4$ : C, 70.04; H, 6.61. Found: C, 69.04; H, 6.69.

**6b:** yield, 44.5 mg (27.4%); yellow oil; contains 5% of *Z,E* isomer;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.16-8.07 (m, 1 H), 7.90-7.38 (m, 6 H), 7.4 (d,  $J = 15$  Hz, 1 H), 6.90 (dd,  $J = 15, 10$  Hz, 1 H), 6.48

(dd,  $J = 15.5, 10$  Hz, 1 H), 6.29 (d,  $J = 15.5$  Hz, 1 H), 3.78 (s, 6 H), 1.68 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  171.0, 134.3, 133.7, 133.4, 131.5, 131.4, 130.9, 130.1, 128.4, 127.9, 125.8, 125.6, 125.3, 125.15, 56.6, 52.7, 20.8; calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_4$  324.1356, found 324.1362.

**7.** The reaction was run on a 0.15-mmol scale, 18 mg (38.2%). The compound is only one spot by TLC, but contains impurities visible by NMR:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.44-7.08 (m, 5 H), 6.89-6.74 (m, 1 H), 6.55 (d,  $J = 15.8$  Hz, 1 H), 6.39-6.25 (m, 2 H), 5.91-5.40 (m, 1 H), 5.19-4.81 (m, 2 H), 3.75 (s, 6 H), 2.25-1.85 (m, 4 H); calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_4$  314.1512, found 314.1508.

**Acknowledgment.** We wish to thank the National Science Foundation for their generous support of our programs. The Italian CNR provided partial fellowship support for A.B.

## 2,3,3-Trifluoro-1-cyclobutene and Dimers of 1,1,2-Trifluoro-1,3-butadiene from Tetrafluoroethylene-Vinylsilane Cycloadducts

David C. England,\* Frank J. Weigert, and Joseph C. Calabrese

Central Research and Development Department,<sup>1</sup> E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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(Tetrafluorocyclobutyl)silanes prepared by thermal cycloaddition of tetrafluoroethylene (TFE) to vinylsilanes were pyrolyzed at 600 °C to give mixtures containing dimers of 1,1,2-trifluoro-1,3-butadiene. The monomeric diene **1** was undoubtedly an intermediate formed by ring opening of initially formed 2,3,3-trifluoro-1-cyclobutene (**9**). This cyclobutene has been prepared by fluoride ion catalyzed removal of trimethylfluorosilane from (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane (**8**) at room temperature. One of the dimers of the diene was saturated and was shown by X-ray crystallography to have the tricyclo[3.3.0.0]octane structure (**3**) corresponding to a previously reported structure for a perfluorobutadiene dimer. The cyclooctadiene **2** presumed to be the precursor to dimer **3** and Diels-Alder dimers (vinylcyclohexenes) **4** and **7** were characterized by  $^{19}\text{F}$  NMR analyses of liquid fractions.

Perfluorobutadiene, its dimers, and its relation to isomeric perfluorocyclobutene were first explored by W. T. Miller and co-workers.<sup>2</sup> A saturated dimer of the diene which they isolated was found by I. L. Karle and co-workers<sup>3</sup> to have the tricyclo[3.3.0.0]octane structure with two five-membered and one four-membered ring instead of the initially postulated three four-membered rings. We have now found a convenient, high-yield route to 2,3,3-trifluorocyclobutene (**9**) and have prepared dimers of 1,1,2-trifluoro-1,3-butadiene in low yield by pyrolysis of cyclobutanes prepared by cycloaddition of TFE to vinylsilanes. One of the dimers was saturated and was shown by X-ray crystallography to have structure **3** analogous to the perfluorobutadiene dimer characterized by Karle and co-workers. Other Diels-Alder dimers (vinylcyclohexenes) were characterized by  $^{19}\text{F}$  NMR.

### Results and Discussion

Five (tetrafluorocyclobutyl)silanes were prepared in high yield by cycloaddition of the corresponding vinylsilanes to TFE in sealed tubes at 180 °C (Table I). Three of these (expt 1, 2, and 3) were prepared earlier by Russian workers<sup>4</sup> by passing the same reactants through a quartz tube at atmospheric pressure and elevated temperatures (400-500 °C). Their yields were lower and decreased further at 600

°C. We have found that passing the cycloadducts through a quartz tube at 600 °C gives much decomposition and low yields of mixtures containing dimers of 1,1,2-trifluoro-1,3-butadiene (**1**). One of these dimers proved to be saturated and crystalline and was characterized by X-ray crystallography as having the tricyclo[3.3.0.0]octane structure **3**. Presumably pyrolysis of the (tetrafluorocyclobutyl)silanes proceeded partly through loss of fluorosilane to give 2,3,3-trifluoro-1-cyclobutene (**9**) as an intermediate which may ring open to the diene. The diene can dimerize in several ways (Scheme I). Examination of distilled fractions by NMR has provided evidence for the presence of the cyclooctadiene **2**, saturated dimer **3**, and the vinylcyclohexenes **4** and **7** with a trace of **5** (see below for structure identification).

Preparation of the presumed pyrolysis intermediate, 2,3,3-trifluoro-1-cyclobutene (**9**) has been accomplished by Park and co-workers in 21% yield by dehydrochlorination<sup>5</sup> and in 70% yield (63% conversion) by dechlorination<sup>6</sup> of the corresponding chlorofluorocyclobutanes. We have found that (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane (**8**) (Table I, expt 3) in the presence of fluoride ion catalyst, loses trimethylfluorosilane to give the cyclobutene **9** in nearly quantitative yield at room temperature. As reported,<sup>5</sup> a white polymer separates from the uninhibited cyclobutene on standing.

**Structure Identification of Dimers.** Three fractions of the dimer mixture were analyzed: (A) bp 92 °C (100

(1) Contribution No. 3399.

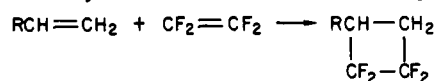
(2) Prober, M.; Miller, W. T. *J. Am. Chem. Soc.* **1949**, *71*, 598.

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(4) Mironov, V. F.; Sheludyakov, V. D.; Rad'kova, O. M.; Shcherbinin, V. V.; Viktorov, N. A. *Zh. Obshch. Khim.* **1973**, *43*(8), 1856.

(5) Park, J. D.; Holler, H. V.; Lacher, J. R. *J. Org. Chem.* **1960**, *25*, 992.

(6) Park, J. D.; Croft, T. S.; Groppelli, G. *J. Fluorine Chem.* **1975**, *5*, 301.

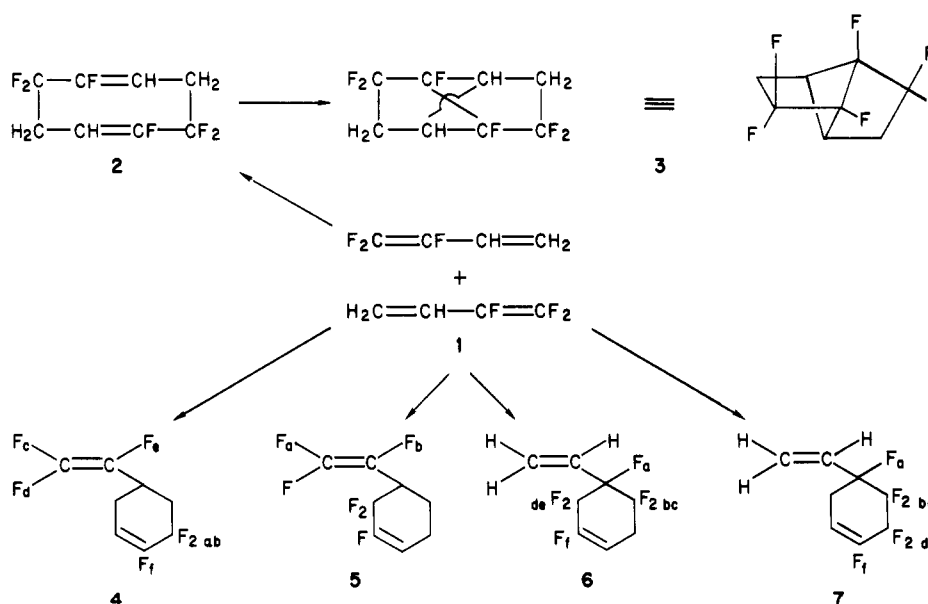
Table I. Cycloadditions of Tetrafluoroethylene<sup>a</sup>

expt	R	RCH=CH <sub>2</sub> , g (mol)	TFE, g (mol)	no. of tubes	product <sup>b</sup>			
					weight, g	bp, °C (mm)	% conversn <sup>c</sup>	yield, %
1	SiCl <sub>3</sub>	30 (0.19)	20 (0.2)	8	155	85 (135)	40	84
2	SiCl <sub>2</sub> CH <sub>3</sub>	14 (0.1)	15 (0.15)	2	17	62 (50)	35	70
3	Si(CH <sub>3</sub> ) <sub>3</sub>	13 (0.13)	22 (0.22)	8	128	75 (120)	62	86
4	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	19 (0.1)	17 (0.17)	4	66	49 (0.6)	58	77
5	Si(OCH <sub>3</sub> ) <sub>3</sub>	15 (0.1)	15 (0.15)	2	27	59 (8)	54	75

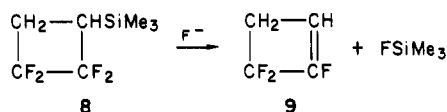
<sup>a</sup>Run at 180 °C for 8 h in 150-mL Carius tubes with 0.1 g of phenothiazine and 1 drop of limonene as polymerization inhibitors.

<sup>b</sup>Satisfactory carbon, hydrogen, and fluorine analyses were obtained on all products. <sup>c</sup>Conversion based on silane charged, yield on silane consumed.

Scheme I



mm), (B) 97 °C (100 mm), and (C) 85 °C (22 mm) (see Experimental Section). Gas chromatography and <sup>19</sup>F NMR showed that both A and B were predominantly mixtures of the same two compounds, though in different proportions. The fluorine NMR chemical shifts and coupling constants of these major isomers are given in the Experimental Section. The proton NMR and IR are consistent with the major isomer of A having a CF=CF<sub>2</sub> group and that of B having a CH=CH<sub>2</sub> group.



Four-membered ring structures for both isomers can be eliminated by the geminal CF<sub>2</sub> coupling constants of 270–280 Hz which are consistent only with unstrained structures. Eight-membered rings can be eliminated by symmetry considerations. All six fluorines in each isomer are in different environments, a feature impossible to reconcile with cyclooctadienes or their derivatives.

Four Diels–Alder adducts of trifluorobutadiene are possible (4, 5, 6, and 7 above). The presence of a vinyl or a trifluorovinyl group narrows the choices. Fraction A is either mainly 4 or 5, while fraction B is either mainly 6 or 7. Further distinctions follow from chemical shifts and coupling constant considerations of the ring CF<sub>2</sub> groups.

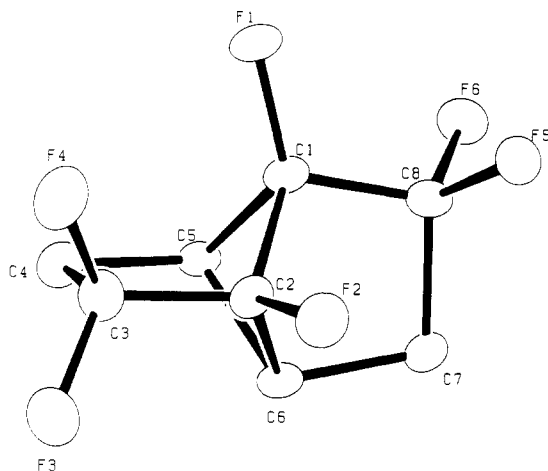
The vicinal=CFCF<sub>2</sub> couplings can be unambiguously assigned in isomer A as 19 and 22 Hz. A distinction be-

tween 4 and 5 can be made based on the expectation that there should be a long range FF coupling between CF<sub>2</sub>=CF and at least one of the CF<sub>2</sub> fluorines in 5, while no such coupling would be expected in 4. No coupling is seen in the major isomer of A. We thus assign structure 4 to the major isomer of fraction A.

To assign a structure for the major isomer in B we consider the distinction between 6 and 7. There is no reason to expect the vicinal=CFCF<sub>2</sub> couplings (19 and 22 Hz) to change with different ring substituents, so the =CFCF<sub>2</sub> group is matched with the resonances at –131 ppm and –115 ppm (F<sub>2de</sub>). These are significantly upfield from the –95 ppm and –109 ppm (F<sub>2ab</sub>) for the major isomer 4 in A. The CF<sub>2</sub> group derived from the dienophile is therefore at –124 ppm and –137 ppm, at even higher field. The assignments for F<sub>2de</sub> are more consistent with 7 than 6. The fluorine at –137 ppm is coupled to all the others in the molecule, and all of the long-range couplings are comparable. This is plausible in 7, but a 10 Hz, 5-bond coupling, which would be required if the structure were 6, is less reasonable. The upfield shift of the dienophile CF<sub>2</sub> group is also more consistent with 7 than 6.

A third, very minor component is present in fraction B. It has a trifluorovinyl group as indicated by resonances at –101.9 ppm and –182 ppm. The –182 ppm resonance shows coupling to three fluorines as might be expected from structure 5.

Fraction C, a crystalline solid (mp 48–50 °C), was characterized by X-ray analysis (see Experimental Sec-



**Figure 1.** 1,2,2,5,6,6-Hexafluorotricyclo[3.3.0.0<sup>6,8</sup>]octane (numbers indicated on carbon and fluorine atoms in the figure are those which were used in the X-ray analysis).

tion). It is interesting to note that in this structure there does not appear to be any significant differences as previously observed<sup>3</sup> between the average C–F bond distances when the carbon is attached to one or two fluorines. In either case the distances range from 1.363 (8) Å. Also there appears to be only a slight effect of the fluorine substitution on the carbon skeleton. The C–C bonds flanked by the fluorine substitution are slightly shorter than those on the opposite side of the molecule. For example, in Figure 1 compare C(2)–C(3), 1.498 (8) Å, vs. C(4)–C(5), 1.527 (9) Å, and C(1)–C(8), 1.502 (8) Å, vs. C(6)–C(7), 1.516 (8) Å. Otherwise the carbon skeleton is quite symmetric with the largest C–C bond length differences involving the central four-membered ring vs. the external five-membered ring distances as expected. The central ring distances average 1.554 Å vs. 1.511 Å for the six external C–C ring distances.

A minor component was seen in the fluorine NMR spectrum of fraction C with a doublet at –97 ppm and a triplet at –121.2 ppm coupled by 23 Hz. These resonances are consistent with the head-to-tail cyclooctadiene structure 2, the potential precursor to the crisscross cyclobutane 3.

### Experimental Section

Melting points and boiling points are uncorrected. <sup>1</sup>H NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as external standard with the downfield direction taken as positive. <sup>19</sup>F NMR spectra were obtained with a Varian XL-100 spectrometer operating at 94.1 MHz with CFCl<sub>3</sub> as internal standard. Upfield shifts are reported as negative values.

**2,3,3-Trifluoro-1-cyclobutene.** A mixture of 25 g of (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane (See Table I, expt 3), 1 g of CsF, and 5 mL of tetraglyme was sealed in each of two 50-mL Carius tubes and rotated at room temperature overnight. The volatile contents of the tubes were transferred with warming to 100 °C under vacuum to a 200 mL tube containing 100 mL of 2 N KOH which was then heated for 4 h in a steam bath. The KOH had been neutralized and Me<sub>3</sub>SiF was still present, so the volatiles were again transferred to another tube containing 100 mL of 2 N KOH and heated overnight in a steam bath. Volatile material was then distilled from P<sub>2</sub>O<sub>5</sub> to give 26 g (96%) of 2,3,3-trifluoro-1-cyclobutene, bp 33 °C, and 16.5 g (81%) of Me<sub>3</sub>SiOSiMe<sub>3</sub>, bp 94 °C, formed by alkaline solvolysis of the Me<sub>3</sub>SiF, bp 19 °C. Separation of the cyclobutene from Me<sub>3</sub>SiF was difficult by distillation, and therefore avoided in this treatment.

For Me<sub>3</sub>SiF: <sup>1</sup>H NMR –0.20 ppm (d, 8.0 Hz, 9 H); <sup>19</sup>F NMR –157.96 ppm (decet, 8.0 Hz, 1 F).

For Me<sub>3</sub>SiOSiMe<sub>3</sub>: <sup>1</sup>H NMR –0.23 ppm (s, 18 H).

For 2,3,3-trifluoro-1-cyclobutene-1: IR 5.94 μm (C=C); <sup>1</sup>H NMR 5.13 ppm (m, 1 H) and 2.20 ppm (m, 2 H); <sup>19</sup>F NMR (decoupled from H) –107.36 ppm (t, 7.5 Hz, 1 F) and –114.11 ppm (d, 7.5 Hz, 2 F).

A finely divided, acetone-soluble polymer slowly separated from purified (acid and base washed and distilled) samples of the cyclobutene.

Anal. Calcd for C<sub>4</sub>H<sub>3</sub>F<sub>3</sub>: C, 44.46; H, 2.79; F, 52.75. Found: C, 44.10; H, 3.01; F, 51.41.

**Pyrolysis of (2,2,3,3-Tetrafluorocyclobutyl)trichlorosilane. Dimers of 1,1,2-Trifluoro-1,3-butadiene.** A total of 151 g of the above silane (see Table I, expt 1) was pyrolyzed at 600 °C in a slow current of nitrogen by dropwise addition into an 18 in. × 1 in. quartz tube packed with 1/4 in. sections of 8-mm quartz tubing and heated by a 12-in. split-type furnace. There was considerable charring in the tube. Volatile products were collected in a dry ice cooled trap, and low boilers were allowed to escape at room temperature leaving 63 g which was distilled. There was obtained a fraction (11.7 g) with bp 64–70 °C (22 mm) and one (12.3 g) with bp 85 °C (22 mm). These fractions appeared by gas chromatography to contain two different pairs of isomers. The former fraction (11.7 g) was redistilled to give partial separation into A (1.4 g, bp 92 °C (100 mm)) and B (1.0 g, bp 97 °C (100 mm)). The latter fraction above (12.3 g) partially solidified on standing and was recrystallized from CCl<sub>4</sub> to give C (4.4 g, mp 48–50 °C).

Fractions A, B, and C analyzed as diene dimers. Only A and B showed unsaturation, absorbing at 5.55 μm and 5.83 μm in the infrared with different intensities. <sup>19</sup>F NMR analyses indicated that fraction A was about 78% compound 4 and 22% compound 7. Fraction B was about 10% compound 4, 89% compound 7, and 1% compound 5. Fraction C was largely compound 3 with a trace of compound 2.

For A: IR 5.55 μm (s) and 5.83 μm (s).

For B: IR 5.55 μm (w) and 5.83 μm (s).

Anal. Calcd for C<sub>8</sub>H<sub>6</sub>F<sub>6</sub>: C, 44.45; H, 2.80; F, 52.75.

For A Found: C, 44.50; H, 2.63; F, 52.42.

For B Found: C, 44.31; H, 2.75; F, 52.41.

For C Found: C, 44.43; H, 2.86; F, 52.89.

For compound 2: <sup>19</sup>F NMR –96.95 ppm (d, 23 Hz, 2 F) and –121.18 ppm (t, 23 Hz, 1 F).

For compound 3: <sup>19</sup>F NMR –109.0 ppm (*J*<sub>AB</sub> = 226 Hz, *J*<sub>AX</sub> = 7 Hz, 2 F), –113.6 ppm (*J*<sub>AB</sub> = 226 Hz, 2 F) and –195.7 ppm (m, 2 F).

For compound 4: <sup>19</sup>F NMR –95 ppm (F<sub>a</sub>), –109 ppm (F<sub>b</sub>, *J*<sub>ab</sub> = 270 Hz), –104 ppm (F<sub>c</sub>), –121 ppm (F<sub>d</sub>, *J*<sub>cd</sub> = 85 Hz), –183 ppm (F<sub>e</sub>, *J*<sub>ce</sub> = 33 Hz, *J*<sub>de</sub> = 115 Hz) and –135 ppm (F<sub>f</sub>, *J*<sub>af</sub> = 22 Hz, *J*<sub>bf</sub> = 19 Hz).

For compound 5: <sup>19</sup>F NMR –101.9 ppm (dd, 36 Hz, 78 Hz, F<sub>a</sub>) and –182 ppm (ddd, 36 Hz, 120 Hz, 15 Hz, F<sub>b</sub>).

For compound 7: <sup>19</sup>F NMR –175 ppm (F<sub>a</sub>), –137 ppm (F<sub>b</sub>, *J*<sub>ab</sub> = 16 Hz), –124 ppm (F<sub>c</sub>, *J*<sub>ac</sub> = 3 Hz, *J*<sub>bc</sub> = 271 Hz), –131 ppm (F<sub>d</sub>, *J*<sub>bd</sub> = 10 Hz, *J*<sub>cd</sub> = 10 Hz), –115 ppm (F<sub>e</sub>, *J*<sub>ae</sub> = 20 Hz, *J*<sub>be</sub> = 10 Hz, *J*<sub>de</sub> = 285 Hz) and –135 ppm (F<sub>f</sub>, *J*<sub>bf</sub> = 10 Hz, *J*<sub>df</sub> = 19 Hz, *J*<sub>ef</sub> = 22 Hz).

Further characterization of these fractions is reported above under "Structure Identification of Dimers".

Similar pyrolyses of methyl and chloromethylsilanes (See Table I, expt 2 and 3) gave similar mixtures.

**X-ray Characterization of 1,2,2,5,6,6-Hexafluorotricyclo[3.3.0.0<sup>6,8</sup>]octane.** A colorless, crystalline fragment of fraction C, 0.24 mm × 0.09 mm × 0.50 mm, obtained by sublimation in a sealed tube, was wedged in a glass capillary and placed on a Syntex R3 X-ray diffractometer equipped with a Mo K<sub>α</sub> source, graphite monochromator, and LT-1 low temperature device operating at –100 °C. The preliminary Syntex routines based on 39 reflections indicated an orthorhombic cell with dimensions *a* = 14.963 (3) Å, *b* = 5.671 (1) Å, and *c* = 9.559 (1) Å. With *Z* = 4 the calculated density is 1.770 g/cm<sup>3</sup>. Systematic absences were

(7) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; York, England and Luvain-la-Neuve, Belgium, 1978.

consistent with space group  $Pna2_1$ . A total of 1171 reflections were collected with the  $\omega$  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)<sup>7</sup> to yield the structure. With  $\mu = 1.919 \text{ cm}^{-1}$  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  $0.2e/\text{\AA}^3$  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;  $\text{Cl}_3\text{SiCH}=\text{CH}_2$ , 75-94-5;  $\text{MeCl}_2\text{SiCH}=\text{CH}_2$ , 124-70-9;  $\text{Me}_3\text{SiCH}=\text{CH}_2$ , 754-05-2;  $(\text{EtO})_3\text{SiCH}=\text{CH}_2$ , 78-08-0;  $(\text{MeO})_3\text{SiCH}=\text{CH}_2$ , 2768-02-7;  $\text{CF}_2=\text{CF}_2$ , 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

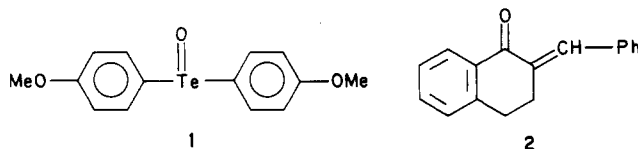
Mitsuo Akiba, M. V. Lakshmikantham, Kwan-Yue Jen, and Michael P. Cava\*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received April 6, 1984

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.

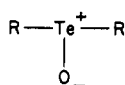
Several years ago, it was found in our laboratories that bis(*p*-methoxyphenyl) telluroxide (1) functioned as a selective aldol catalyst in boiling toluene.<sup>1</sup> This reaction appeared to be particularly promising for the condensation of aromatic aldehydes with active methylene compounds under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



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

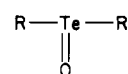
Telluroxides should exhibit a certain degree of basic character by virtue of the polar nature of the tellurium-oxygen bond in telluroxide monomers. Indeed, in 1977



a  $pK_a$  of  $\sim 14.9$  in acetonitrile was reported for telluroxide 1,<sup>2</sup> 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.

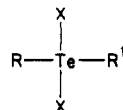
In the present study, we have synthesized a number of structurally varied telluroxides (3-8) with the aim of as-

sessing, albeit qualitatively, their relative propensity to promote aldol-type reactions. For the purposes of this investigation the condensation of benzaldehyde with  $\alpha$ -tetralone to give the readily isolated benzylidene derivative 2 was chosen as the standard reaction.

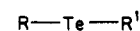


- 3,  $R = R^1 = \text{Ph}$
- 4,  $R = \text{Ph}; R^1 = \text{Me}$
- 5,  $R = p\text{-methoxyphenyl}; R^1 = p\text{-(dimethylamino)phenyl}$
- 6,  $R = R^1 = p\text{-(dimethylamino)phenyl}$
- 7,  $R = R^1 = m\text{-methoxyphenyl}$
- 8,  $R = R^1 = \text{mesityl}$

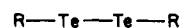
**Synthesis of Telluroxides.** Telluroxides 3-7 were made by the base treatment of the Te dichloro or dibromo derivatives 9-13. The dibromo derivative 9, 10, and 13 were made from the corresponding monotellurides 14-16 by the action of bromine. The known dichloro derivatives



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



- 14,  $R = R^1 = \text{Ph}$
- 15,  $R = \text{Ph}; R^1 = \text{Me}$
- 16,  $R = m\text{-methoxyphenyl}$
- 17,  $R = R^1 = \text{mesityl}$



- 18,  $R = \text{Ph}$
- 19,  $R = R^1 = m\text{-methoxyphenyl}$
- 20,  $R = R^1 = \text{mesityl}$

11 and 12 were prepared by reported procedures.<sup>3,4</sup> Telluroxide 8 was made by periodate oxidation of telluride 17.

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