New and Selective Method for Deoxygenating Epoxides: Use of the Organic Tellurium Reagent Sodium *OO*-Diethyl Phosphorotelluroate

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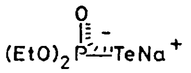
Summary Sodium OO-diethyl phosphorotelluroate (**1**), which can be used as a stoicheiometric reagent or generated continuously *in situ* from a catalytic portion of Te, converts terminal epoxides efficiently into the corresponding olefins.

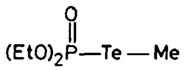
Although there is substantial literature on organic compounds containing Te[1] the subject has never before provided any mild and general reagents for synthetic transformations that are difficult by classical methods. We report the first example of such a reagent.[2]

When terminal epoxides are treated with (**1**) they are converted into olefins at room temperature (see Table). To test for double bond mobility, 1,2-epoxyoctane was



$(\mathrm{EtO})_2\overset{\mathrm{O}}{\mathrm{P}}\text{---}\mathrm{TeNa}^{+}$

(1)



$(\mathrm{EtO})_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\text{—}\mathrm{Te}\text{—}\mathrm{Me}$

(2)

chosen because the isomers of n-octene are easy to separate.[3] Only oct-1-ene was produced, and the reaction is, therefore, regiospecific.

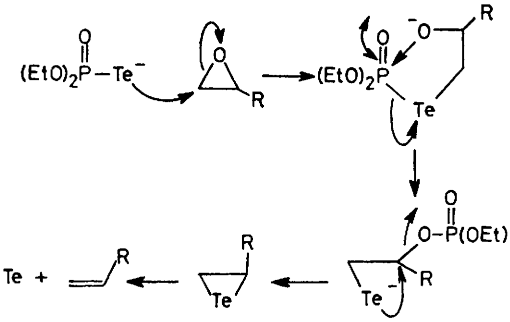
TABLE

Epoxide	Equiv. Te	Equiv. $(EtO)_2PONa$	Addition time	Total reaction time/h	% Yield of olefin[a]
1,2-Epoxyeicosane	0·16	1·69	2 h[b]	12	91·9
1,2-Epoxyoctane	0·018	1·13	11 h[c]	24	73
1,2-Epoxydecane	0·24	1·4	6 h[c]	26	70
Limonene diepoxide	0·063	2·01	11 h[b]	24	76[d,e]
Epoxycyclohexane	0·23	1·13	1 min[f]	48	88·6[d]
trans-4,5-Epoxyoctane ..	0·15	1·2	1 min[f]	12	$\leqslant 1$[d]

[a] Isolated material except where stated. [b] Added in portions. [c] Continuous addition. [d] Absolute yield determined by g.l.c. using an internal standard. [e] 1,2-Epoxy-*p*-menth-8-ene is formed. [f] The epoxide was added rapidly to a mixture of Te and $(EtO)_2PONa$.

Compound (**1**) {^{31}P n.m.r. $\delta([^2H_8]\text{-THF})$ (THF = tetrahydrofuran) $-19{\cdot}6$ p.p.m. (quintet); $^1J(P\text{–}Te)$ 2114·9 Hz; $^3J(P\text{–}OCH_2)$ 9·5 Hz}† can be prepared by stirring elemental Te with $(EtO)_2PONa$ (1 equiv.) in anhydrous EtOH.‡ Most (>81%) of the metal dissolves to give a colourless solution and evaporation leaves (**1**) as a white crystalline solid that is destroyed very rapidly by air. Addition of MeI to a solution of (**1**) generates the ester (**2**) {^{31}P n.m.r. $\delta([^2H_8]\text{-THF})$ $-1{\cdot}50$ p.p.m. (m); ^1H n.m.r. $\delta([^2H_8]\text{-THF})$ 1·9 [d, ^3J (*P*–Te–*Me*) 12·2 Hz]}§ but this compound is too sensitive to be isolated in a pure form. However, the n.m.r. characteristics of (**1**), taken together with the following chemistry, establish the structure shown.

When a terminal epoxide is added to a solution of (**1**) (1 equiv.) in EtOH an exothermic reaction occurs, Te is deposited, sodium diethyl phosphate is produced, and the epoxide is converted into the corresponding olefin. Deoxygenation does not occur in the absence of Te. A reasonable mechanism to account qualitatively for these observations is summarised in the Scheme. There is an analogy in selenium chemistry[2,4] for the pathway shown and epitellurides have been detected spectroscopically.[5]



SCHEME.

Under our reaction conditions $(EtO)_2PONa$ reacts very slowly with epoxides but rapidly with added Te. Therefore, this deoxygenation can be carried out as a catalytic process. The following experimental procedure is typical: a solution of $(EtO)_2PONa$ (1—2 equiv.) in EtOH is added at a uniform rate (usually *ca.* 0·2 equiv. h^{-1}) to a stirred mixture of Te (0·1—0·25 g. equiv.) and a solution of the epoxide (1 equiv.) in EtOH. Cooling is needed to maintain the temperature below 25 °C. After the addition is complete the mixture is left, usually overnight, and the olefin is then isolated. This procedure gives the results shown in the Table.

During the deoxygenation most, or all [depending on the rate at which $(EtO)_2PONa$ is added], of the tellurium dissolves and, if an excess of $(EtO)_2PONa$ is avoided, the Te precipitates towards the end of the reaction. If the $(EtO)_2PONa$ solution is added rapidly, but in small portions, rather than continuously, then the Te alternately passes into and out of solution and acts as a rough indicator of the progress of the reaction.

Non-terminal epoxides react slowly and, therefore, selective deoxygenations are possible: limonene diepoxide[6] gave 1,2-epoxy-*p*-menth-8-ene[6] (76% yield).

In comparison, the selenium salt corresponding to (**1**) is much less reactive and less suitable for catalytic deoxygenations.

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† The ^{31}P n.m.r. spectrum of the corresponding selenium compound has δ ($[^2H_8]$THF) — 59·3 (quintet) p.p.m.; $^2J(P\text{–}Se)$ 794·1 Hz; $^3J(P\text{–}O\text{–}CH_2)$ 9·5 Hz.

‡ The selenium salt corresponding to (**1**) is made analogously (O. Foss, *Acta Chem. Scand.*, 1947, **1**, 8).

§ $(EtO)_2P(:O)\text{–}SeMe$ has ^{31}P δ ($[^2H_8]$-THF) $-24{\cdot}0$ (m); ^1H δ ($[^2H_8]$-THF) 2·1 p.p.m. (d, J 13 Hz). For the preparation of this ester see B.P. 691, 267 (*Chem. Abs.*, 1954, **48**, 7047e).

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