tained with the adsorbed material permits the radical species to be identified (Figure 2). The spectrum obtained with adsorbed H₂ (trace a) is attributed to the addition of H' to I; the hyperfine pattern consists of a 1:1:1 triplet due to ¹⁴N, further split into 1:2:1 triplets due to two equivalent β protons. With D₂ (trace b), the addition product of D' to I gives a triplet-doublet-triplet splitting pattern, with the smaller triplet due to the β deuteron.

Figure 2 (b) also shows small amounts of the hydrogen addition product and another unidentified radical which was not present if a non-hydrogen-containing solvent such as carbon tetrachloride was used. Adsorption of hydrogen on this sample gave a spectrum showing the hydrogen addition product with a very small contribution from the deuteration addition product.

Table I compares the hyperfine splitting constants that we have observed with those reported in the literature for the addition products of H' and D' to I. The solution spectra are certainly those of I with R = H' or D'. The similarity of the adsorbed phase spectra to those from solution indicates that the addition products are formed on the ZnO surface by reaction of I with adsorbed hydrogen or deuterium.

It has been shown by infrared spectroscopy that adsorption of H₂ on ZnO at room temperature involves a reversible dissociative chemisorption to form Zn–H and O–H species. Our experiments indicate that hydrogen adsorbed on ZnO can be abstracted by PBN. Further experiments are needed to determine which hydrogen is abstracted and to determine the mechanism of abstraction. Trapping of the adsorbed hydrogen by PBN does not necessarily imply the presence of free hydrogen atoms on the ZnO surface, but does indicate that the reactivity of adsorbed hydrogen resembles that of hydrogen atoms produced in radiolysis or electrolysis experiments. The question of the extent of the radical character of hydrogen adsorbed on ZnO has still to be answered. Nevertheless, PBN is clearly a valuable spin trap to use in studying surface species having radical character. We envisage many systems of catalytic importance in which the presence of radical intermediates may be investigated by this technique.

References and Notes

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Asymmetric Reductions with a
Chiral 1,4-Dihydropyridine Crown Ether¹

Sir:

We are interested in the catalytic cycle shown in eq 1. A 1,4-dihydropyridine (DHP) is contained in a segment (for example a crown ether) capable of complexing a metal ion, M⁺. The encapsulated M⁺ then complexes with a carbonyl compound, forming a ternary complex in which the carbonyl group is activated toward hydride acceptance through its complexation to M⁺. The pyridinium salt (Pyr⁺) formed on reduction of the carbonyl group is reduced back to 1,4-DHP with Na₂S₂O₇. Such a cycle has attractive synthetic and biomimetic aspects, especially if the 1,4-DHP–crown combination is chiral and is capable of carrying out reductions with a significant degree of asymmetric induction. We report here the preliminary results of work intended toward the achievement of the above goals.

The synthetic route to the desired 1,4-DHP–crown compounds is shown in Scheme I. Chiral starting materials were the tert-butyl esters of optically pure L-alanine (2a) and L-

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Thus far only overall, 26% for ring closure, mp 259.1-262.3 °C dec, [α]23D +26.8° (c 1.00, C2H502CCH3). The product were then converted to ethers and macrolides. There was obtained colorless oil (lit. mp 65.5-66.5 °C for the pure enantiomer), and was pure by both 'H NMR and LC. In C6H6. C2H50H. 'In CH3COCH3.

Reactions of these amino acid esters with 3-oxopentane in DMF. The cesium salt method, first developed with sodium dithionite in a pH 7 phosphate buffer afforded the alcohol. In all cases care was taken to avoid optical fractionation of the alcohol during workup. The recovered perchlorate of pyridinium salt could be reduced by dithionite back to the alcohol. In the absence of Mg(ClO4)2·1.5H2O either with or without oxygen no significant oxidation of 6 or reduction of substrate occurred.

Reduction by 6 of 2-benzoylpyridine (7) to alcohol 8 proceeded only slowly (72 h) even at the relatively high temperature of 55 °C. Data for the maximum rotation of 8 as well as its absolute configuration have not been reported and therefore this reaction was not examined further. Optical data are, however, available for the alcohol 10 derived from trifluoroacetonophenone (9), which is a popular substrate for reductions by 1,4-dihydropyridines. We found the reaction to be very sluggish, taking 5 days at 55 °C to go to completion. The degree of asymmetric induction in 10, 68%, is, however, quite satisfying. The reductions of the ethyl ester (11) and amide (13) of phenylglyoxylate proceeded exceptionally smoothly. The optical inductions in 12 and 14 of, respectively, 86 and 64% are also very good indeed considering that the chiral centers in 6 are five bonds removed from the site of hydride donation. The reduction of the N-ethylamide (15) to alcohol 16 has been attended thus far by experimental difficulties: the isolated compound is not very pure, and could be reduced by dithionite back to alcohol. In C6H6. C2H50H. In CH3COCH3. For optically pure material (S). *Reference 15. *Reference 16. *Reference 17. *Reference 18.
Communications to the Editor

Dedicated to Professor E. Havinga, University of Leiden, on the occasion of his 70th birthday.


Reference and Notes


A reduction of thiones by such a catalytic cycle has been reported recently; N. Kuskamakana, A. Ohno, Y. Yasui, and S. Oka, Tetrahedron Lett., 4815 (1978).


For interpreting the complex biochemistry of 1, we are studying the chemistry of the model endoperoxide 2 and homologues. We now report that the abnormally large solvent effects found for thermal decompositions of 2 are not observed for decomposition of the less strained homologue, 2,3-dioxabicyclo[2.2.2]octane (7). Furthermore, activation enthalpies and entropies for thermal decomposition of 2, of the homologue 7, and of tert-butyl peroxide in cyclohexane are remarkably different. ∆H° increases with decreasing strain in the series.

Thermal decompositions of 2 and 7 were monitored by 1H NMR. Relative rates in various solvents are listed in Table I. Both reactions follow first-order kinetics. As reported previously, the rate of decomposition of 2 increases with solvent polarity and is exceptionally rapid in protic solvents owing primarily to an extraordinary dependence of the rate of rearrangement to levulinaldehyde (8) on solvent polarity. The parallel first-order rearrangement of 2 to 9 is a nonpolar process which shows only a small dependence on solvent polarity.

In contrast, the rate of decomposition of 7 varies only slightly and erratically with changes in solvent polarity. The modest acceleration found for decomposition of 7 in protic solvents

Extraordinary Reactivity of the Prostaglandin Endoperoxide Nucleus. Nonpolar Rearrangement of 2,3-Dioxabicyclo[2.2.2]heptane and -[2.2.2]octane

Sir:

Occasionally Nature provides us with molecules which not only have unusual structures, but which also exhibit extraordinary chemical reactivity. Prostaglandin (PG) endoperoxides (e.g., 1) possess an unusual bicyclic peroxide nucleus. They are a branch point in the oxidative transformation of polyunsaturated fatty acids into a vast array of physiologically active metabolites. The biological role of 1 depends in large measure on enzymatic conversion into prostaglandins (e.g., 3, 4), thromboxane A₂ (5), and prostacyclin (6).

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