Table I. Secondary Tritium Isotope Effects in E2 Reactions of $ArCLTCH_2X$ and $ArCL_2CH_2X$ (L = H or D) at 50 °C

reaction	k_H/k_T	k_D/k_T	$(k_H/k_T)_{calcd}$[c]
1[a] + EtONa/EtOH	1.204 ± 0.015	1.0314 ± 0.010	1.106 ± 0.033
2[b] + *t*-BuOK/*t*-BuOH	1.191 ± 0.012	1.0274 ± 0.008	1.092 ± 0.026

[a] 2-Phenylethyltrimethylammonium bromide. [b] 2-(*p*-Chlorophenyl)ethyl tosylate. [c] From the relation $k_H/k_T = (k_D/k_T)^{3.26}$ (ref 8 and 9).

transferred hydrogen are coupled with the stretching motion of the transferred hydrogen. The calculations also predict that the tunnel correction to the secondary tritium isotope effect should be diminished when the transferred atom is deuterium rather than protium. We report here experimental evidence that this is indeed the case.

The experiments were modeled after the earlier ones by using 2-arylethyl derivatives tracer labeled with tritium in the β-position. The resulting mixture can undergo the following elimination reactions

$$ArCL_2CH_2X + RO^- \xrightarrow{2k_1} ArCL{=}CH_2 + ROL + X^-$$

$$ArCLTCH_2X + RO^- \begin{cases} \xrightarrow{k_2} ArCL{=}CH_2 + ROT + X^- \\ \xrightarrow{k_3} ArCT{=}CH_2 + ROL + X^- \end{cases}$$

When L = H, $k_1/k_3 = (k_H/k_T)_{sec}$, and when L = D, $k_1/k_3 = (k_D/k_T)_{sec}$. We determined $(k_H/k_T)_{sec}$ and $(k_D/k_T)_{sec}$ in the manner previously described[2] for the reactions of 2-phenylethyltrimethylammonium ion (**1**) with ethoxide in ethanol and 2-(*p*-chlorophenyl)ethyl tosylate (**2**) with *tert*-butoxide in *tert*-butyl alcohol, both at 50 °C. The results are given in Table I.

The secondary k_H/k_T values are both substantial.[5] We pointed out earlier[2] that the fractionation factors of Hartshorn and Shiner[6,7] predict $k_H/k_T = 1.17$ at 50 °C for *complete* rehybridization. Since proton transfer is incomplete in the transition state, it is unlikely that rehybridization would be complete, so the actual contribution of rehybridization to k_H/k_T is probably well below 1.17. The k_D/k_T are very much smaller than the k_H/k_T and remain smaller when converted to k_H/k_T (last column of Table I) by the relationship[8,9]

$$k_H/k_T = (k_D/k_T)^{3.26} \quad (1)$$

This relationship is obeyed by the calculated *semiclassical* (without tunneling) primary (error ≤ 3.8%) and secondary (error ≤ 1.1%) isotope effects reported in ref 4. If masses are assumed to be in the ratio of reduced masses of C-H, C-D, and C-T instead of 1:2:3, the exponent in eq 1 becomes 3.34, but an exponent of ca. 6 is required to bring our calculated and directly measured k_H/k_T values into agreement. Any protium in the deuteriated substrate (<2% by NMR) would make k_D/k_T appear too large rather than too small.

That both measured $(k_H/k_T)_{sec}$ values in Table I are larger than predicted for rehybridization and larger than the $(k_H/k_T)_{sec}$ values calculated from $(k_D/k_T)_{sec}$ is consistent only with model calculations that include tunneling.[4] The disagreements between columns 2 and 4 of Table I also constitute violations of the rule of the geometric mean.[10] The principle behind the rule is that the isotope effect for a doubly labeled species should be very close to the product of the isotope effects for the corresponding singly labeled species. In other words, the two isotopes should exert their effects independently. This statement can be expressed algebraically in eq 2, where the subscript refers to the transferred and the superscript to the nontransferred atom

$$k_H^H/k_D^T = (k_H^H/k_H^T)(k_H^H/k_D^H) \quad (2)$$

But eq 2 can be true only if

$$k_H^H/k_H^T = k_D^H/k_D^T \quad (3)$$

The values in column 2 of Table I are k_H^H/k_H^T and in column 4 are k_D^H/k_D^T. It is evident that eq 3 does not hold and hence neither does eq 2. Specifically, k_D^H/k_D^T is less than k_H^H/k_H^T. Qualitatively similar effects of the mass of the transferred atom on secondary deuterium isotope effects have been observed in reactions involving NAD^+ and NAD^+ analogues,[11-13] but only in the nonenzymatic reactions[11] can one be reasonably sure that the hydride transfer is wholly rate determining. We continue to explore other predictions of the calculations.

(5) We believe our previously reported (ref 2) k_H/k_T for **1** + EtONa (1.259 ± 0.010 at 40 °C) is somewhat high, for the two present workers agree on a lower value (1.189 ± 0.008 at 40 °C, R.C.P., and the present value at 50 °C, M.A.).

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Triticones A and B, Novel Phytotoxins from the Plant Pathogenic Fungus *Drechslera tritici-repentis*

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Fungi of the genus *Drechslera* (*Helminthosporium*) attack a variety of plants.[1] The attack is usually chemical, and the disease symptoms are caused by plant toxins emanating from the fungal hyphae.[2] Phytotoxins produced by fungi are interesting for several reasons: they are often new structural types, they can be used in studying plant physiology, they can serve as models for new herbicides, and they can be used in screening programs for resistant plant strains.[3-5] *D. tritici-repentis* attacks crested wheat grass (*Agropyron cristatum*), quackgrass (*A. repens*), rye (*Secale cereale*), and wheat (*Triticum vulgare*), and the wheat disease is currently a major agricultural problem.[6] The symptons of fungal attack are lesions which appear as light to reddish brown elliptical spots 1-2 weeks after inoculation. These lesions suggest that *D. tritici-repentis* produces one or more phytotoxins, but no

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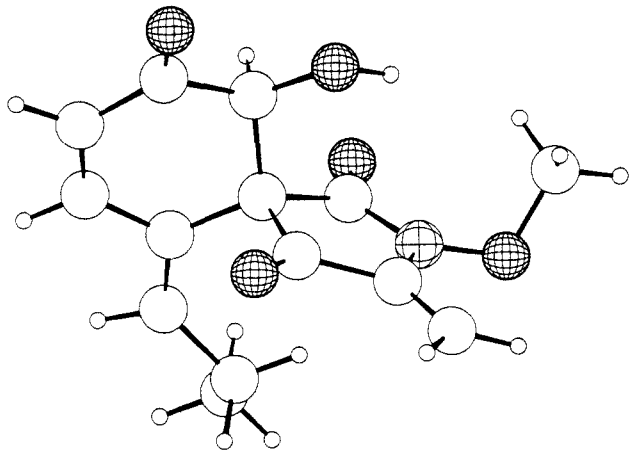
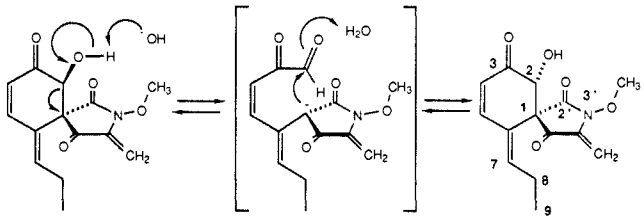


Figure 1. A computer-generated drawing of the final X-ray model of triticone A (1). No absolute configuration is implied (see text).

Scheme I



1 3 2

chemical studies have appeared. Our studies on *D. tritici-repentis*, the isolation and the characterization of unusual spirocyclic γ-lactams trivially named triticone A (**1**) and B (**2**), are the subject of this report.

D. tritici-repentis was grown in shake culture on a modified M-1-D medium for 3 weeks,[7] and a simple leaf puncture assay on wheat guided the toxin purification.[4] Extraction of the culture broth with ethyl acetate, flash chromatography, and chromatography on Sephadex LH-20 led to the isolation of the most active fraction as a mixture of triticones A and B (12 mg/L).[8] The mixture was active in a leaf assay at 10^{-5} M, and the assay symptoms closely resembled those of the natural infection.

Work on the active fraction was hampered by its ready decomposition; heating above 35 °C or silica gel TLC led to extensive decomposition. A fortuitous slow evaporation of an ethyl acetate solution in the cold led to the formation of crystals which belonged to space group $P2_12_12_1$ ($z = 8$) with $a = 9.026$ (2), $b = 13.387$ (3), and $c = 23.214$ (4) Å. The molecular structure was analyzed by single-crystal X-ray diffraction, and a drawing of the final X-ray model is shown in Figure 1. The molecule shown was called triticone A (**1**), and there were two independent enantiomeric molecules in the asymmetric unit.

The spectral data for the active fraction indicated the presence of two very similar molecules, which we were unable to separate chromatographically, in the approximate ratio of 10:9. The ^{1}H NMR signal for the proton on C2 was typical. It appeared as two doublets at δ 4.74 and 4.66 both with $J = 2.1$ Hz, and a 2-D NOESY spectrum indicated the cross peaks for interconversion between the two molecular forms. The optical rotation for the mixture varied from $[\alpha]_D$ of 0° to -9° depending on the sample's history. The most plausible interpretation of these and other observations is shown in Scheme I. Triticone A (**1**) could be converted to **3** in a retro-aldol type reaction. Intermediate **3** is achiral, so reversion to **1** would give racemization. Intermediate **3** could close in an alternate manner to generate **2**. Thus Scheme I interconverts **1** and **2** as well as racemizing both. Compound **1** is the diastereoisomer which crystallized and is trivially named triticone A; triticone B is **2**. The observed optical rotation indicates that *D. tritici-repentis* produces optically active **1** or **2** (or both) and that racemization or interconversion is an artifact of the isolation. The ultimate plant toxin may well be the putative intermediate **3**.

The triticones are new chemotypes, and no closely related molecules have been described. They are not only active in the leaf assay but also have an LD_{50} in a wheat protoplast assay 4.0 μM after 2 h.[9]

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, interatomic and torsional angles for **1** and spectral data for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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Catalysis of Alkene Oxidation by Nickel Salen Complexes Using NaOCl under Phase-Transfer Conditions

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The selective oxidation of hydrocarbons by inexpensive oxidants is an area of intensive study. In particular, catalysis of alkene oxidation by soluble transition-metal complexes is of interest in both biomimetic and synthetic chemistry.[1] The use of hypochlorite ion for the epoxidation of alkenes was initially limited to the activated carbon–carbon double bonds of certain arenes[2] or α,β-unsaturated ketones.[3] More recently, OCl^- has been effectively used in the presence of manganese porphyrin catalysts to epoxidize a variety of olefins.[4] Only a few non-porphyrinic metal complexes have been studied; these reactions generally yield a large amount of C=C bond cleavage products when either OCl^- or IO_4^- is employed as oxidant.[5,6]

As part of our interest in hydrocarbon oxidation catalyzed by nickel[II] complexes,[7] we report here the ability of Ni^{II}(salen)[8] and

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