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METAL-ASSISTED REACTIONS. PART 16.1 INVESTIGATION OF MECHANISMS OF HETEROGENEOUS LIQUID PHASE CATALYTIC TRANSFER HYDROGENOLYSIS THROUGH DEUTERIUM-LABELLING.

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Abstract - Hydrogen isotope studies have shown that heterogeneous catalytic transfer hydrogenolysis of C-O bonds in tetrazolyl ethers of phenols (1) in the liquid phase proceeds via direct transfer of hydrogen from an active hydrogen donor centre to the ether on the catalyst surface and not through transfer of hydrogen atoms from the catalyst surface.

# INTRODUCTION

Heterogeneous gas- and liquid-phase catalytic reduction of substrates using 2,4-7 molecular hydrogen has been studied widely and mechanisms are broadly understood. Similarly, many mechanisms of reduction entailed in the use of homogeneous (soluble) organometallic catalysts have been elucidated. However, heterogeneous liquidphase catalytic reduction using hydrogen donor molecules (transfer reduction) rather than molecular hydrogen is not nearly so well understood and, indeed, there are very few studies of mechanistic aspects. 6,7 There is a tendency to regard catalytic transfer hydrogenation as simply a slight extension from catalytic hydrogenation with molecular hydrogen whereby the hydrogen donor serves only to provide an alternative (in situ) source of hydrogen for the catalyst. This simplistic approach ignores the complex chemistry associated with binding of donor and substrate to the catalyst surface. There is sufficient evidence to suggest that the hydrogen donor should not be regarded as just an incidental source of hydrogen<sup>8</sup> but, rather, that the donor has a central role to play in mechanism. For example, selectivity and reactivity in transfer hydrogenation is usually different from that observed in hydrogenation with 'molecular' hydrogen.8 If vigorous evolution of hydrogen gas is observed when the donor and catalyst are in contact, usually the system proves to be poor for reduction; conversely, where hydrogen evolution is not observed, the system may be excellent for hydrogenation.

Hydrogen isotope studies have been used widely to investigate mechanisms of catalytic reduction by, for example, hydrogen/deuterium exchange, examination of adsorption onto catalyst surfaces and the adsorbed state, and reaction pathways.<sup>4</sup> In the present work, we have used hydrogen and deuterium isotopes to probe the mechanism of catalytic transfer hydrogenolysis of tetrazolyl ethers of phenols (1).

Hydrogenolysis of phenolic C-O bonds has been shown to be an effective, rapid means for converting phenols into arenes, a reaction of value in organic synthesis (equation 1.)<sup>9</sup> In all these reactions, the phenol is converted first into an ether in which the group (R; equation 1) is strongly electron withdrawing and, for convenience, is often 1-phenyltetrazolv1. With this ether group, it has been shown that phenolic C-O bond hydrogenolysis occurs in 10 - 15 min. when using a Pd/C catalyst and a benzene/ethanol/water/formic acid biphasic system.<sup>9</sup> Because of the simplicity of this reaction (very few or no side-products) and

(1)

the ease of preparation of a wide variety of substituted 1-phenyltetrazolyl

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Equation 1

ethers, it was decided to investigate the mechanism of this hydrogenolysis through isotope studies. Compound (2; equation 2),the 1-phenyltetrazolyl ether of 4-methoxycarbonylphenol was chosen as the substrate in these investigations



Equation 2

because it was easy to isolate the resulting arene (3) from any reaction mixture and the  ${}^{1}$ H-,  ${}^{13}$ C-nmr and mass spectra made analysis easy.

# METHOD

All isotopically labelled substrates were obtained commercially except for  $\begin{bmatrix} 2\\H \end{bmatrix}_2$ -formic acid and a, a, a- $\begin{bmatrix} 2\\H \end{bmatrix}_3$ -toluene which were synthesized as described in the experimental section. The formation of the arene (3; methylbenzoate) from the tetrazolyl ether (2) was followed by gas and thin-layer chromatographic The degree of incorporation of deuterium into methyl benzoate, was analysis. obtained by comparison of the molecular ion region of the mass spectrum of nondeuteriated and deuteriated material. The specificity of incorporation of deuterium into the ring positions of methyl benzoate was obtained from  $^{1}$ H- and  $^{13}$ C-nmr spectroscopy. In the  $^{1}$ H-nmr spectrum of methyl benzoate, the hydrogens at the 2-, 3- and 4-positions appear as a doublet, a triplet and a triplet respectively at & 8.15, 7.5 - 7.55, 7.4 - 7.5; incorporation of deuterium at any of these positions is readily inferred both by changes in the integrals for numbers of hydrogens and by a change in the coupling pattern at the 3-position from a triplet to a doublet. Similarly, in <sup>13</sup>C-nmr, the 2-, 3- and 4-carbon atoms appear as doublets at  $\delta$  130.0, 128.4 and 133.0 respectively; incorporation of deuterium at any of these positions leads to a change from a doublet to a triplet because of the difference between the nuclear spin quantum number for  $^{1}\mathrm{H}$  and  $^{2}\mathrm{H}$ .

In a typical experiment, the 1-phenyltetrazolyl ether (2) was hydrogenolysed until thin-layer chromatography showed that no starting material remained. After separation from catalyst by filtration and removal of 1-phenyl-5-hydroxytetrazole<sup>14</sup> by extraction into aqueous alkali, the organic layer was evaporated to leave an oil, methyl benzoate. The purity (> 95%) of this methyl benzoate was checked by gas chromatography, mass spectrometry and <sup>1</sup>H-nmr spectroscopy. <sup>1</sup>H-, <sup>13</sup>C-nmr and mass spectroscopy were carried out on the methyl benzoate as isolated.

Hydrogenolysis was carried out in a two-phase liquid medium consisting of water and benzene, with ethanol added to improve miscibility. For the deuterium experiments, deuteriated or non-deuteriated solvents were used in various combinations with deuteriated or non-deuteriated hydrogen donor (formic acid), as summarised in the Table. Some of the experiments were designed to invert the availability of hydrogen and deuterium so that specificity of incorporation could be double-checked. For example, the results from use of non-deuteriated solvents with deuteriated formic acid were compared with those obtained by use of deuteriated solvents and non-deuteriated formic acid. Such comparative experiments also yielded overall isotope effects.

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# RESULTS AND DISCUSSION

In all experiments using deuteriated solvents or hydrogen-donors, deuterium was incorporated only into the 4-position of the product, methyl benzoate. This specificity of incorporation indicates that hydrogenolysis involves only the position to which the 1-phenyltetrazolyl ether is attached and that one of the possible mechanisms, suggested earlier (Scheme 1),<sup>9</sup> is unlikely to be correct because such a mechanism, involving ring positions ortho to the 1-phenyltetrazolyl group, would be expected to lead also to incorporation of deuterium into the 3-position of methyl benzoate by rapid exchange with ring hydrogens.<sup>4</sup>





### Scheme 1

Oxidative addition and reductive elimination, as implied by the second suggested mechanism (Scheme 2), $^9$  would be compatible with the observed results.

Although, in all experiments, hydrogen (or deuterium) was incorporated into only the 4-position of methyl benzoate, further experiments were required to determine whether or not the hydrogen-donor transferred its hydrogens specifically or randomly. Specific incorporation implies complex formation involving donor, tetrazolyl ether and catalyst; random incorporation indicates either that the



# Scheme 2

donor does not form a specific complex with the acceptor or that its hydrogens exchange rapidly with other hydrogens in the systems before complex formation. The results of various deuterium-labelling experiments are collated in the Table.

To obtain figures for the calculated random incorporations shown in the Table it was necessary to decide on the number of hydrogen atoms contributed by each molecular species. Thus, entries 6,7 in the Table show that incorporation of Table

EXPERIMENTAL CONDITIONS AND RESULTS FOR HYDROGEN/DEUTERIUM INCORPORATIONS.

ENTRY	RE- ACTION TIME (min)	EXPERIMENTAL CONDITIONS <sup>8.</sup>	ACTUAL % INCORP- ORATION INTO ARENE (3) <sup>b.</sup>		ADJUSTED ACTUAL % INCORPOR- ATION INTO ARENE (3)		THEORETICAL RANDOM % INCORPOR- ATION INTO ARENE (3)		
			Ħ	D	Ħ	٩	<u>н</u>	D	
1	10	HCO <sub>2</sub> H/H <sub>2</sub> O/CH <sub>3</sub> CH <sub>2</sub> OH/C <sub>6</sub> H <sub>6</sub> (0.1)	100	0	-	-	100	0	
2	15	DCO2D/H20/CH3CH20H/C6H6 (0.1)	81	19	69	31	84	16	ĺ
3	10	DCO2D/D20/CH3CH2OH/C6H6 (0.1)	43	57	31	69	15	85	
4	10	DCO <sub>2</sub> D/D <sub>2</sub> O/CH <sub>3</sub> CH <sub>2</sub> OD/C <sub>6</sub> H <sub>6</sub> (0.1)	12	88	0	100	0	100	
5	10	HCO <sub>2</sub> H/D <sub>2</sub> O/CH <sub>3</sub> CH <sub>2</sub> OH/C <sub>6</sub> H <sub>6</sub> (0.1)	90	10	78	22	32	68	
6	10	HCO2H/H2O/CD3CD2OD/C6H6(0.085)	97	3	87	13	84	16	
7	15	HCO2H/H2O/CH3CH2OD/C6H6 (0.085)	97	3	87	13	84	16	
8	10	HCO2H/H2O/CH3CH2OH/C6D6 (0.057)	94	6	100	0	100	0	
9	10	DCO <sub>2</sub> D/H <sub>2</sub> O/CH <sub>3</sub> CH <sub>2</sub> OH/C <sub>7</sub> H <sub>8</sub> (0.066)	94	6			90	10	
10	15	HCO2H/D2O/CH3CH2OH/C7H8 (0.066)	97	3			60	40	
11	150	DCO2D/D20/CH3CH20D/C7D8 (0.05)	8	92			0	100	
12	75	DCO2D/D20/CD3CD20D/C7H8 (0.076)	86	14	:		59	41	
13	15	HCO2H/H2O/CH3CH2OH/C7D8 (0.044)	52	48	1		70	30	
14	15	HCO2H/H2O/CH3CH2OH/C7H5D3(0.064)	53	47			62	38	
15	180	$D_{20}^{0} D_{2}^{0/CH_{3}^{-}CH_{2}^{-}OD/C_{8}^{-}H_{10}}$ (0.060)	62	38			55	45	

<sup>a.</sup> All experiments were carried out under the same conditions as described in the Experimental Section using only one batch of Pd/C catalyst (Koch-Light; 10%). In each case, the following quantities were used : formic acid (0.03 mol), water (0.11 mol), ethanol (0.05 mol), aryl ether (2) (300 mg), Pd/C catalyst (350 mg). The quantity of aromatic solvent is shown in parentheses (mol). The individual entries show the various combinations of deuteriated and non-deuteriated substrates used in these experiments.
<sup>b</sup> Incorporations were determined by mass spectrometry (see experimental).
<sup>c</sup> Incorporations adjusted to allow for non-specific incorporation from benzene

solvent, as described in the discussion section.

<sup>d</sup> Random incorporations calculated as described in the discussion section.

deuterium from either  $CH_3CH_2OD$  or  $CD_3CD_2OD$  was identical in the two experiments. This result demonstrates that the alkyl hydrogens of ethanol do not contribute to the reaction 'pool' and that each molecule of ethanol contributes one hydrogen. Similarly, entries 13,14 show that incorporation of hydrogen from toluene arises mainly from the three hydrogens in the methyl side-chain, but that there must be some small incorporation also from ring hydrogens. Incorporation of aromatic ring hydrogens into the reaction product can be inferred from entries 4,8. Thus, entry 4 indicates that 12% of hydrogen in the reduction product (3) arose from the large excess of benzene used as solvent. However, the efficiency of incorporation is low because the benzene provides 65% of 'available' hydrogen and yet only 12% was incorporated. If efficiency of incorporation is defined as equal to the actual percentage incorporation divided by the molar percentage of available hydrogen (or deuterium) for any one component, then the efficiency of benzene as a donor is 0.18. Entry 8 confirms this low efficiency since only 6% of the 48% of available deuterium is incorporated into the product. To simplify further discussion of the results presented in the Table, the low incorporation of hydrogen arising from benzene solvent into the reaction product has been subtracted from the observed incorporations of hydrogen and deuterium.

With the contribution of hydrogen from benzene removed from the observed incorporations, the specific incorporation from formic acid becomes more readily apparent. Entry 2 shows that the efficiency of incorporation of deuterium from DCO<sub>2</sub>D is 2.21 and that the incorporation is specific.

Entry 3 shows that only 69% of deuterium is incorporated into the reaction product with an expected random incorporation of 85%. If it is assumed (from entry 2) that 31% of this incorporation arises from formic acid then 38% must arise from the  $D_2O$ , a figure much less than random. Therefore, there must be competitive incorporation of hydrogen from ethanol, possibly a result of kinetic isotope effects leading to very slow reaction (see below). The low efficiency of incorporation of hydrogen from water is confirmed by entry 5 which shows that, despite providing 68% of available deuterium, only 22% was incorporated, again much less than random and giving an incorporation efficiency of 0.32. Similarly, entries 6,7 show that ethanol provides 13% of incorporation of deuterium with an efficiency of 0.72 i.e., about twice that of water.

In summary, entries 2 - 8 demonstrate that the efficiency of incorporation of hydrogen from formic acid into the reduction product is much greater (more specific) than incorporation from water, ethanol or benzene and suggests direct transfer of hydrogen to the ether (2) from a formate complex adsorbed on the catalyst.

Entries 9 - 14 concern experiments in which toluene replaced benzene in the reaction mixture and changed the relative efficiencies of incorporation strikingly. Comparison of entries 2,9 shows that incorporation of deuterium from DCO<sub>2</sub>D drops to only 6% on changing from benzene to toluene even though there is proportionately much less aromatic solvent present in the toluene experiments Entry 12 indicates that specific incorporation of hydrogen from toluene is much greater than that for formic acid, water or ethanol. Confirmation of this finding is seen in entry 13 which reveals a 48% incorporation of deuterium from toluene compared with a random expected incorporation of 30%. For the tcluene experiments, incorporation efficiencies fall in the order, toluene (1.66), formic acid (0.60), ethanol (0.54) and water (0.07). Therefore, unlike the experiments which utilized benzene, these experiments with toluene as solvent lead to the aromatic solvent being a much more efficient donor of hydrogen than Further, as shown by entries 13, 14, the active hydrogens in is formic acid. toluene are almost entirely those in the methyl side-chain; changing the solvent from  $C_6D_5CD_5$  to  $C_6H_5CD_3$  leads to only a small decrease in incorporation of deuterium.

Apart from the striking alterations in efficiency or specificity of hydrogen donation on change of solvent from benzene to toluene, it is noteworthy that, in the absence of formic acid, toluene is not a hydrogen donor, v.i.z. without formic acid, the water /ethanol / toluene / Pd system is not capable of effecting hydrogenolysis of compound (2). These results strongly suggest that direct (specific) transfer of hydrogen from the side-chain methyl of toluene occurs and that another supply of hydrogen ('sacrificial') is needed also to maintain reaction. One possible mechanism whereby this could occur is shown in the Scheme (3).

Scheme (3) depicts a reversible chemical adsorption of toluene onto the catalyst surface by oxidative addition (hydrogen and benzyl ) to a palladium atom. At the next stage, the hydrogen acceptor (A) occupies an adjacent site so that hydrogen can be transferred from the chemically bonded benzyl group to the acceptor. This step would result in a benzylidene species forming two bonds to the palladium metal and stops further hydrogen transfer until the benzylidene is reduced once more to benzyl by hydrogen provided from a second hydrogen source (formic acid in this case). Rate controlling steps might occur at the transfer of hydrogen from benzyl to acceptor or at the transfer of hydrogen from the secondary source to benzylidene. If the adsorption of toluene onto the catalyst surface involves an equilibrium as shown (Scheme 3) then, although hydrogen from the formic acid gradually replaces that lost by the toluene, this does not become significant as a change in isotopic purity of the toluene because of its large excess as a solvent.



In separate experiments, the hydrogenolysis system was examined in the absence of the substrate acceptor (2) but with the use of deuteriated toluene,  $C_6D_5CD_3$ . Samples of the mixture were subjected to gc/ms at intervals to determine how much hydrogen became incorporated by exchange into the toluene. Over the same length of time as taken by a normal hydrogenolysis of ether (2), i.e., about 15 min., only 37% exchange of hydrogen for deuterium was observed. Thus, the rate of exchange of hydrogen for deuterium in toluene was not faster than hydrogenolysis and indicated that the results of the deuterium studies could be interpreted without taking account of isotope exchange. Oxidative adsorption of toluene onto palladium is well documented<sup>4</sup> as is the relative inactivity of ring compared with side-chain a-hydrogens towards hydrogen exchange on a catalytic metal surface in the gas phase.<sup>4</sup>

Entry 15 in the Table is interesting in that, although the ortho-xylene, used in place of toluene, has twice as many side-chain hydrogens, its specificity

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for incorporation of hydrogen into the hydrogenolysis product is not as good as that of toluene. This effect may be due to the two methyl groups being adjacent, leading to steric interference in either the initial adsorption onto the catalyst or in the transfer of hydrogen to an adjacent acceptor.

Finally, the Table gives approximate times for the reactions to go to completion, as monitored by the continued appearance of reduction product (3) or disappearance of the starting material (2). Whilst these times are no substitute for accurate kinetic data, one fact stands out very clearly. In experiments with various deuterium-labelled components in the benzene series (entries 1 - 8), all reaction rates are very similar, even where most of the components are deuteriated (entry 4). However, in the toluene series, very slow reaction rates are observed when a substantial proportion of the medium is deuteriated. For example, reaction becomes so slow in the case of entry 11 that some hydrogen incorporation from the normally 'inactive' alkyl hydrogens of ethanol is observed. These rate results point to a change in mechanism between the benzene and toluene series and support the deductions made on the basis of the hydrogen/deuterium incorporations.

The slowing up of the reaction by about ten times in changing from a hydrogen to a deuterium system suggests that hydrogen transfer is a rate-For example, relative rate constants for CH/CD, OH/OD and controlling step. NH/ND bond-breaking reactions, <sup>10</sup> in which the transferred hydrogen is part of a symmetrically bonded transition state, are respectively 6.9, 11.5 and 9.2 at 25°. This considerable decrease in reaction rate is observed even for entry 12 where specific transfer of hydrogen from non-deuteriated toluene occurs and suggests that the rate-controlling step is transfer of hydrogen from the secondary hydrogen source (formic acid, water and ethanol). This step, involving O-H or C-H bond breaking or formation, could be subject to extensive kinetic isotope effects. Since the greatest slowing of reaction rate occurs when deuteriated formic acid, ethanol and water are used and the rate is relatively unchanged if only one of these components is deuteriated, the rate controlling step appears to be common for each component. The only likely common entity is hydrogen itself, and this indicates that the rate-controlling step may be the transfer of hydrogen from the catalyst to the active benzylidene centre (Scheme 3).

#### CONCLUSION

Hydrogen isotope studies of the hydrogenolysis of the 1-phenyltetrazolyl ether of a phenol (2) indicate that, with palladium catalyst, in a formic acid/ water/ethanol/benzene biphasic system, specific incorporation of hydrogen into the arene product occurs primarily from formic acid. Contrariwise, with the same substrates and catalyst in a formic acid/water/ethanol/toluene system, specific incorporation of hydrogen occurs primarily from the methyl side-chain of toluene but that, in the absence of formic acid, toluene does not serve as a hydrogen donor. The results indicate that, for the toluene system, direct transfer of hydrogen occurs, from an active centre derived from toluene to the substrate acceptor. Rates of reaction in deuteriated and non-deuteriated toluene systems suggest that the rate controlling step in these hydrogenolyses results from a relatively slow transfer of a hydrogen atom from the catalyst surface to an active (benzylidene) centre and not to the substrate acceptor directly. The mechanism inferred from these results for heterogeneous catalytic transfer hydrogenolysis is similar to a general mechanism proposed for catalytic hydrogenation of alkenes<sup>11</sup> in that the latter also involves indirect transfer of hydrogen atoms from the catalyst surface to an undefined carbonaceous active site which, in turn, transfers hydrogen to the alkene. In the mechanism proposed here, no attempt has been made to specify the number of palladium atoms involved with the

active site. Thus, the scheme can be taken to imply addition of the substrate acceptor (A) either to the same or to a different palladium atom from that to which the toluene active centre is attached.

#### EXPERIMENTAL

Preparation of 5-(4-carboxyphenoxy)-1-phenyltetrazole. To a solution of 4-hydroxybenzoic acid (1.4g; 10.14 mmole) in dimethyl sulphoxide (25 ml), under nitrogen, was added potassium t-butoxide (2.47g; 22.0 mmole) with stirring at room temperature. After 10 min, 5-chloro-1-phenyltetrazole (2g; 11.04 mmole) was added and the mixture was heated to 75° for 2 hours before being cooled and poured into ice/water (200 ml). This alkaline solution was acidified (conc. HC1) and the precipitated 5-(4-carboxyphenoxy)-1-phenyltetrazole was recrystallized (2.5g), m.p. 215 - 216° (EtOAc/petroleum ether, b.p.  $60-80^{\circ}$ );  $v_{max}$ . 3200 - 2390 (v.broad), 1720, 1560, 1250, 1130, 870, 770 cm<sup>-1</sup>;  $\delta$  (DMSO-d<sub>6</sub>; <sup>1</sup>H), 7.6 - 7.7 (5H, m), 7.85 (2H, d, J 9 Hz), 8.08 (2H, d, J 9 Hz), 13.1 (1H, broad s, exchanges in D<sub>2</sub>O); m.s., m/z 282 (M<sup>++</sup>).

5-(4-Methoxycarbonylphenoxy)-1-phenyltetrazole (2). The above acid (1.5g; 5.3 mmole) in diethyl ether (20 ml) was reacted with a solution of diazomethane in ether with stirring at room temperature for 1.5 hours to yield a thick white precipitate. A small excess of acetic acid was added to destroy excess of diazomethane (discharge of yellow colour) and then the solvent was evaporated <u>in</u> <u>vacuo</u>. The residue was dissolved in methylene chloride, washed with aqueous sodium bicarbonate and water, and dried (MgSO<sub>4</sub>). Evaporation of the solvent and recrystallization gave 5-(4-methoxycarbonylphenoxy)-1-phenyltetrazole (1.5g) m.p. 90 - 91° (EtOAc/petroleum ether, b.p. 60 - 80°). Found: C, 61.0; H, 4.3; N, 18.7.  $C_{15}H_{12}N_{4}O_{3}$  requires C, 60.8; H, 4.1; N, 18.9%;  $v_{max}$ . 1740, 1600, 1570, 1510, 1465, 1295, 1100, 760 cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>; <sup>1</sup>H), 3.8( $\Xi$ H,s), 7.5 - 7.7 (5H,m), 7.85(2H, d, J 9.7 Hz), 8.20 (2H, d, J 9.7 Hz); m.s., m/z 320 (M<sup>++</sup>).

 $\begin{bmatrix} 2H \\ 2 \end{bmatrix}_2$ -Formic acid. NaCN (5g; 0.11 mole) and D<sub>2</sub>O (6 ml; 0.33 mole) were heated in a sealed vessel to about 180° for 20 hours to give sodium  $\begin{bmatrix} 2H \\ -1 \end{bmatrix}_2$ -formate (100% yield; 99.5% isotopic purity).  $\begin{bmatrix} 2H \\ -1 \end{bmatrix}_3$ -Phosphoric acid was prepared by addition of D<sub>2</sub>O (8.4 ml; 0.42 mole) to fresh P<sub>2</sub>O<sub>5</sub> (20.05g; 0.14 mole) over a period of 15 min. in a dry-box. The resulting viscous solution of  $\begin{bmatrix} 2H \\ -1 \end{bmatrix}_3$ -phosphoric acid was added to dry sodium  $\begin{bmatrix} 2H \\ -1 \end{bmatrix}_2$ -formate (12.3g; 0.18 mole) and then heated to 70° at 0.1 mm for 3 hours to drive off the  $\begin{bmatrix} 2H \\ -1 \end{bmatrix}_2$ -formic acid which was collected in a cold-trap (4.54g; 58% yield; 95% isotopic purity).

 $a,a,a-\begin{bmatrix}2\\H\end{bmatrix}_3$ -Toluene. A solution of lithium pheny  $\mathbf{1}^3$  in diethyl ether was prepared in the usual way from bromobenzene (0.07 mole). To this solution at room temperature was added dropwise a solution of  $\begin{bmatrix}2\\H\end{bmatrix}_3$ -methyl iodide (10g; 0.07 mole) in diethyl ether (25 ml). After 0.5 hours the solution was refluxed gently for a further 0.5 hours and then poured onto ice to give, after distillation,  $a,a,a-\begin{bmatrix}2\\H\end{bmatrix}_3$ -toluene, b.p. 110° (80% yield). To remove traces of halide (which inhibits catalytic transfer reduction), the trideuteriotoluene was refluxed for 2 hours over, and then distilled from, a small quantity of Na/K (1:3 molar ratio) alloy.<sup>12</sup>

<u>Typical catalytic transfer hydrogenolysis of 5-(4-methoxycarbonylphenoxy)-1-phenyltetrazole</u>. EtOH (3 ml; 0.05 mole) and 10% Pd-on-charcoal catalyst (450 mg) were added to a vigorously stirred solution of the ether (2; 400 mg; 1.25 mmole) in benzene (8 ml; 0.1 mole). To this mixture,under reflux (80<sup>0</sup>), was added dropwise a solution of formic acid (1 ml; 26.5 mmole) in distilled water (2 ml; 0.11 mole). The reaction was monitored by t.l.c. on silica (solvent, benzene

acetone, 9:1) to determine the point of disappearance of the starting ether (2), with simultaneous formation of 1-pheny1-5-hydroxytetrazole and methyl benzoate (R, : methyl benzoate 0.95; starting ether, 0.70; l-phenyl-5-hydroxytetrazole, At the end of the reaction, the catalyst was filtered off and washed 0.05). The filtrate and washings were extracted with cold with hot diethyl ether. aqueous NaOH to remove 1-pheny1-5-hydroxytetrazole and then dried  $(MgSO_h)$  to give, on evaporation of solvent, methyl benzoate (3) in 92% yield.

Mass spectrometry of methyl benzoate. Mass spectra of methyl benzoate from each of the various deuteriation experiments were measured by electron impact at 70v. Peak heights corresponding to the molecular ion at m/z 136, 137 were measured and the natural  $^{13}$ C-isotope contribution from m/z 136 was subtracted from the peak height at m/z 137; the residual peak height at m/z 137 corresponded to mono-From the peak height at m/z 136 and the residual deuteriated methyl benzoate. at m/z 137, the percentage incorporation of deuterium was determined. On subtracting the  $^{13}$ C-isotope contribution due to m/z 137 from the peak height at m/z 138 there was no residual peak height, thereby showing that no more than monodeuteriation had occurred.

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- J.C.W.Evans and C.F.H.Allen in, "Organic Syntheses", Collected Vol. II, Ed., A.H.Blatt, Wiley, New York, 1969, pp. 517 518. This product is described as a 5-hydroxytetrazole to emphasise the hydro-genolytic C-O bond cleavage. Infrared evidence suggests that the compound exists in two tautomeric forms, 1-phenyl-5-hydroxytetrazole (strong, broad OH absorption, 3300 2500 cm<sup>-1</sup>) and 1-phenyl-1,2,3,4-tetraaza-3-en-5-one (strong C=O absorption, 1730 cm<sup>-1</sup>).