The differences may arise from the differences in the intermediates generated in the two experiments. In Bauld's thermal experiment, presumably radical cations of the dienes are first generated which subsequently react with available cisoid diene. However, in the photochemical experiment, free radical cations may not form, but rather a tightly bound complex, either an exciplex or radical cation/radical anion pair, reacts directly with cisoid diene to form dimer products, perhaps through an intermediate such as a "triplex" or "exterplex".[1b,12] Although radical cations and anions are known to form in sufficiently polar solvents such an CH_3CN, CH_2Cl_2 is much less polar and presents an intermediate polarity where the degree of solvent penetration and dissociation of the exciplex could be far less. Thus, differences in the structures of the dienes might mean differences in the structure of the subsequently formed complex, which could lead to very different reactivities with another diene. Current data, however, cannot rule out the possibility that identical intermediates form in both the photochemical and thermal oxidative experiments and that although DMHD efficiently quenches DCNA fluorescence, the lifetime of any intermediate complex formed may be too short to undergo subsequent dissociation and bimolecular chemistry.

We are currently studying the mechanism of this reaction in greater depth. Our preliminary findings are that the lack of reactivity and quenching behavior of DMHD is the exception rather than the rule, and other olefins and dienes do undergo [4 + 2] cycloadditions.

Registry No. 1, 703-35-5; **2**, 703-36-6; DMHD, 764-13-6; CHD, 592-57-4; DCNA, 1217-45-4.

(11) Unpublished results.

(12) "Triplexes" have been proposed in authracene dimerizations in the presence of aromatic amines and dienes: (a) Saltiel, J.; Townsend, D. E.; Watson, D. D.; Shannon, P.; Finson, S. L. *J. Amer. Chem. Soc.* **1977**, *99*, 884-896. (b) Yang, N. C.; Shold, D. M.; Kim, D. *J. Am. Chem. Soc.* **1976**, *98*, 6587-6596. (c) Saltiel, J.; Townsend, D. C.; Watson, B. D.; Shannon, P. *J. Am. Chem. Soc.* **1975**, *97*, 5688-5695. (d) Saltiel, J.; Townsend, D. D. *J. Am. Chem. Soc.* **1973**, *95*, 6140-6142. (e) Campbell, R. O.; Lie, R. S. *Mol. Photochem.* **1974**, *6*, 207-223.

(13) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.

Halonium-Initiated Cyclizations of Allylic Urethanes: Stereo- and Regioselectivity in Functionalizing the Olefinic Bond[1]

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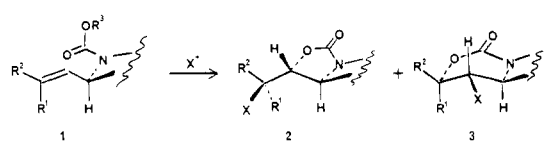
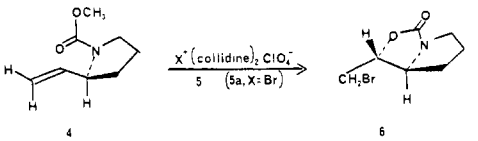
Studies of relative asymmetric induction in acyclic systems have served as the basis of conceptually new strategies for synthesis.[2] We viewed a stereo- and regiospecific addition to the olefinic bond of an acyclic allylamine as the key step in an approach to some highly functionalized alkaloids, for example, naphthyridinomycin.[3] We have now shown that the halonium-initiated cyclization of urethane **1** gives the cyclic urethanes **2**[4] and/or **3** (R^1 = H, R^2 = Ar or R^1 = Ar, R^2 = H). Each process (**1** → **2** and **1** → **3**) is stereospecific. Furthermore, the regioselectivity of the cyclization depends on the electronic properties of the olefinic substituents (R^1 and R^2).



The cyclization of allylic methyl urethane **4**[5] with brominium dicollidine perchlorate (**5a**)[6] proceeded in refluxing methylene chloride (3 h) to afford an 82% yield of a single oxazolidone, IR 1750 cm^{-1}. This product was shown to be the trans-isomer **6**.[7]

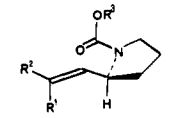


(1) These studies were reported at the Chemical Society Symposium on Synthesis, Oxford, England, July, 1981.

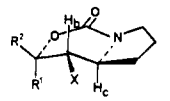
(2) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3.

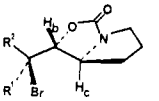
(3) (a) Sygusch, J.; Brisse, F.; Hanessian, S.; Kluepfel, D. *Tetrahedron Lett.* **1974**, 4021; **1975**, errata no. 3. (b) Sygusch, J.; Brisse, F.; Hanessian, S. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1139.

Chart I



7a, R^1 = H; R^2 = C_6H_5; R^3 = CH_3
7b, R^1 = C_6H_5; R^2 = H; R^3 = CH_3
8a, R^1 = H; R^2 = C_6H_5; R^3 = *t*-Bu
8b, R^1 = C_6H_5, R^2 = H; R^3 = *t*-Bu
9a, R^1 = H; R^2 = *o*-C_6H_4CN; R^3 = *t*-Bu
9b, R^1 = *o*-C_6H_4CN; R^2 = H; R^3 = *t*-Bu
10a, R^1 = H; R^2 = *p*-$C_6H_4NO_2$, R^3 = *t*-Bu
10b, R^1 = *p*-$C_6H_4NO_2$, R^2 = H; R^3 = *t*-Bu





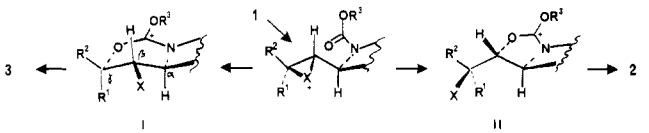
11a, R^1 = H; R^2 = C_6H_5
11b, R^1 = C_6H_5; R^2 = H
12a, R^1 = H, R^2 = *o*-C_6H_4CN
12b, R^1 = *o*-C_6H_4CN; R^2 = H
13a, R^1 = H; R^2 = *p*-$C_6H_4NO_2$
13b, R^1 = *p*-$C_6H_4NO_2$; R^2 = H

12c, R^1 = *o*-C_6H_4CN; R^2 = H
13c, R^1 = *p*-$C_6H_4NO_2$; R^2 = H

Table I. Product Distributions as a Function of Olefin Geometry and Aryl Substituent

allylic urethane	reagent	product(s) (yield, %)	ratio
8a	**5b**	**11a**, X = I (73)	
8b	**5b**	**11b**, X = I (60)	
9a	**5a**	**12a**, X = Br (62)	
9b	**5a**	**12b** + **12c**, X = Br (40)	1:2
10a	**5a**	**13a**, X = Br (60)	
10b	**5a**	**13b** + **13c**, X = Br (70)	1:5

Scheme I



(4) (a) Fraser-Reid has reported the cyclization of an ethyl allyl urethane with iodonium dicollidine perchlorate to afford the oxazolidone product; in the system described, the allyl urethane moiety was part of a ring system and could give only one stereoisomer. See: Pauls, H. W.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1980**, *102*, 3956. (b) Bartlett has observed an iodonium-initiated urethane closure of an acyclic-protected amino acid; however, the stereochemistry of cyclization was not reported. See: Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Tetrahedron Lett.* **1982**, *23*, 619. (c) The bromonium-initiated cyclizations of a urethane that resembles our substrate **4** have been studied by Overman (Overman, L. E.; McCready, R. J. *Tetrahedron Lett.* **1982**, *23*, 4887). We are grateful to Professor Overman for sharing his results with us prior to publication.

(5) The structure of each new compound was assigned by IR and NMR spectroscopy. With the exception of **13a** and **13b**, which were obtained only in minute amounts, each new compound was also characterized by elemental analysis and/or high-resolution mass spectroscopy.

(6) Lemieux, R. V.; Morgan, A. R. *Can. J. Chem.* **1965**, *43*, 2190.

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Having demonstrated that the cyclization was stereospecific in the predicted sense (compare the cyclization of **4** to the iodolactonization of 3-methyl-4-pentenoic acid)[2], we sought to apply this transformation in systems where it would result in the introduction of two new chiral centers and provide intermediates more closely related to our synthetic targets. When allyl methyl urethane **7a**[8] (Chart I) was treated with $I^+(collidine)_2ClO_4^-$ (**5b**, X = I;[6] 12 h, refluxing CH_2Cl_2), only traces of a new compound were detected by TLC. Similarly, **7b**[8] was unreactive. However, under the same conditions, the corresponding *tert*-butyl urethanes **8a** and **8b** did undergo cyclization with **5b**.[9] These reactions were regio- and stereospecific, affording **11a** and **11b** respectively[10] (Table I). The formation of the six-membered ring products was unexpected; the oxazolidones were not detected in these cyclizations. This change in regiochemistry (compare **4** → **6**) corresponds to nucleophilic attack on an intermediate halonium ion at the site of greater positive charge (see additional discussion below).

We reasoned that a substituent that stabilizes a positive charge less effectively than phenyl might be expected to allow closure to the oxazolidone. To test this hypothesis, we prepared urethanes **9** and **10**. Urethane **9b** (the major isomer from the Wittig procedure)[8] gave, as predicted, a significant amount of the oxazolidone **12c**[10] (**12b**:**12c** = 1:2). Urethane **10b** (the major isomer from the Wittig procedure)[8] showed even greater tendency to go to the oxazolidone product (**13b**:**13c** = 1:5).

The trans-compounds **9a** and **10a** did not behave as predicted, however. Each afforded (stereospecifically) only the six-membered ring product[10] (**12a** and **13a**, respectively).

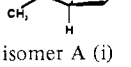
The results of these product studies are consistent with a mechanism (Scheme I) in which two concerted diastereoselective additions to the olefinic bond may occur. Cation I is favored when the aryl substituent is capable of assisting the stabilization of positive charge at the γ-carbon (i.e., when R^1 or R^2 = phenyl and when R_2 = *o*-cyanophenyl or *p*-nitrophenyl).[11] Cation II is favored in the absence of this stabilization (i.e., when $R^1 = R^2$ = H) or when the stabilization afforded by the substituent is counterbalanced by the steric interaction of R^1 and the α-hydrogen (R^1 = *o*-cyanophenyl or *p*-nitrophenyl) in I. Either cation, I or II, may lose the R^3 group (*tert*-butyl easily or methyl more slowly) to afford a cyclic urethane product.

The potential of the halonium-initiated cyclization of allylic urethanes, a reaction that is not only stereospecific but subject to regiochemical control, will be investigated for the synthesis of stereochemically complex natural products.

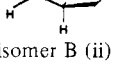
Acknowledgment. We would like to acknowledge helpful discussion with Professor Bert Fraser-Reid. Robert E. Babine assisted in acquiring decoupled spectra on Brown University's Bruker WM250 spectrometer, which was purchased with funds from the National Science Foundation and from Montedison, SPA (Milan, Italy). This work was supported by the National Institutes of Health (AI-18665). K.A.P. is pleased to acknowledge additional support in the form of a Teacher-Scholar Award from the Camille and Henry Dreyfus Foundation.

Supplementary Material Available: Partial ^1H NMR data for the debrominated urethane A and its stereoisomer and ^1H NMR data for halourethanes **11a,b**, **12a-c**, and **13a-c** (2 pages). Ordering information is given on any current masthead page.

(7) Raney nickel hydrogenolysis afforded the debrominated urethane, designated here as isomer A. A mixture of isomer A and its epimer had been prepared (by Grignard addition to the protected prolinal) and subjected to NMR analysis. At 250 MHz the proton spectrum of the mixture showed two completely nonsuperimposable sets of signals (data in supplementary material). The isomer with the smaller coupling constant between protons on the oxazolidone ring and the higher field chemical shifts for these protons (the isomer obtained by debromination of **6**) was tentatively assigned the trans structure by analogy to assignments in the literature (see: Herweh, J. E.; Foglia, T. S.; Swern, D. *J. Org. Chem.* **1968**, *33*, 4029. Spassow, S. L.; Stefanovsky, J. N.; Kurtev, B. J.; Fodor, G. *Chem. Ber.* **1972**, *105*, 2462). This assignment was confirmed by inspection of the ^{13}C NMR spectrum of the mixture ($\delta(CH_3)$ 21.1 and 15.8) and that of isomer A ($\delta(CH_3)$ 21.1). For an analogous ^{13}C assignment, see: Overman, L. E.; Bell, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 1851.



isomer A (i)



isomer B (ii)

(8) All cyclization substrates were prepared by Wittig condensation of the required phosphorane with the urethane of prolinal. Geometric isomers were separated by chromatography on silica gel or by fractional crystallization.

(9) A similar effect of the alkyl "leaving group" on halonium-initiated cyclizations of γ,δ-unsaturated ethers to tetrahydrofurans has been noted by Bartlett. See: Tychnovsky, S. D.; Bartlett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3963.

(10) The cyclic urethanes **11a-13a** and **11b-13b** exhibited carbonyl absorption in the 1690-1705-cm^{-1} range. Stereochemistry was assigned on the basis of proton-proton coupling constants (see supplementary material). For **12c** and **13c**, IR 1750 cm^{-1}, the trans relationship of H_b and H_c was assigned on the basis of coupling constants (see supplementary material); the threo relationship of the centers bearing H_a and H_b was assigned by assuming that addition to the double bond was anti as it was in cyclizations affording the isomeric **12b** and **13b** as well as **12a** and **13a**.

(11) This is reminiscent of substituent effects that control ring size in concerted, cationic polyolefin cyclizations; see the discussion in the following: Parker, K. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 2556. A substituent effect in the *intermolecular* opening of iodonium and bromonium ions has previously been noted; see: Hassner, A. *Acc. Chem. Res.* **1969**, *4*, 9. L'abbe, G.; Hassner, A. *J. Org. Chem.* **1971**, *36*, 258.

(12) **Note Added in Proof**: For the stereochemistry of cyclization of some homoallylic urethanes, see the following: Wang, Y.-F.; Izawa, T.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1982**, *103*, 6465.

Unusual Ligand Replacement: Displacement of η^5-Cyclopentadienyl by η^6-Arenes in the Syntheses of $H_3(\eta^6\text{-X})RhOs_3(CO)_9$ (X = C_6H_6, $C_6H_5CH_3$). Crystal and Molecular Structure of $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$

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We recently described general approaches to the preparation of mixed metal clusters that contain a triosmium unit.[1] Among the compounds reported is the paramagnetic cluster $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$ (Figure 1), obtained from the reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $H_2Os_3(CO)_{10}$ in the presence of H_2. Attempts to prepare the rhodium analogue gave only very small amounts of a paramagnetic substance for which analytical data could not be obtained. However, in the course of this work we did observe displacement reactions that we believe to be without precedent in mono-η^5-cyclopentadienyl complexes.

We find that when $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ reacts with $H_2Os_3(CO)_{10}$ in the presence of H_2 in a solvent that is a potential η^6 ligand (benzene and toluene), the cyclopentadienyl molecule is replaced by a solvent molecule (eq 1; X = C_6H_6, $C_6H_5CH_3$). The second

$$H_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)Rh(CO)_2 \xrightarrow[H_2]{X} H_3(\eta^6\text{-X})RhOs_3(CO)_9 + H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10} \quad (1)$$

product of the above reaction, $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$, has been reported previously[1] from the reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with $H_2Os_3(CO)_{10}$ in the absence of H_2.

In a typical reaction $H_2Os_3(CO)_{10}$ was allowed to react with a 2-fold excess of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in toluene with prepurified hydrogen slowly bubbled through the reaction mixture at 90 °C for 72 h. Orange-red $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ (25% based on $H_2Os_3(CO)_{10}$) and greenish brown $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ (8%) were isolated by TLC (silica 80:20 hexane/benzene). Or-

(1) Shore, S. G.; Hsu, W. L.; Weisenberg, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* **1982**, *1*, 1405.

0002-7863/83/1505-0655$01.50/0