methanesulfonic acid by heating to 70 °C. After the mixture cooled to 50 °C, 2.50 mL of 90% H_2O_2 was added during 15 min (ice bath cooling to maintain the temperature at 45–55 °C). During the addition, the color of the solution changed from orange to green and then to yellow. After the solution was stirred at ambient temperature for 19 h, it was extracted with two 60-mL portions of methylene chloride. The combined extracts were stirred with 15 g of $MgSO_4$ for 5 h to remove trifluoromethanesulfonic acid. After filtration, the filtrate was concentrated to dryness under reduced pressure, leaving 0.55 g of pale yellow solid which was crystallized from 6.0 mL of pure, dry chloroform to yield 0.49 g (90%) of hexanitrobenzene (**23**), mp 24–262 °C (phase transition at 115 °C), identical with an authentic sample.[4]

Hexanitrobenzene (23). Procedure C.[36] Pentanitroaniline (**9**; 1.0 g, 3.14 mmol) was dissolved in 80 mL of trifluoromethanesulfonic acid by heating to 70 °C. The mixture was cooled to 24 °C, 2.60 g (9.62 mmol) of potassium persulfate was added in one portion, and the resulting solution was stirred at ambient temperature for 18 h. After extraction with two 75-mL portions of methylene chloride, the combined extracts were stirred with 20 g of $MgSO_4$ for 6 h to remove trifluoromethanesulfonic acid. After filtration, the solvent was removed from the filtrate under reduced pressure, leaving 0.63 g of a yellow solid. This material, a mixture of pentanitroaniline and hexanitrobenzene, was stirred with CCl_4 for 19 h and filtered; removal of solvent from the filtrate gave 0.23 g (21%) of hexanitrobenzene, mp 239–258 °C.

Treatment of pentanitroaniline with potassium persulfate in sulfuric acid gave recovered pentanitroaniline only. To pentanitroaniline (**9**; 1.0 g, 3.14 mmol) in 50 mL of 20% oleum was added 6.5 g of potassium persulfate, and the mixture was stirred at 25 °C for 24 h. The mixture was extracted three times with methylene chloride. After being dried with $MgSO_4$, the combined extracts were concentrated to dryness to yield 0.53 g of crude pentanitroaniline as yellow crystals; trituration of this product with pure chloroform gave 0.40 g of recovered pentanitroaniline, mp 193–199 °C. The sulfuric acid solution remaining when poured onto ice gave a trace of orange solid. No hexanitrobenzene could be isolated from the reaction products.

Acknowledgment. The authors are indebted to M. Finger and R. R. McGuire of Lawrence Livermore Laboratory and to D. W. Moore and D. A. Fine of the Naval Weapons Center for helpful discussions. This work was supported in part by Lawerence Livermore Laboratory. The support of L. A. Roslund and the Naval Sea Systems Command is gratefully acknowledged.

Registry No. 1, 64884-81-7; **2**, 606-22-4; **3**, 73333-89-8; **4**, 73333-90-1; **5**, 489-98-5; **6**, 32650-52-5; **7**, 22603-58-3; **8**, 3698-54-2; **9**, 21985-87-5; **10**, 51168-33-3; **11**, 17215-44-0; **12**, 53517-46-7; **13**, 73333-91-2; **14**, 73333-92-3; **15**, 73333-93-4; **16**, 603-13-4; **17**, 73333-94-5; **18**, 73333-95-6; **19**, 3698-53-1; **20**, 5967-26-0; **21**, 73333-96-7; **22**, 68630-38-6; **23**, 13232-74-1; **24**, 73347-63-4; **25**, 73333-97-8; **26**, 73333-98-9; **27**, 73333-99-0; **28**, 73334-00-6; **29**, 122-28-1; **30**, 60956-27-6; **31**, 73334-01-7; **32**, 610-41-3; **33**, 73334-02-8; 3,5-dinitroaniline, 618-87-1; 3,5-diacetamido-2,4,6-trinitrotoluene, 73334-03-9; 3,5-diamino-2,4,6-trinitrotoluene, 73334-04-0; peroxydisulfuric acid, 13445-49-3.

Alkali Metal *O,O*-Diethyl Phosphorotelluroates, a Reagent Class for Deoxygenation of Epoxides, Especially Terminal Epoxides

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Epoxides are deoxygenated to olefins by alkali metal *O,O*-diethyl phosphorotelluroates. These reagents can be used in stoichiometric quantities or they can be generated continuously in situ from tellurium under conditions that approach a catalytic nature with respect to the metal. Terminal epoxides are deoxygenated most readily, but the reaction does work for other types. In the case of epoxides formally derived from acyclic olefins, the *Z* compound reacts more easily than the *E* isomer and the deoxygenation is stereospecific. 1,2-Epoxycyclohexanes react faster than 1,2-epoxycyclopentanes. Selective deoxygenations, especially those in favor of terminal epoxides, are possible.

Introduction

While a large number of well-established synthetic methods depend on special properties of organic sulfur compounds,[1] the utility of selenium-based procedures was recognized only in the recent past. This area is being studied, however, in a very intensive manner, and one of its characteristic features is the rapidity with which the new selenium reactions have been accepted into the repertoire of standard methodology.[2] In contrast, the relevance of tellurium chemistry to synthesis is very largely undefined. The *organic* chemistry of the metal is described in a substantial primary literature, and extremely detailed reviews are available.[3] However, this large and active subject has made little contribution to synthesis by way of providing organic compounds that function as reagents. Species of the type $ArTe_xAr'$ ($x = 1$ or 2) can be used to convert vicinal dibromides into olefins,[4] and certain telluronium salts have been examined[5] as catalysts for oxi-

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[1] Trost, B. M.; Melvin, L. S., Jr. "Sulfur Ylides—Emerging Synthetic Intermediates"; Academic Press: New York, 1975. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978.

[2] Clive, D. L. J. *Tetrahedron* **1978**, 1049; *Aldrichimica Acta* **1978**, *11*, 43. Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9. Reich, H. J. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter 1. *Acc. Chem. Res.* **1979**, *12*, 22.

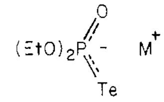
[3] Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974. Irgolic, K. J. *J. Organomet. Chem.* **1978**, *158*, 267. Zingaro, R. A.; Irgolic, K. In "Tellurium"; Copper, W. C., Ed.; Van Nostrand-Reinhold: New York, 1971. Petragnani, N.; De Moura Campos, M. *Organomet. Chem. Rev.* **1967**, *2*, 61. Petragnani, N. *Ann. N.Y. Acad. Sci.* **1972**, *192*, 10; Houben-Weyl, "Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1955; Chapter IX, 917.

[4] De Moura Campos, M.; Petragnani, N.; Thomé, C. *Tetrahedron Lett.* **1960**, *No. 15*, 5. De Moura Campos, M.; Petragnani, N. *Chem. Ber.* **1961**, *94*, 1759.

[5] Ohkubo, K.; Kanaeda, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 11. Fukui, K.; Ohkubo, K.; Yamabe, T. *Ibid.* **1969**, *42*, 312.

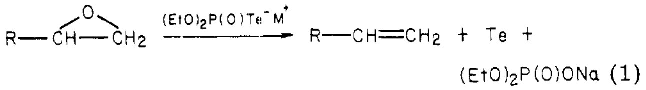
0022-3263/80/1945-2347$01.00/0

dation of hydrocarbons. It is also clear from recent publications[6] that organic tellurium chemistry is being reexamined carefully, and extended, with the definite intention of discovering new reactions and reagents. Therefore, the status of the subject is likely to change, but, up till now, it has never provided any reagents that can be used for transformations that are difficult by classical methods. Alkali metal *O,O*-diethyl phosphorotelluroates (**1**) are the



1

first examples of such reagents. These substances are highly effective for deoxygenating epoxides (eq 1), and we report here full details of our experimental work on this reaction.[7]



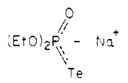
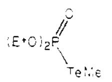
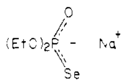
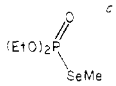
$$\text{R—CH(O)CH}_2 \xrightarrow{(\text{EtO})_2\text{P(O)Te}^-\text{M}^+} \text{R—CH=CH}_2 + \text{Te} + (\text{EtO})_2\text{P(O)ONa} \quad (1)$$

The potassium salt **1** (M = K) was actually reported a long time ago,[8] but synthetic applications for it were not recognized and no study of its properties was undertaken beyond observing that it released elemental tellurium in the presence of air, acids, or iodine.

We have made all three alkali metal salts **1** (M = Na, K, Li). Each is a white solid and, although it is extremely sensitive to air, it can be generated without difficulty. The preparation itself is straightforward: one simply stirs tellurium powder with a solution of the appropriate salt of diethyl phosphite. Ethanol is a convenient solvent, but our early experiments with sodium diethyl phosphite make us regard tetrahydrofuran as superior. In most of the work using equimolar amounts of tellurium and sodium diethyl phosphite not all the metal dissolved if the reaction was conducted in ethanol. With tetrahydrofuran, dissolution always was complete, and so we have routinely used this solvent to generate the salts **1** when we wished to use them in a stoichiometric manner (vide infra). In such cases the solvent must be removed and replaced by anhydrous ethanol before the reagent is ready for use. In a number of preliminary attempts to deoxygenate epoxides according to eq 1, essentially no olefin was formed when tetrahydrofuran was the solvent; however, in comparable experiments using ethanol, substantial reaction did occur.

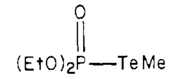
We noticed at the beginning of our work that tellurium powder dissolves quite rapidly in solutions of sodium diethyl phosphite and that the deoxygenation of terminal epoxides (eq 1) is also a fast process. On the other hand, sodium diethyl phosphite does not attack epoxides at a comparable rate, and so it has been possible to refine the experimental procedure nearly to the level of a catalytic process. The terminal epoxide and a small amount of tellurium[9] are stirred in ethanol under nitrogen and an ethanol solution of sodium diethyl phosphite is added slowly. The tellurium dissolves to generate the active[10] species **1** which then deoxygenates some of the epoxide. In this process (eq 1) tellurium is liberated; it combines with more of the phosphite and the whole sequence is repeated. If the phosphite solution is added in small portions at intervals, then the tellurium alternately dissolves and precipitates. However, when the phosphite solution is injected more rapidly, the reaction mixture stays clear until the epoxide has been deoxygenated and at about that stage the metal is deposited. This indicates a rough end point for the reaction.

Table I[a]

	$\delta_{^{31}\text{P}}$ -14.09 (q, $^1J_{\text{P-Te}}$ = 2114.9 Hz, $^3J_{\text{P-OCH}_2}$ = 9.5 Hz) $\delta_{^1\text{H}}$ 1.32 (t, J = 7.2 Hz, 6 H), 3.6-4.3 (m, 4 H)
 **2**	$\delta_{^{31}\text{P}}$ +4.04 (m) $\delta_{^1\text{H}}$ 1.16 (t, J = 7 Hz, 6 H), 1.87 (d, $^3J_{\text{P-TeCH}_3}$ = 12.2 Hz, 3 H), 3.66-4.28 (m)
 **3**[b]	$\delta_{^{31}\text{P}}$ -53.8 (q, $^1J_{\text{P-Se}}$ = 794.1 Hz, $^3J_{\text{P-OCH}_2}$ = 9.5 Hz) $\delta_{^1\text{H}}$ (D$_2$O) 1.29 (t, J = 7.2 Hz, 6 H), 3.73-4.3 (m, 4 H)
 **4**[c]	$\delta_{^{31}\text{P}}$ -18.5 (m) $\delta_{^1\text{H}}$ 1.3 (t, J = 7.2 Hz, 3 H), 2.1 (d, $^3J_{\text{P-TeCH}_3}$ = 13 Hz, 3 H), 3.89-4.29 (m, 4 H)

[a] All spectra were run in THF-d_8 except where stated. Negative values of $\delta_{^{31}\text{P}}$ refer to parts per million downfield from 85% H_3PO_4 as external standard. $\delta_{^{31}\text{P}}$ values reported here replace those given in ref 7. [b] See ref 12. [c] For preparation see: British Patent 691 267, 1953; *Chem. Abstr.* 1954, *48*, 7047e.

Structure of the Reagent. We assign structure **1** to our reagent,[11] in part because of the method of preparation and the chemical reaction with epoxides and, in part, on the basis of the NMR characteristics that we have measured for the sodium salt and for the ester **2**. This ester



$$(\text{EtO})_2\overset{\text{O}}{\overset{\|}{\text{P}}}\text{—TeMe}$$

2

may be generated in situ by adding methyl iodide to a solution of **1**, but the compound was too sensitive for us to isolate in a pure form. The spectroscopic data for **1** and **2** are shown in Table I together with corresponding particulars for the selenium analogues.[12]

Deoxygenations with the Tellurium Reagents: Special Features and Preparative Runs. The tellurium salts **1** must be protected from oxygen, and so we did examine the selenium analogue **3**[13] (see Table I) which is a far more stable material that can be weighed out in air. Treatment of 1,2-epoxyoctane with a stoichiometric amount of **3** does slowly produce the required olefin.[14] However, in a comparison experiment, the tellurium salt **1** (M = Na) proved to be more effective even when it was generated in situ from less than 8 mol % of the stoichiometric amount of tellurium. Therefore, we do not think

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[6] Barton, D. H. R.; Glover, S. A.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1977**, 266. Spencer, H. K.; Cava, M. P. *J. Org. Chem.* **1977**, *42*, 2937. Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314. Bergman, J.; Engman, L. *Tetrahedron Lett.* **1978**, 3279. Cuthbertson, E.; MacNicol, D. D. *J. Chem. Soc., Chem. Commun.* **1974**, 498. Barrett, A. G. M.; Barton, D. H. R.; Read, R. W. *Ibid.* **1979**, 645.

[7] Clive, D. L. J.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1977**, 658.

[8] Foss, O. *Acta Chem. Scand.* **1950**, *4*, 1241.

[9] We have used between 1.8 and 24 mmol of tellurium per 100 mmol of epoxide.

[10] Epoxides are not deoxygenated by $(EtO)_2PONa$ or by a mixture (in EtOH) of EtONa and Te. For equilibria involving $(EtO)_2PONa$ in EtOH, see: Moedritzer, K. *J. Inorg. Nucl. Chem.* **1961**, *22*, 19.

[11] This formulation is not meant to exclude $(EtO)_2P(:Te)O^-M^+$.

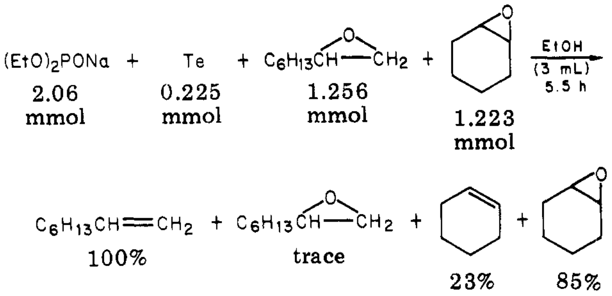
[12] Cf. Glidewell, C.; Leslie, E. J. *J. Chem. Soc., Dalton Trans.* **1977**, 527.

[13] Foss, O. *Acta Chem. Scand.* **1947**, *1*, 8.

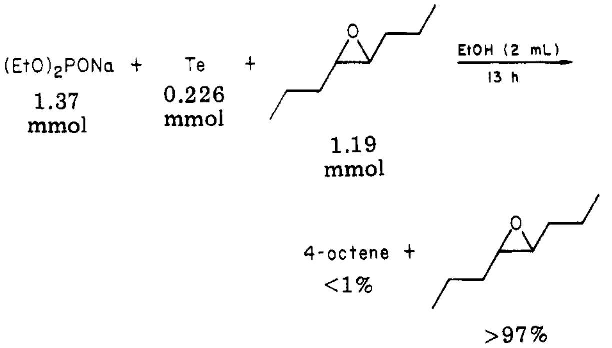
[14] For $(EtO)_2P(O)Se^-Na^+$ both EtOH and HMPA were evaluated as solvents; EtOH is much better.

that the selenium compound is sufficiently reactive to be a useful reagent.

The tellurium salts 1 can discriminate between different types of epoxides and the reactivity of the salts depends on the nature of the cation, the lithium reagent being the most reactive. Our observations are the following: (a) Terminal epoxides are deoxygenated faster than other types, as shown by the experiments summarized in eq 2 and eq 3.

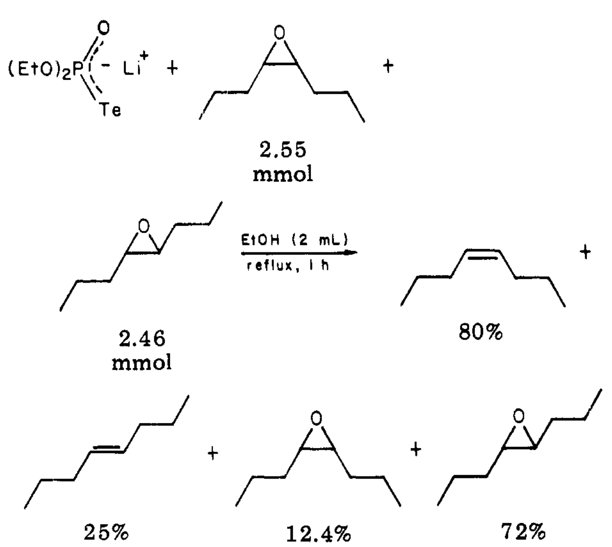


(2)



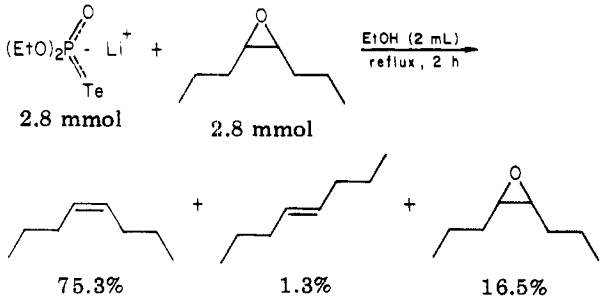
(3)

(b) Among geometrical isomers, the *Z* isomer is the more reactive (eq 4).



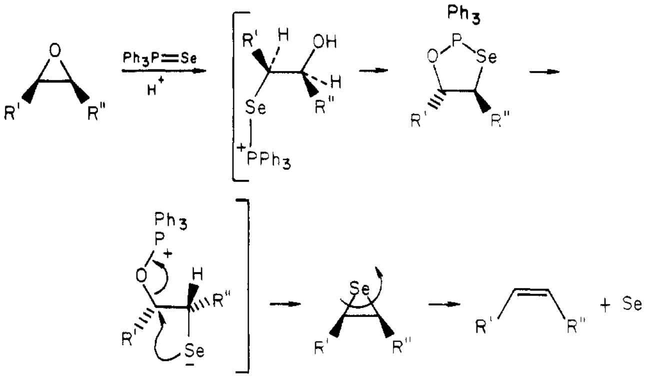
(4)

(c) The deoxygenation is stereospecific: a *Z* epoxide gives a *Z* olefin (eq 5).[15]

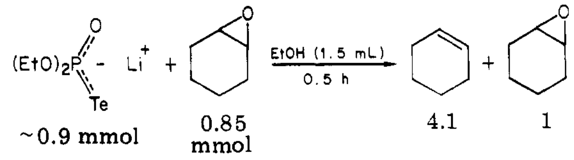


(5)

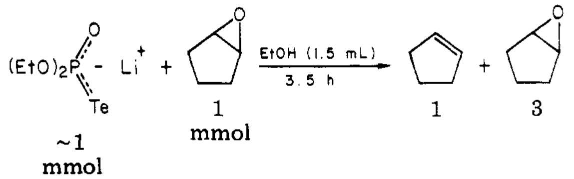
Scheme I



(d) Cyclohexene oxide is deoxygenated more easily than cyclopentene oxide (eq 6[16] and eq 7[17]).



(6)



(7)

The properties of the tellurium reagent, as revealed by the above analytical survey, were also evaluated by preparative runs listed in Table II. Terminal epoxides are deoxygenated efficiently and much less than the stoichiometric amount of tellurium can be used. 1,2-Epoxycyclohexanes require longer reaction times or higher temperatures, and selective deoxygenations are possible as shown by the case of limonene bisepoxide (experiment 7, Table II) and by the more demanding example of the dodecene bisepoxide (experiment 4, Table II). The steroidal epoxide of the estrone series (experiment 8, Table II) reacted less efficiently than any of the other examples because two factors combine to render the process difficult with respect to competing reactions. The substrate is a cyclopentene oxide, and attack from the β face of the molecule is sterically hindered by the C-18 methyl group.

Mechanistic Considerations. Deoxygenation of epoxides by triphenylphosphine selenide[18] occurs by the mechanism shown in Scheme I. This pathway was proposed[18] on the basis of analogy to the thoroughly studied reaction of triphenylphosphine sulfide with epoxides[19] but has been made secure by direct evidence revealing the presence of a selenirane.[20] It is reasonable to suggest a similar pathway (Scheme II) for the tellurium reagents described here. An initial nucleophilic stage is consistent with the enhanced reactivity of terminal epoxides over other types, and the greater facility of deoxygenating *Z*

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[15] The epoxide used for this experiment contained ~2% of the *E* isomer.

[16] A black precipitate of tellurium formed immediately. The numbers written beneath the products are relative peak areas (VPC).

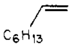
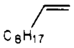
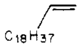
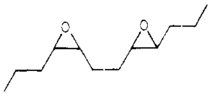
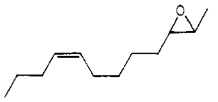
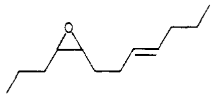
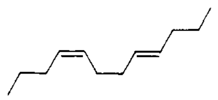
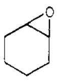
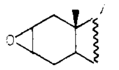
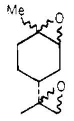
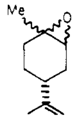
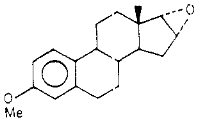
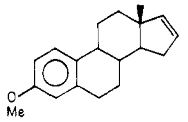
[17] A black precipitate of tellurium formed after 30 min. The numbers written beneath the products are relative peak areas (VPC).

[18] Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1973**, 253. Incorporation of the phosphorus atom into a five-membered ring enhances the reactivity of the reagent: Mathey, F.; Muller, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *281*, 881.

[19] Chan, T. H.; Finkenbine, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2880.

[20] Chan, T. H.; Finkenbine, J. R. *Tetrahedron Lett.* **1974**, 2091.

Table II[a]

expt	epoxide	mmol	Te, mmol	phosphite (mmol)	reaction time, h[b]	product(s)	% yield	procedure
1		95	1.7	$(EtO)_2PONa$ (107)	24		72	*c*
2		64	15.7	$(EtO)_2PONa$ (91)	26		70	*d*
3		6.6	1	$(EtO)_2PONa$ (11)	12		91	*e*
4		4		$(EtO)_2P(O)TeLi$ (4.4)	17		46.8[f]	
							5.2[g]	*g*
							6.6	
5		1.2	0.28	$(EtO)_2PONa$ (1.4)	42		88 (VPC)	*h*
6		0.26	0.26	$(EtO)_2POLi$ (0.29)	5.5 (reflux)	5α-cholest-2-ene	90	*j*
7		1.5	0.1	$(EtO)_2PONa$ (3.0)	18.5		76 (VPC)	*k*
8		0.6	1.6	$(EtO)_2POLi$ (1.9)	46 (reflux)		39	*l*

[a] Unless otherwise stated, reactions were run in ethanol at room temperature and yields refer to isolated products. [b] This includes the time taken to add the reagent. [c] $(EtO)_2PONa$ added continuously over 11 h. [d] $(EtO)_2PONa$ added in portions during 20 h. [e] $(EtO)_2PONa$ added in portions over 2 h. [f] Ratio of *Z*:*E* olefins was 9:1 as judged by the ^1H NMR spectrum of the mixture. [g] $(EtO)_2P(O)TeLi$ added in portions over 15 h. [h] Epoxide added in one lot to mixture of the other ingredients. [i] 5α-Cholestane skeleton. [j] See Experimental Section. [k] $(EtO)_2PONa$ added in portions over 17 h. [l] Tellurium reagent generated in presence of epoxide (with THF) and solvent then replaced by EtOH.

epoxides, as compared with the *E* isomers, is the same kind of behavior observed[21] in the reduction of isomeric epoxides by lithium aluminum hydride. Formation of a cyclic intermediate (see Scheme II) accounts for the slowness of reactions involving cyclopentene oxides because for these compounds such an intermediate is geometrically unfavorable.[22] The epitelluride proposed is a compound class that has been detected spectroscopically[23] and, lastly, in accordance with the scheme, we find that one of the reaction products is sodium diethyl phosphate. We isolated diethylphosphoric acid from the deoxygenation of ethylene oxide and characterized the material spectroscopically (^1H and ^{31}P NMR).

Conclusions

The results of our preparative experiments show that the use of *O*,*O*-diethyl phosphorotelluroates for deoxygenation is a general process. The method is very mild for terminal epoxides and it can be run for these cases, as well as for certain others, under conditions that approach a catalytic nature with respect to tellurium.[24]

Experimental Section

Ethanol was dried by the Lund–Bjerrum method and THF was dried by distillation from sodium (benzophenone indicator). HMPA was distilled (oil pump vacuum) from sodium. Oven-dried apparatus was used for all deoxygenations. Nitrogen was purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[25] and then through a similar column of Drierite. All reactions, even when not specifically stated, were done under nitrogen. Inlet and

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(21) Mihailović, M. Lj.; Andrejević, V.; Milovanović, J.; Janković, J. *Helv. Chim. Acta* **1976**, *59*, 2305.

(22) It is appreciated that transfer of phosphorus from tellurium to oxygen may be intermolecular.

(23) Connor, J.; Greig, G.; Strausz, O. P. *J. Am. Chem. Soc.* **1969**, *91* 5695. Connor, J.; van Rooselaar, A.; Fair, R. W.; Strausz, O. P. *J. Am. Chem. Soc.* **1971**, *93*, 559.

(24) For other methods of deoxygenating epoxides see: Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538. Vedejs, E.; Fuchs, P. L. *Ibid.* **1971**, *93*, 4070. Dervan, P. B.; Shippey, M. A. *Ibid.* **1976**, *98*, 1265. Reetz, M. T.; Placky, M. *Synthesis* **1976**, 199. Fujisawa, T.; Sugimoto, K.; Ohta, H. *Chem. Lett.* **1974**, 883. Calō, V.; Lopez, L.; Mincuzzi, A.; Pesce, G. *Synthesis* **1976**, 200. Rosenblum, M.; Saidi, M. R.; Madhavarao, M. *Tetrahedron Lett.* **1975**, 4009. Alper, H.; Des Roches, D. *Ibid.* **1977**, 4155. Dowd, P.; Kong, K. *J. Chem. Soc., Chem. Commun.* **1974**, 384.

(25) An American supplier of this BASF catalyst is Chemical Dynamics Corp., Hadley Industrial Plaza, South Plainfield, NJ 07080.

exit needles for nitrogen were passed through a septum on the apparatus and, after a few minutes (provided no gas was to be generated in the reaction) the exit needle was removed so as to keep the contents under a slight static pressure of nitrogen. For yields evaluated by VPC an internal standard was used. Silica gel for TLC was Merck Type 60-PF-254. For TLC plates impregnated with silver nitrate, the % $AgNO_3$ refers to (weight of $AgNO_3$)/(weight of silica gel).

Standard Solution of Sodium Diethyl Phosphite. Diethyl phosphite (14.24 g, 103 mmol) was injected over 15 min into a magnetically stirred solution of sodium (2.39 g, 104 mmol) in anhydrous ethanol (150 mL). The solution was stirred for at least 30 min prior to use and was stored under a slight static pressure of nitrogen.

Standard Solution of Lithium Diethyl Phosphite in THF. Diethyl phosphite (5.375 g, 38.92 mmol) was stirred overnight with dry THF (20 mL) and lithium (270.1 mg, 38.92 mmol, cut into small pieces). All the lithium dissolved and the solution was stored under a slight static pressure of nitrogen.

Standard Solution of Potassium Diethyl Phosphite in THF. The method used for the corresponding lithium salt was followed but with potassium (315.7 mg, 8.074 mmol) and diethyl phosphite (1.125 g, 8.146 mmol).

Preparation of (4*E*,8*Z*)-4,5:8,9-Diepoxydodecane. (4*E*,8*Z*)-Dodecadiene[26] (392.5 mg, 2.36 mmol) was dissolved in dichloromethane (50 mL) and the solution was cooled in an ice bath. *m*-Chloroperbenzoic acid (982.2 mg, 4.83 mmol) in dichloromethane (20 mL) was added over 20 min with stirring. The temperature was kept near 0 °C for 2 h more and stirring was continued overnight at room temperature. The solution was washed with aqueous sodium hydroxide (50 mL, 1 N) and then with water. The organic layer was dried (Na_2SO_4) and evaporated at room temperature (water pump). The colorless residue was distilled in a Kugelrohr apparatus (oven temperature 73 °C, 0.05 mm) to give the diepoxide (406.7 mg, 86%) as a colorless, homogeneous (TLC, silica gel, chloroform) liquid: NMR ($CDCl_3$) δ 0.6–1.2 (m, 6 H), 1.2–2 (m, 12 H), 2.5–2.8 and 2.8–3.1 (two partially overlapping m, each 2 H); ^{13}C NMR ($CDCl_3$) δ 58.9, 58.7, 58.3, 58, 57.2, 57.1, 56.7, 56.4, 34.1, 29.8, 29.6, 29.2, 24.8, 24.4, 19.9, 19.4, 14.0; exact mass 198.1618 [calcd for $C_{12}H_{22}O_2$, 198.1627]. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.82; H, 11.28. The ^{13}C NMR confirms the expectation that the material is a mixture of the syn and anti diastereoisomers.

1,2:8,9-Diepoxy-*p*-menthane. This compound, as a mixture of isomers, was prepared from *d*-limonene by the literature[27] procedure.

Comparative Reactivity of $(EtO)_2P(O)SeNa$ and $(EtO)_2P(O)TeNa$. A. Reactions of $(EtO)_2P(O)SeNa$ with 1,2-Epoxyoctane. (a) Sodium diethyl phosphite (243.8 mg, 1.523 mmol) in ethanol (1 mL of a stock solution) was injected into a 5-mL septum-closed flask containing selenium powder (27.3 mg, 0.346 mmol). The mixture was stirred for a few minutes until all the metal had dissolved and then 1,2-epoxyoctane (197.6 mg, 1.541 mmol) was injected. Stirring was continued for 13 h and the mixture was then examined by VPC with the following result: (relative peak areas) epoxide:olefin 12:1.

(b) With the exception noted below the above experiment was repeated using selenium (114.9 mg, 1.455 mmol), sodium diethyl phosphite (243.8 mg, 1.523 mmol) in ethanol (1 mL), and 1,2-epoxyoctane (164.1 mg, 1.280 mmol). (Prior to injection of epoxide the selenium–sodium diethyl phosphite mixture was stirred 1.5 h. Not all the selenium dissolved.) Stirring was continued for 13 h and the mixture was then examined by VPC with the following result: (relative peak areas) epoxide:olefin 7:23.

B. Reaction of $(EtO)_2P(O)TeNa$ with 1,2-Epoxydecane. (a) Sodium diethyl phosphite (219.3 mg, 1.37 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (10 mg, 0.0784 mmol). The mixture was stirred for a few minutes until all the metal had dissolved and then 1,2-epoxydecane (160 mg, 1.024 mmol) and octane (130.4 mg, as internal standard) were injected. The mixture remained clear and periodic analysis by VPC showed that the epoxide was being converted into olefin. After 1.5 h a black precipitate started to form. After 7.5 h all the epoxide had reacted (VPC) and the absolute yield of olefin was 71.8%.

(b) The experiment was repeated with the ethanol stock solution (2 mL), tellurium powder (30 mg, 0.235 mmol), 1,2-epoxydecane (172.4 mg, 1.103 mmol), and octane (149.6 mg). This reaction differs from that just described only in the increased amount of tellurium. A black precipitate formed 30 min after addition of the epoxide and reaction was complete within 2 h (VPC control). The yield of olefin (VPC) was 90.2%.

Reaction of $(EtO)_2P(O)TeNa$ with a Mixture of 1,2-Epoxyoctane and 7-Oxabicyclo[4.1.0]heptane. Sodium diethyl phosphite (110 mg, 0.687 mmol) in ethanol (1 mL of a stock solution) was injected into a 5-mL septum-closed flask containing tellurium powder (28.7 mg, 0.225 mmol). The mixture was stirred and after a few minutes all the metal had dissolved. 1,2-Epoxyoctane (161.1 mg, 1.256 mmol) was then injected, followed immediately by 7-oxabicyclo[4.1.0]heptane (120 mg, 1.223 mmol) and dodecane (129.5 mg, as internal standard). Within 3 min a black precipitate formed, and after 30 min (from the time of addition of the epoxides) more sodium diethyl phosphite (55 mg, 0.344 mmol) in ethanol (0.5 mL) was injected. After a further 30 min had elapsed, a black precipitate formed again and another identical portion of the stock solution of sodium diethyl phosphite was injected. The mixture was examined by VPC 15 min later, the following relative peak areas being found: 1-octene (14), 1,2-epoxyoctane (7), cyclohexene (1), 7-oxabicyclo[4.1.0]heptane (14). More sodium diethyl phosphite (110 mg, 0.687 mmol) was injected in two equal portions, one at this stage and the other after 1 h, bringing the total quantity used to 330 mg (2.06 mmol). Stirring was continued 3 h beyond the last addition and the following yields (based on the dodecane internal standard) were measured by VPC: 1-octene (103.9%), 1,2-epoxyoctane (trace), cyclohexene (23.0%), 7-oxabicyclo[4.1.0]heptane (85%).

Reaction of $(EtO)_2P(O)TeNa$ with (*E*)-4,5-Epoxyoctane. Sodium *O,O*-diethyl phosphite (219.9 mg, 1.37 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (28.8 mg, 0.226 mmol) and the mixture was stirred magnetically until all the metal had dissolved. (*E*)-4,5-Epoxyoctane (152.6 mg, 1.19 mmol) was added by syringe followed by dodecane (172.4 mg, as internal standard). After 13 h at room temperature analysis by VPC showed that the absolute yield of 4-octene was <1% and that >97% of the epoxide remained.

General Method for Preparation of *O,O*-Diethyl Phosphorotelluroates. The apparatus consisted of a 5-mL round-bottomed flask fused onto the end of a small condenser which carried a straight vacuum takeoff. Tellurium powder and a small magnetic stirring bar were placed in the flask. The apparatus was assembled and evacuated to 0.05 mm. The tap of the vacuum takeoff was closed and the tip of the hose connector portion was capped with a septum. The space between the tap and the septum was flushed with nitrogen, and nitrogen was then allowed to leak slowly into the flask. The appropriate diethyl phosphite in THF (from a stock solution) was injected into the vessel followed, sometimes, by a small volume of pure, dry THF. The mixture was stirred (under nitrogen) until all the tellurium had dissolved (1 to 2 h). The solvent was evaporated at room temperature through the vacuum takeoff (using an oil pump) to leave a white residue. The vacuum takeoff was capped with a septum and, by the same procedure as before, nitrogen was introduced into the flask. Anhydrous ethanol was injected to afford a colorless, and usually clear, solution.

Reaction of $(EtO)_2P(O)TeLi$ with a Mixture of (*Z*)- and (*E*)-4,5-Epoxyoctane. Solid lithium *O,O*-diethyl phosphorotelluroate was prepared as described above from tellurium powder (520 mg, 4.075 mmol) and lithium diethyl phosphite (629.9 mg, 4.373) in THF (1.5 mL of a stock solution). The salt was dissolved in anhydrous ethanol (2 mL). (*Z*)-4,5-Epoxyoctane (327 mg, 2.550 mmol) and then the *E* isomer (315 mg, 2.457 mmol) were injected into the reaction vessel. The mixture was refluxed for 1 h and then partitioned between hexane (20 mL) and water (30 mL). The hexane layer was washed with water (5 × 10 mL) and dried (Na_2SO_4). Dodecane (391.3 mg) was added as an internal standard and the mixture was analyzed by VPC using ordinary and silver nitrate impregnated columns.[28] The absolute yield/recoveries

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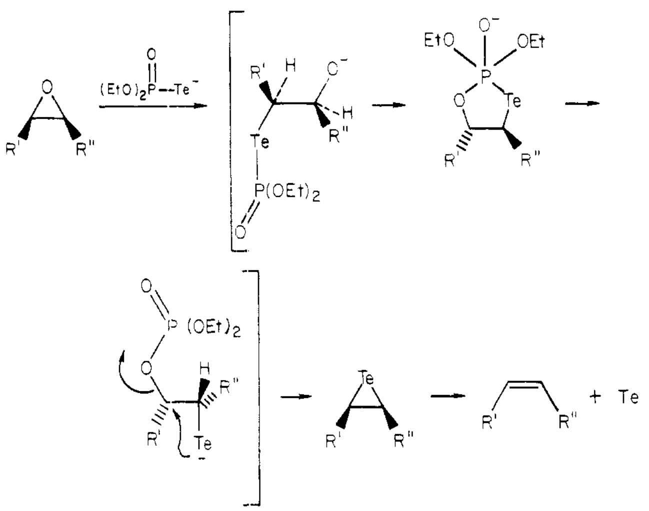
[26] Mochel, V. D.; Lawson, D. F.; Farrar, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6202.

[27] Anderson, W. K.; Veysoglu, T. *J. Org. Chem.* **1973**, *38*, 2267.

Scheme II



were as follows: (*E*)-4,5-epoxyoctane, 72.2%; (*Z*)-4,5-epoxyoctane, 12.4%; (*Z*)-oct-4-ene, 80.6%; (*E*)-oct-4-ene, 25.2%.

Comparison of the Reactivity of Potassium, Sodium, and Lithium *O,O*-Diethyl Phosphorotelluroates. (a) Reaction of $(EtO)_2P(O)TeK$ with (*Z*)-4,5-Epoxyoctane. Solid potassium *O,O*-diethyl phosphorotelluroate was prepared by the special technique described above from tellurium powder (31 mg, 0.243 mmol), potassium diethyl phosphite (59.3 mg, 0.337 mmol) in THF (0.25 mL of a stock solution), and a portion (1 mL) of dry THF. The solid residue was stirred with anhydrous ethanol (1.5 mL) to give a clear colorless solution. (*Z*)-4,5-Epoxyoctane (37.1 mg, 0.289 mmol) was introduced by syringe and the mixture was stirred (nitrogen atmosphere) for 22 h. At this stage a tellurium mirror had been deposited and analysis of the reaction mixture by VPC showed the following relative mole ratios: olefin:epoxide 1:3. The mixture was refluxed for 7.5 h and VPC analysis then showed new relative mole ratios: olefin:epoxide 5:3.

(b) Reaction of $(EtO)_2P(O)TeNa$ with (*Z*)-4,5-Epoxyoctane. Tellurium powder (175.7 mg, 1.38 mmol) was added to a stirred solution of sodium diethyl phosphite [from diethyl phosphite (308.9 mg, 2.24 mmol), sodium (51.6 mg, 2.24 mmol), and dry ethanol (3 mL)]. After 2 h all but a trace of tellurium had dissolved and (*Z*)-4,5-epoxyoctane (260 mg, 2.03 mmol) was injected. After 12 h at room temperature analysis of the reaction mixture by VPC showed the following relative mole ratio: epoxide:olefin 5.29:1. After 24 h the ratio was 3.2:1.

(c) Reaction of $(EtO)_2P(O)TeLi$ with (*Z*)-4,5-Epoxyoctane. Solid lithium *O,O*-diethyl phosphorotelluroate was prepared in the usual way from tellurium powder (68.1 mg, 0.53 mmol) and lithium diethyl phosphite (140.1 mg, 0.973 mmol) in THF (1 mL of a stock solution). The reagent was stirred with anhydrous ethanol (1.5 mL) and (*Z*)-4,5-epoxyoctane (108 mg, 0.842 mmol) was added. After 12 h at room temperature analysis of the reaction mixture by VPC showed the following relative mole ratios: epoxide:olefin 0.95:1.

Stereochemistry of the Deoxygenation. (a) Reaction of $(EtO)_2P(O)TeLi$ with (*Z*)-4,5-Epoxyoctane. The previous experiment was repeated using tellurium powder (363.2 mg, 2.846 mmol) and lithium *O,O*-diethyl phosphite (419.9 mg, 2.915 mmol) in THF (1 mL of a stock solution). The solid tellurium reagent was stirred with anhydrous ethanol (2 mL) and (*Z*)-4,5-epoxyoctane (359.9 mg, 2.807 mmol) was added. The mixture was then refluxed for 2 h and partitioned between hexane (20 mL) and water (10 mL). The hexane layer was washed with water (3 × 10 mL) and was then dried ($MgSO_4$). Dodecane (311.6 mg) was added to the solution as an internal standard and VPC analysis showed the absolute yields of olefin and epoxide to be 76.7% and 16.5%, respectively. Analysis by VPC on a silver nitrate impregnated column[28] showed that the ratio of (*Z*)- to (*E*)-oct-4-ene was 56.1:1.

(b) Reaction of $(EtO)_2P(O)TeLi$ with (*E*)-4,5-Epoxyoctane. The previous experiment was repeated using tellurium powder (315.5 mg, 2.47 mmol) and lithium diethyl phosphite (419.9 mg, 2.92 mmol) in THF (1 mL of a stock solution). The solid tellurium reagent was stirred with anhydrous ethanol (2 mL) and (*E*)-4,5-epoxyoctane (362.5 mg, 2.83 mmol) was added. The mixture was refluxed for 19 h and it was then partitioned between hexane (20 mL) and water (10 mL). The hexane layer was washed with water (5 × 8 mL), dried ($MgSO_4$), and analyzed by VPC using a silver nitrate impregnated column. The mole ratio of *E*:*Z* olefin was 62:1. Dodecane (308.1 mg, as an internal standard) was added to the hexane solution and VPC analysis showed that the yield of olefin was 46.6% and the recovery of epoxide 27.9%.

Deoxygenation of 1,2-Epoxyoctane. Nonstoichiometric Procedure with $(EtO)_2P(O)TeNa$. Tellurium powder (214.9 mg, 1.684 mmol) was placed in a 250-mL round-bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and then kept under a slight static pressure of the gas. 1,2-Epoxyoctane (12.180 g, 95.01 mmol) was added by syringe and a stock solution of sodium diethyl phosphite [170 mL, 107.4 mmol of $(EtO)_2P(O)Na$] was added with stirring at a uniform rate (syringe pump) over 11 h. The mixture was then stirred overnight, after which it was filtered through cotton wool, diluted with water (1 L), and extracted with isopentane (3 × 300 mL). The combined organic extract was dried (Na_2SO_4) and, with a spinning-band apparatus, it was concentrated and distilled. 1-Octene (7.763 g, 72%) was obtained as a colorless liquid, bp 112 °C. Analysis by VPC (on two different silver ion impregnated columns)[29] showed that the material was better than 99% pure. (The columns were able to separate all octene isomers.)

Deoxygenation of 1,2-Epoxydecane. Nonstoichiometric Procedure with $(EtO)_2P(O)TeNa$. Tellurium powder (2.00 g, 15.67 mmol) was placed in a 100-mL round-bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and kept under a slight static pressure of the gas. 1,2-Epoxydecane (10.00 g, 63.99 mmol) was added by syringe and a stock solution of sodium *O,O*-diethyl phosphite [47.0 mL, 71.6 mmol of $(EtO)_2P(O)Na$] was added with stirring at a uniform rate (syringe pump) over 1.5 h. After a further 2 h (stirring) an additional portion of stock solution [5 mL, 7.62 mmol of $(EtO)_2P(O)Na$] was added rapidly. Stirring was continued 8.5 h and, since epoxide was still present (VPC control), a further portion [5 mL, 7.62 mmol of $(EtO)_2P(O)Na$] was added rapidly. After 8 h a final addition [3 mL, 4.57 mmol of $(EtO)_2P(O)Na$] of stock solution was made and stirring was continued for 6 h. At this stage [i.e., total reaction time of 26 h; total reagent 91.41 mmol of $(EtO)_2P(O)Na$] the mixture was poured into water (100 mL) and extracted with dichloromethane (5 × 30 mL). The combined extracts were washed with water, dried (Na_2SO_4), and concentrated by slow distillation (1 atm) using a Vigreux column (1 × 15 cm). Spinning-band distillation of the residue gave 1-decene (6.286 g, 70%) as a colorless liquid, bp 70 °C (water pump vacuum). The material was 99.9% pure by VPC.

Deoxygenation of 1,2-Epoxyeicosane. Nonstoichiometric Procedure with $(EtO)_2P(O)TeNa$. Tellurium powder (130 mg, 1.019 mmol) and 1,2-epoxyeicosane (1.956 g, 6.596 mmol) were placed in a 25-mL round-bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and then kept under a slight static pressure of the gas. A stock solution of sodium diethyl phosphite [110 mg of $(EtO)_2P(O)Na$ mL^{-1}] was injected in portions in the following manner. Each injection caused the tellurium to dissolve; the next injection was not made until the metal had precipitated. The

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(28) The silver nitrate impregnated column was prepared as follows: Silver nitrate (40 g) was dissolved in ethylene glycol (40 g) and a portion (20 g) of the solution was distributed over Chromosorb P (acid washed 60–80 mesh, 40 g). The packing was used to fill a stainless steel column (20 ft × 1/8 in. o.d.). Use of test mixtures showed that this column could separate cleanly the *Z* and *E* isomers of 4-octene and could also resolve most of the other octene isomers. The column was used at temperatures in the range 60–80 °C. Cf.: Gil-Av, E.; Herling, J.; Shabtai, J. *J. Chromatogr.* **1958**, *1*, 508. Bendel, E.; Fell, B.; Gartzen, W.; Kruse, G. *Ibid.* **1967**, *31*, 531.

(29) One of the columns was that described in ref 28. The other was made as follows: Silver tetrafluoroborate (3 g) was dissolved in 3,3'-oxybis[propionitrile] (20 g) and a portion (12 g) of the solution was distributed over Chromosorb P (acid washed, 60–80 mesh, 48 g). The packing was used to fill a stainless steel column (40 ft × 1/8 in. o.d.).

portions and addition times of the stock solution were 5.00 mL (0 min), 5.00 mL (20 min), 2.00 mL (55 min), 2.00 mL (85 min), 2.00 mL (115 min); i.e., 16.00 mL containing 1.760 g (10.994 mmol) of sodium diethyl phosphite was added over ca. 2 h. The mixture was stirred overnight, the tellurium was removed by filtration through a plug of cotton wool, and the filtrate was partitioned between dichloromethane (50 mL) and water (50 mL). The aqueous layer was washed with dichloromethane (50 mL) and the combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed over neutral grade I alumina (3 × 18 cm) with pentane to afford eicosene (1.697 g, 91%) as a colorless liquid that crystallized on standing. The material was homogeneous by TLC (silica impregnated with 15% silver nitrate, benzene) and was identified by spectroscopic comparison with an authentic sample of eicosene.

Selective Deoxygenation of (4*E*,8*Z*)-4,5:8,9-Diepoxydodecane. Stoichiometric Procedure with $(EtO)_2P(O)TeLi$. Lithium *O,O*-diethyl phosphorotelluroate was prepared by the general procedure described above from tellurium powder (588.1 mg, 4.609 mmol) and lithium diethyl phosphite (627 mg, 4.353 mmol) in THF (2.25 mL of a stock solution), the mixture being diluted with dry THF (5 mL). The crystalline reagent was generated in the usual way and then dissolved in dry ethanol (5 mL). (4*E*,8*Z*)-4,5:8,9-Diepoxydodecane (733.5 mg, 4.023 mmol) was placed in a 10-mL round-bottomed flask closed with a septum. The flask was purged with nitrogen and kept under a slight static pressure of the gas. By use of a syringe the solution of tellurium reagent (3 mL) was added, with magnetic stirring, to the diepoxide. After 12 h a further portion of the solution (1 mL) was added and, after 3 h, the remainder of the tellurium reagent solution was injected, using dry ethanol (2 × 1 mL) as a rinse. The reaction mixture was stirred 2 h more and was then partitioned between pentane (100 mL) and water (50 mL). The aqueous phase was washed with pentane (50 mL) and the combined organic extracts were dried (Na_2SO_4) and evaporated at room temperature (water pump). The residue was chromatographed over silica gel (1.5 × 40 cm) with chloroform to afford two fractions. The less polar was a colorless oil which, after Kugelrohr distillation, weighed 40.9 mg (6.6%). Its NMR and IR spectra were identical with those of (4*E*,8*Z*)-4,8-dodecadiene. The second fraction was distilled (Kugelrohr, oven temperature 62 °C, 0.15 mm) to afford monoepoxide (357 mg, 52.94%) as a colorless liquid. Examination by TLC (silica, 5% $AgNO_3$, chloroform) showed a large spot (jet black with hot sulfuric acid) at $R_f \sim 0.5$ and a faint spot (dark with hot sulfuric) at $R_f \sim 0.55$. Bisepoxide was absent. The material had NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J = 7.4 Hz, 3 H), 0.96 (t, J = 4 Hz, 3 H), 1.3–1.7 (m, 8 H, incorporating s, J = 7.3 Hz, 2 H), 2.01 (q, J = 6.8 Hz, 2 H), 2.19 (q, J = 6.8 Hz, 2 H), 2.68 (approximate t, J = 4.9 Hz, 2 H), 5.3–5.5 (m, 2 H); [a weak multiplet centered at δ 2.92 indicated (by comparison with signal at δ 2.68) that 10.8% of (4*Z*,8*E*)-4,5-epoxydodec-8-ene was present; NMR spectra ($CDCl_3$) on authentic (*Z*)- and (*E*)-4,5-epoxyoctanes showed the vinyl multiplets at δ 2.8 and 2.65, respectively]; ^{13}C NMR ($CDCl_3$) δ 130.6, 128.6, 58.7, 58.3, 34.2, 32.4, 29.3, 23.9, 22.8, 19.4, 14.0, 13.8. The ^{13}C NMR spectrum showed weak signals at 131.2, 129.2, 57.0, 56.6, 34.7, 30.0, 29.7, 28.1, 22.7, 20.0. Exact mass 182.1671 (calcd for $C_{12}H_{22}O$ 182.1669).

Deoxygenation of 7-Oxabicyclo[4.1.0]heptane. Nonstoichiometric Procedure with $(EtO)_2P(O)TeNa$. Sodium diethyl phosphite (219.9 mg, 1.374 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (35.3 mg, 0.277 mmol) and the mixture was stirred magnetically until all the metal had dissolved. 7-Oxabicyclo[4.1.0]heptane (119.5 mg, 1.218 mmol) was added by syringe followed by dodecane (153.7 mg). The progress of the reaction was monitored by VPC and after 42 h of stirring at room temperature no epoxide remained. The absolute yield of cyclohexene was 88.6%.

Deoxygenation of 2β,3β-Oxido-5α-cholestane. Stoichiometric Procedure with $(EtO)_2P(O)TeLi$. Lithium *O,O*-diethyl phosphorotelluroate was prepared by the general procedure described above from tellurium powder (33.0 mg, 0.259 mmol) and lithium diethyl phosphite (41.9 mg, 0.29 mmol) in THF (0.15 mL of a stock solution), the mixture being diluted with dry THF (1 mL). The crystalline reagent was generated in the usual way and then dissolved in dry ethanol (0.2 mL). Another unit of the special apparatus used to generate the tellurium reagent was charged with 2β,3β-oxido-5α-cholestane (100.0 mg, 0.259 mmol) and filled with nitrogen by the special technique described above for use with such apparatuses. By means of a syringe, the ethanol solution of the tellurium reagent was injected, with magnetic stirring, into the reaction vessel with further portions (3 × 0.2 mL) of ethanol as a rinse. (This protocol was adopted because the steroid is insoluble in ethanol, which is a good reaction solvent.) The reaction mixture was refluxed for 5.5 h and the black mixture was partitioned between ether (50 mL) and water (50 mL). The ether layer was washed with water (2 × 10 mL) and once with saturated aqueous sodium chloride solution and it was then dried ($MgSO_4$). Evaporation and chromatography of the residue over silica gel (2.5 × 10 cm) with toluene gave 5α-cholest-2-ene (86.4 mg, 90%): mp 73–75 °C; $[\alpha]_D$ 66.7° (c 2.745, $CHCl_3$).[30] The material was homogeneous by TLC (silica impregnated with 5% $AgNO_3$; 2:98 benzene–hexane). The ^{13}C NMR spectrum showed a 1:1 correspondence with the published data.[31]

Selective Deoxygenation of 1,2:8,9-Diepoxy-*p*-menthane. Nonstoichiometric Procedure with $(EtO)_2P(O)TeNa$. Tellurium powder (12.1 mg, 0.095 mmol) was placed in a 10-mL round-bottomed flask equipped with a magnetic stirring bar and closed by a rubber septum. The flask was purged with nitrogen and kept under a slight static pressure of the gas. 1,2:8,9-Diepoxy-*p*-menthane (255.1 mg, 1.516 mmol) and dodecane (122.2 mg, internal standard) were injected followed by sodium diethyl phosphite (487.6 mg, 3.046 mmol) in ethanol (2 mL of a stock solution). The phosphite solution was added in 0.20-mL portions over 17 h, each portion being added only when tellurium had precipitated after the previous addition. The time needed for the black precipitate to appear changed from 20 min (after the first addition) to 7 h (after the last addition). The mixture was stirred 1.5 h after the final appearance of the tellurium deposit, and analysis of the solution by VPC showed that the absolute yield of 1,2-epoxy-*p*-menth-8-ene[32] was 76%. A portion was isolated and its NMR spectrum confirmed the gross structure.

Deoxygenation of 16α,17α-Epoxy-3-methoxyestra-1,3,5(10)-triene. Stoichiometric Procedure with $(EtO)_2P(O)TeLi$. The tellurium reagent was generated in the usual way, but in the presence of 16α,17α-epoxy-3-methoxyestra-1,3,5(10)-triene[33] (169.5 mg, 0.60 mmol), from tellurium (201 mg, 1.58 mmol) and lithium diethyl phosphite (275 mg, 1.91 mmol) in THF (2 mL of a stock solution). The solid reagent, admixed with the epoxide, was stirred with dry ethanol (1.5 mL) and the mixture was refluxed for 46 h. It was then applied (without removal of solvent) to a column of silica gel (2.5 × 20 cm). Development with 1:1 hexane–benzene gave 62.8 mg (39%) of 3-methoxyestra-1,3,5(10),16-tetraene as a homogeneous (TLC, silica, 1:1 hexane–benzene) solid: mp 65–68 °C; $[\alpha]_D$ 108° (c 2.38, $CHCl_3$) [lit.[33] mp 66–68 °C; $[\alpha]_D$ 109°].

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Registry No. 1 (M = K), 72726-64-8; 1 (M = Na), 65857-68-3; 1 (M = Li), 72726-65-9; sodium diethyl phosphite, 2303-76-6; lithium diethyl phosphite, 72726-66-0; potassium diethyl phosphite, 54058-00-3; (4*E*,8*Z*)-4,5:8,9-diepoxydodecane, isomer 1, 72726-67-1; (4*E*,8*Z*)-4,5:8,9-diepoxydodecane, isomer 2, 72776-96-6; (4*E*,8*Z*)-dodecadiene, 38926-02-2; 1,2-epoxyoctane, 2984-50-1; 1,2-epoxydecane, 2404-44-6; 7-oxabicyclo[4.1.0]heptane, 286-20-4; (*E*)-4,5-epoxyoctane, 1689-70-9; tellurium, 13494-80-9; (*Z*)-4,5-epoxyoctane, 1439-06-1; (*Z*)-oct-4-ene, 7642-15-1; (*E*)-oct-4-ene, 14850-23-8; 1,2-

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[30] Reported values of melting points are in the range 66–75 °C; and for $[\alpha]_D$ ($CHCl_3$), 66 ± 2: Jacques, J.; Kagan, G.; Ourisson, G. In "Tables of Constants and Numerical Data"; Allard, S., Ed.; Pergamon Press: Oxford, 1965; Vol. 14.

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epoxyeicosane, 19780-16-6; 2β,3β-oxido-5α-cholestane, 2789-50-6; 1,2:8,9-diepoxy-*p*-menthane, 96-08-2; 16α,17α-epoxy-3-methoxyestra-1,3,5(10)-triene, 28336-32-5; 1-octene, 111-66-0; 1-decene, 872-05-9; 1-eicosene, 3452-07-1; (4*Z*,8*E*)-8,9-epoxydodec-4-ene, 72726-68-2; (4*Z*,8*E*)-4,5-epoxydodec-8-ene, 72776-97-7; cyclohexene, 110-83-8; 5α-cholest-2-ene, 570-73-0; 1,2-epoxy-*p*-menth-8-ene, isomer 1, 4680-24-4; 3-methoxyestra-1,3,5(10),16-tetraene, 28336-31-4; 1,2-epoxy-*p*-menth-8-ene, isomer 2, 6909-30-4.

Thermolyses of 3-Alkyl-4-phenyl-2-oxetanones and Related Compounds

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Thermolyses of *cis*- and *trans*-3-methyl-4-phenyl-2-oxetanones (**1c** and **1t**), *cis*- and *trans*-3-isopropyl-4-phenyl-2-oxetanones (**2c** and **2t**), and *cis*- and *trans*-3-*tert*-butyl-4-phenyl-2-oxetanones (**3c** and **3t**) resulted in quantitative formation of the corresponding styrene which kept stereochemical uniformity. The strict stereospecificity suggests the concerted nature of the fragmentation. The rates of reaction of these 2-oxetanones and related compounds, including 3,3-dimethyl-4-phenyl-2-oxetanone (**4**), 3,3-dimethyl-4,4-diphenyl-2-oxetanone (**5**), 4,4-dimethyl-3-phenyl-2-oxetanone (**6**), and *cis*- and *trans*-3,4-diphenyl-2-oxetanones (**7c** and **7t**), in decane and/or dodecane were studied. The reactivity of 4-phenyl-2-oxetanone (**8**) was estimated from that of *p*-nitro derivative **9**. The relative rates at 150 °C were **1c**/**2c**/**3c**/**1t**/**2t**/**3t**/**4**/**5**/**6**/**7c**/**7t**/**8**, 1.0:0.31:0.028:11.4.3:2.1:0.29:6.9:3.8:(1.7):(13):(17). The least substituted **8** exhibited the highest reactivity. In 3,4-disubstituted derivatives, the trans isomer reacted more rapidly than the corresponding cis isomer without exception. For **1**–**3**, it is shown that the bulkier the alkyl group, the slower the fragmentation. Since significant positive charge development has been previously shown to occur only at C-4, but not at C-3, the reactivity sequence cannot be attributed to the electronic effect of the alkyl group. On the other hand, if an assumption that the important factor is the increased steric strain at the concerted $2_s + 2_a$ transition state is accepted, the results can be explained reasonably. Indeed, log k_1 values of **1c**, **2c**, **3c**, and **8** correlated quite linearly with the steric parameter E_s or υ. The relative reactivities of **4**–**7** are also discussed.

Since the concerted nature may be anticipated in the decarboxylation of 2-oxetanones,[1] mechanistic studies of such reactions should be of great interest. Up to the present time there have been several papers describing the stereospecific fragmentation of certain 2-oxetanones,[2] but kinetic studies are rather deficient, only a limited number of works having appeared.[3] We have recently uncovered the substituent electronic effects at both the C-3 and C-4 positions,[3c] but our results themselves are still insufficient to account for certain well-documented behavior of 2-oxetanones. In particular, the observations that heavily substituted compounds, such as tetrasubstituted derivatives, are relatively stable[4] whereas those substituted by a smaller number of groups at times result in easy fragmentation[2a–c,3b,5,6] are hardly explained by the electronic effects.[3c] Because our previous results predict that the substitution of a hydrogen at C-4 by an electron-releasing group should *increase* the reactivity while any group at C-3 could not influence the reactivity, it is, therefore, highly desirable to carry out a systematic study which can provide a further clarification to the structure–reactivity relationship of 2-oxetanones. In this paper, we studied the thermal behavior of geometrically pure 3-alkyl-4-phenyl-2-oxetanones **1**–**3** and related compounds **4**–**9**.

The scarcity of the kinetic data, in particular those of the 4-phenyl derivatives, should be, at least in part, due to the extreme sensitivity of such compounds toward acidic impurities in the reaction system. We have previously developed a method to overcome these difficulties.[3c]

Results

Substrates. 2-Oxetanones, including *cis*- and *trans*-3-methyl-4-phenyl- (**1c** and **1t**), *cis*- and *trans*-3-isopropyl-4-phenyl- (**2c** and **2t**), *cis*- and *trans*-3-*tert*-butyl-4-phenyl- (**3c** and **3t**), 3,3-dimethyl-4-phenyl- (**4**), 3,3-dimethyl-4,4-diphenyl- (**5**), 4,4-dimethyl-3-phenyl- (**6**), and *cis*- and *trans*-3,4-diphenyl-2-oxetanones (**7c** and **7t**), were prepared by the cyclization of the corresponding 3-hydroxypropionic acid according to the method developed by Adam, Baeza, and Liu.[2c] The geometrical isomers were separated at the

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[6] The instability of 2-oxetanones of low molecular weight is also due to their tendency to form polyesters.[5a–d]

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