1:1 (v/v) acetonitrile–water gave colorless crystals of **1**: yield 0.11 g (40%); mp 273–277 °C dec; IR (KBr) ν_{max} 3020, 2960, 1480, 1300, 1130, 1040 cm^{-1}; NMR (Me$_2$SO-d_6) δ 7.30 (s, 16 H, arom), 3.96 (s, 16 H, CH$_2$), 3.18 (s, 24 H, CH$_3$). Anal. Calcd for $C_{40}H_{56}N_4B_4F_{16}\cdot 2H_2O$: C, 49.08; H, 6.15. Found: C, 49.22; H, 5.78.

***N,N,N',N',N'',N''*-Hexamethyl-*p*-xylylenediammonium tetrafluoroborate (9)** was prepared from 1.54 g (8 mmol) of *N,N,N',N'*-tetramethyl-*p*-xylylenediamine and 2.5 g (17 mmol) of trimethyloxonium tetrafluoroborate in dry methylene chloride in a similar manner as described for **1**. Recrystallization from 1:1 (v/v) acetonitrile–water gave colorless needles of **9**: yield 2.53 g (80%); mp >280 °C dec.

Kinetic Measurements. A 2.0-mL solution of 9.9×10^{-6} M *p*-nitrophenyl chloroacetate (**7a**), α-naphthyl chloroacetate (**7b**), β-naphthyl chloroacetate (**7c**), or α-chloro-β-naphthyl chloroacetate (**14**) in a phosphate ($^1/_{15}$ or $^1/_{60}$ M) (pH 6.96 or 8.10) or in a borate ($^1/_{15}$ or $^1/_{60}$ M) buffer solution (pH 6.96 or 8.10) was put into a quartz cuvet. The cuvet was placed in a cell holder of a Union high-speed UV spectromonitor Model SM-303, a cell chamber of which was thermostated at 20.2 ± 0.1 °C by circulating thermostated water. Heterocyclophane (7.4×10^{-5} to 3.0×10^{-5} M) was added to the above solution of the ester substrate to start the hydrolysis. The reaction was followed by monitoring the increase in the absorbance of phenol (*p*-nitrophenol, α-naphthol, β-naphthol, and α-chloro-β-naphthol) at 400, 321, 328, and 331 nm, respectively. Each kinetic run followed pseudo-first-order kinetics up to the second half-life: correlation coefficients of the lines obtained were 0.9999–0.9770 (8 points). The dependence of pseudo-first-order rate constants on the heterocyclophane concentration was analyzed by the use of eq 2.

Kinetic measurements for CTAB-catalyzed hydrolyses of ester substrates (**7b–c**) were similarly carried out as described above under the following conditions of concentrations: ester substrate, 9.9×10^{-6} M; CTAB, 9.5×10^{-3} to 3.7×10^{-3} M. The effective concentration of micellar particles was calculated by the following equation

$$[\text{micellar particles}] = \frac{[\text{CTAB}] - [\text{cmc}]}{\text{aggregation no.}}$$

where a reported value of 5×10^{-5} M was used as the critical micellar concentration, [cmc], and a reported number, 61, was employed for the aggregation number. Treatment of kinetic data was the same as described above for the heterocyclophane-catalyzed hydrolysis reactions.

Temperature–Jump Experiments. Temperature–jump experiments were carried out with a Union rapid-reaction analyzer RA-1200. A solution of 0.5×10^{-4} M sodium hydroxynaphthalenecarboxylate (**11** or **12**) and the water-soluble heterocyclophane (1.0×10^{-3} to 0.167×10^{-3} M) in 0.067 M borate + 0.1 M KCl buffer solution at pH 7.0 was put into the temperature–jump cell, and the cell compartment was thermostated at 27 °C by circulating thermostated water. Under a standard experimental condition, a 27-kV voltage was applied to raise the temperature of the solution by ca. 2 °C in a few microseconds. The signal output from the photomultiplier was recorded with a Hitachi memoriscope V-038.

Communications to the Editor

[2,3]-Wittig Rearrangement of Unsymmetrical Bis-Allylic Ethers. A Facile Method for Regio- and Stereoselective Synthesis of 1,5-Dien-3-ols

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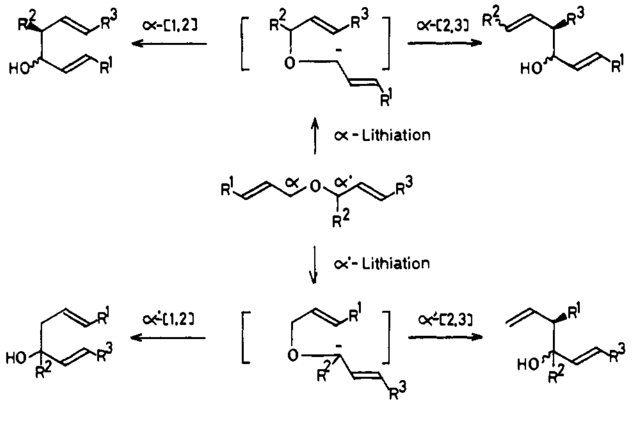
Conceptually, the [2,3]-Witting rearrangement[1] of bis-allylic ethers is a convenient, general vehicle to 1,5-dien-3-ols which are valuable as substrates for the oxy-Cope rearrangement.[2] In order to establish the feasibility of such an approach within *unsymmetrical* frameworks, however, many questions must be elucidated which remain largely unexplored.[3,4] There are positional ambiguities at both the migrating termini in terms of the possibilities for [2,3] vs. [1,2] shift[5] and for α vs. α' lithiation, providing at least four reaction pathways (Scheme I). Furthermore, stereochemical problems also arise when the migrating allylic moiety has substituents at the α and/or γ position; the [2,3]-process might produce geometric and/or diastereomeric isomers.

Scheme I



As part of our general interest in the synthetic potential of [2,3]-sigmatropic rearrangements,[6] we have now systematically studied carbanion rearrangements of unsymmetrical bis-allylic ethers having different substitution patterns. Herein we wish to report that these rearrangements proceed exclusively in a [2,3]-sigmatropic fashion with remarkably higher levels of regio- and stereoselectivity than previously anticipated. The genuine [2,3]-Wittig process provides an exceedingly facile procedure for regio- and stereocontrolled synthesis of a broad variety of 1,5-dien-3-ols from nonidentical allylic alcohols which in many instances will be superior to current procedures.[7]

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(1) For reviews on carbanion rearrangements, see: Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763. Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter VI.

(2) Recent reviews include: Marvell, E. N.; Whalley, W. In "Chemistry of the Hydroxy Group", Patai, S., Ed.; Interscience: New York, 1971; Vol. 2; Chapter 13. Bennett, G. B. *Synthesis* **1977**, 589.

(3) For the [2,3]-Wittig rearrangement of symmetrical bis-allylic ethers with or without the [1,2]-shift, see: (a) Baldwin, J. E.; DeBernard, J.; Patrick, J. E. *Tetrahedron Lett.* **1970**, 353. (b) Rautenstrauch, V. *Chem. Commun.* **1970**, 4.

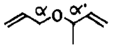
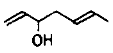
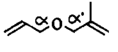
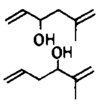
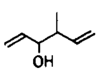
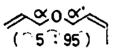
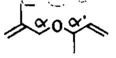
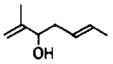
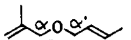
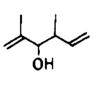
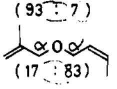
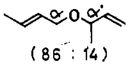
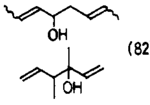
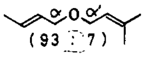
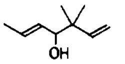
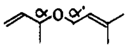
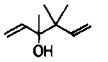
(4) For examples of closely related Wittig variations, see: (a) Schöllkopf, U.; Fellenberger, K.; Rizk, M. *Liebigs Ann. Chem.* **1970**, *734*, 106. (b) Baldwin, J. E.; Patrick, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 3556. (c) Schulte-Elte, K. H.; Rautenstrauch, V.; Ohloff, G. *Helv. Chim. Acta* **1971**, *54*, 1805. (d) Garbers, C. F.; Scott, F. *Tetrahedron Lett.* **1976**, 507. (e) Wada, M.; Fukui, A.; Nakamura, H.; Takei, H. *Chem. Lett.* **1977**, 557.

(5) In addition, a [1,4]-shift is also allowed by orbital symmetry. For examples of the [1,4]-shift under Wittig conditions, see: Felkin, H.; Tambuté, A. *Tetrahedron Lett.* **1969**, 821. Chérest, M.; Felkin, H.; Frajerman, C. *Ibid.* **1977**, 3489. Felkin, H.; Frajerman, C. *Ibid.* **1977**, 3485. Rautenstrauch, V. *Helv. Chim. Acta* **1972**, *55*, 594.

(6) Nakai, T.; Mikami, K. *Chem. Lett.* **1979**, 1081. Nakai, T.; Mikami, K.; Taya, S.; Kimura, Y.; Mimura, T. *Tetrahedron Lett.* **1981**, *22*, 69.

0002-7863/81/1503-6492$01.25/0

Table I. Wittig Rearrangement of Unsymmetrical Bis-Allylic Ethers[a]

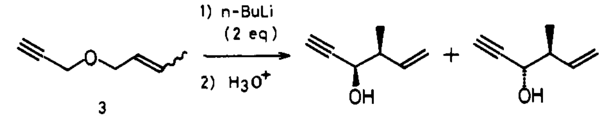
entry	substrate (E:Z)[b]	product[c] (% yield)[d]	regioselectivity[e]	stereoselectivity[f] threo:erythro [E:Z]
1		 (79)	α-[2,3] only	(E, >95%)
2		 (77)	α/α'-[2,3][g] = 4:3	
3	 (93 : 7)	 (81)	α-[2,3] only	79:21 (84:16)[h]
4	 (5 : 95)	(88)		12:88 (8:92)[h]
5		 (60)	α-[2,3] only	[E, >95%]
6	 (93 : 7)	 (70)	α-[2,3] only	67:33 (72:28)[h]
7	 (17 : 83)	(71)		16:84 (5:95)[h]
8	 (86 : 14)	 (82)	α/α'-[2,3] = 1:2	50:50
9	 (93 : 7)	 (65)	α-[2,3] only	
10		 (66)	α-[2,3] only	

[a] All reactions were run as follows. A 1.4 M solution of *n*-BuLi in hexane (1.0 mL/1.0 mmol) was added dropwise to a substrate solution in THF (1.0 mL/1.0 mmol) at -85 °C under N$_2$ and stirred at that temperature for 5-8 h. The mixture was then allowed to warm to 0 °C and quenched with hydrochloric acid. [b] Refers to the geometric ratio of the allylic alcohol or chloride employed. [c] All products were fully characterized by IR and NMR spectra (see the supplementary material). [d] Distilled yields of isomeric mixtures, not optimized yet. [e] For the notation, see Scheme I. [f] Determined by a combination of GLC and NMR analysis with the aid of a NMR shift reagent. [g] In this case, the [1,2]- and [2,3]-shifts are indistinguishable. [h] Refers to the calculated value based on 100% of geometric purity for the substrate.

The rearrangement of bis-allylic ethers (**1**), readily prepared from appropriate combinations of allylic alcohols and allylic halides, is accomplished in tetrahydrofuran (THF) at -85 °C by using a commercial solution of butyllithium in hexane as the base, affording 1,5-dien-3-ols (**2**) in high yields. The examples are given in Table I.

Inspection of Table I reveals several characteristic features of the present [2,3]-Wittig variant which are synthetically valuable. (1) The carbanion rearrangement readily occurs at that low temperature, and the product mixture is free from detectable amounts of the [1,2]- and [1,4]-rearrangement products.[5] (2) The crucial regiochemistry in the lithiation step[8] is remarkably controlled by the difference in total number of α- and γ-alkyl substituents between the two allylic moieties, *giving mostly the single regioisomer resulting from the exclusive lithiation on the less substituted allylic moiety.* In other words, either α- or γ-alkyl substitution considerably depresses the lithiation, while the β-alkyl group has little effect as expected. A direct comparison of the depressive effect of α vs. γ substituent (entry 8) interestingly indicates the latter to be greater. (3) The examples of entries 1 and 5 can be viewed as the otherwise difficult preparations of 6-substituted 1,5-dien-3-ols, since reactions of α,β-unsaturated carbonyl compounds with crotyl-type organometallic reagents generally afford the 4-substituted 1,5-dien-3-ols via complete allylic transposition.[7a] (4) In the rearrangment creating a new olefinic bond, a high *E* selectivity is obtained (entries 1 and 5). While this *E* selection is in sharp contrast to the *Z* selection recently reported for an entirely different [2,3]-Wittig variant,[9] the observed stereoselectivity of the present variant is best explained by essentially the same argument used to rationalize the comparable stereoselectivity observed with a variety of related [2,3]-sigmatropic rearrangements.[6,10] (5) In the rearrangement generating new chiral centers, a high-to-moderate level of diastereoselection is obtained, depending on the substrate geometry (entries 3, 4, 6, and 7); *a high degree of erythro*[11] *selectivity is achieved with the Z substrate whereas a moderate threo selectivity is obtained with the E substrate.*

Interestingly, we have also found that the dianion rearrangement of (*E*)-crotyl propargyl ether (**3**) exhibits a higher degree of threo selectivity while the *Z* substrate shows a comparable level of erythro selectivity as shown below.



3 Erythro-**4** Threo-**4**

E/Z = 93 : 7 7 : 93

E/Z = 2 : 98 88 : 12

The stereochemistry of these diastereomers was unequivocally

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(7) (a) For additions of allylic organometallic reagents to α,β-unsaturated carbonyl compounds, e.g., MgX, see: Viola, A.; Iorio, I. J. *J. Am. Chem. Soc.* **1976**, *89*, 3462. Zn: Grandemar, M. *Bull. Soc. Chim. Fr.* **1962**, 974. Si: Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1978**, 498. An exception: Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) For additions of vinylic or actylenic organometallic reagents to β,γ-unsaturated carbonyl compounds; e.g., vinylic Grignard: Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 7573. Sodium acetylide: Fujita, Y.: Wada, F.; Onishi, T.; Nishida, T. *Chem. Lett.* **1977**, 943.

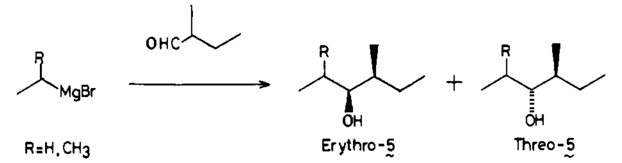
(8) The present reaction is apparently free from the well-known complexity in terms of α vs. γ reactivity of (alkoxyallyl)lithiums. For this problem, see: Still, W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620 and references therein.

(9) Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1927.

(10) For a general review on the stereochemistry of [2,3]-sigmatropic rearrangement, see: Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(11) For the sake of convenience, we have used the prefixes threo and erythro according to the nomenclature of Heathcock: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

determined through NMR and GLC comparisons of their hydrogenation products (**5**) with an erythro-rich mixture independently prepared by the reaction of 2-methylbutanal with ethyl or isopropyl Grignard reagent in which the stereochemistry of the major stereoisomer can be predicted by the Cram's rule.[12-14]



The observed degree of internal asymmetric induction is particularly noteworthy since no great degree of either threo or erythro selectivity has been reported yet for different [2,3]-sigmatropic variations[10,15] except for the [2,3]-Wittig process[3b] of (*Z*)-crotyl benzyl ether exhibiting a high erythro selectivity.[16] Regardless of the origin of the regio- and stereochemical features outlined here,[17] the results of the present study anomalously expand the synthetic potential of the [2,3]-Wittig rearrangement. In particular, the high degree of diastereoselection provides the synthetic chemists with a powerful weapon with which to attack the current problem of acyclic stereocontrol.[15] Further synthetic applications of the [2,3]-Wittig rearrangements are in progress.

Supplementary Material Available: Spectral and physical properties for rearrangement products (5 pages). Ordering information is given on any current masthead page.

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(12) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1971; Chapter 3.

(13) **5** (R = H): 77% yield; 66:34 erythro/threo (by NMR assay); GLC (PEG 20M, 100 °C), t_R 28.8 min (major) and 29.8 min (minor). **5** (R = CH_3): 79% yield; ca. 2.0 erythro/threo (by GLC and NMR assay); GLC (PEG 20M, 80 °C), t_R 47.2 min (major) and 48.7 min (minor).

(14) The stereochemical assignment for **5** (R = H) was further confirmed by NMR and GLC comparisons with an authentic threo-**5** (R = H) independently prepared via reaction of *trans*-3,4-epoxyhexane with lithium dimethylcuprate.

(15) For an excellent review on acyclic stereocontrol, see: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. See also: Jemison, R. W.; Laird, T.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans 1* **1980**, 1436.

(16) In contrast, however, the *E* counterpart has exhibited a low degree of threo selectivity.[3b,4a]

(17) A detailed discussion will be reported in a full paper.

Oxidation of Isopropylamine Coordinated to Ruthenium

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Received April 24, 1981

There has been much recent interest in the oxidative dehydrogenation of coordinated amines to the corresponding imines or nitriles.[1-3] Many of these studies have involved ruthenium as the metal center, and although the formation of complexes containing the α,α'-diimine moiety has been relatively common,[1] complexes containing coordinated simple monodentate imines have not been isolated.[1,2]

We have studied the oxidation of isopropylamine in the complex $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine). Two major processes occur: a two-electron oxidation yielding the corresponding imine complex $[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+}$, which in turn undergoes a further two-electron oxidation to yield a product characterized as $[Ru(tpy)(bpy)(NCMe_2)]^{3+}$. The nature of these two oxidation products is significant, since the two-electron oxidation product represents the first isolated monodentate imine complex of ruthenium, and the structure of the four-electron oxidation product is novel in ruthenium chemistry, as it can be formulated to contain an N-bound isopropylideneamide anion.

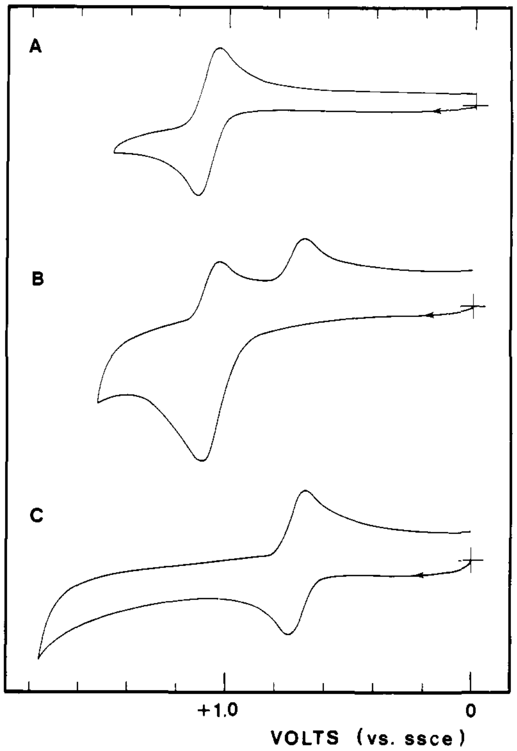

Figure 1. Cyclic voltammograms (200 mV/s) of $[Ru(tpy)(bpy)(isopropylamine)]^{2+}$ (A) and of the two-electron (B) and four-electron (C) oxidation products in acetonitrile solution.[4]

In their study of the oxidation of benzylamine in $[Ru(NH_3)_5(PhCH_2NH_2)]^{2+}$ to the benzonitrile complex, Diamond et al.[2] observed an intermediate which they assumed to be the imine species. In the same work, the oxidation of $[Ru(NH_3)_5(cyclohexylamine)]^{3+}$ yielded $[Ru(NH_3)_6]^{2+}$ and cyclohexanone, presumably by hydrolysis of the coordinated imine complex generated by dehydrogenation. Brown et al.[1] also claimed the generation in situ of nonconjugated chelated diimines in the oxidation of $[Ru(bpy)_2(tn)]^{2+}$ and $[Ru(bpy)_2(aepy)]^{2+}$ (tn = 1,3-propanediamine; aepy = 2-(aminoethyl)pyridine). In none of these cases could the imine complex be isolated.

A spectrophotometric titration of the oxidation of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ by Ce(IV) in 2 M H_2SO_4 indicates an overall four-electron oxidation consisting of two separate two-electron processes which are consecutive. Spectra taken during exhaustive electrolyses (platinum gauze electrode) in 0.1 M HCl (at 0.90 V vs. SSCE) and acetonitrile (at 1.10 V vs. SSCE) indicate similar results. The overall spectrophotometric and coulometric *n* values were slightly less than 4.0 (viz., 3.6–3.8). The second two-electron process can be reversed electrochemically (coulometry at 0.50 V in 0.1 M HCl, 0.55 V in acetonitrile), with *n* for the reduction being exactly half the value for the overall oxidation. The two- and four-electron oxidation products were isolated by precipitation as the hexafluorophosphate salts and purified by ion-exchange chromatography on SP-Sephadex.

For the two-electron oxidation product, the visible spectrum (MLCT transitions) in 2 M H_2SO_4 has ϵ_{474}^{max} 8000 (cf. ϵ_{481}^{max} 8800 for the parent isopropylamine species). Cyclic voltammetry in acetonitrile solution[4] revealed $E_{p,a}$ = 1.10 V (compared with

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(1) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190–196 and references therein.

(2) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661–2664.

(3) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884–1889.

(4) Support electrolyte tetra-*n*-ethylammonium hexafluorophosphate; platinum bead working electrode; saturated sodium chloride calomel electrode (SSCE) as reference.

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