Table II. Rate and Equilibrium Constants for Carbinolamine and Aldimine Formation (T = 25 °C, I = 0.5)

A. Reaction: $H_iPLP^{i-3} + ala^- \rightleftarrows H_iPLP{\cdot}ala^{i-4}{}_{carbinolamine/aldimine}$

i	Carbinolamine formation $k_{a,i}$ (M^{-1} $s^{-1} \times 10^{-5}$)	Aldimine formation Log K_{eq}	Aldimine formation $k_{f,i}$ (M^{-1} s^{-1})
0	2.7	0.53	4.1
1	3.3	4.19	2.8×10^1
2	4.0	4.81	1.7×10^3
3	23	6.69	1.0×10^5
4	6000	8.11	7.0×10^6

B. Reaction: $Cu(H_iPLP)^{i-1} + ala^- \rightleftarrows Cu(H_iPLP{\cdot}ala)^{i-2}{}_{carbinolamine/aldimine}$

i	Carbinolamine formation Log K_{eq}	Carbinolamine formation $k_{a,i}^{Cu}$ (M^{-1} $s^{-1} \times 10^{-5}$)	Aldimine formation Log K_{eq}
0	8.60	8.2	10.74
1	8.87	14	11.46
2	9.32	220	12.56

C. Reaction: $Cu(H_iPLP{\cdot}ala)^{i-2}{}_{carbinolamine} \rightleftarrows Cu(H_iPLP{\cdot}ala)^{i-2}{}_{aldimine} + H_2O$

i	Log K_{eq}	$k^i_{dehydration}$ (s^{-1})
0	2.14	0.001 7
1	2.59	0.000 553
2	3.24	0.000 334

as I. The values of the rate and equilibrium constants resolved from the data are given in Table II, along with values determined for the "direct" conversion of PLP to aldimine. Cu(II) dependent pathways were not observed for these latter reactions.

Equation 2 shows that I is formed from PLP along both Cu(II) independent and Cu(II) dependent pathways. Under the conditions that we have investigated, the former were usually found to be dominant, with the latter becoming important only under conditions where the relatively weak Cu-H_iPLP^{i-1} complexes are formed in appreciable concentrations. This can be seen by comparing the two sets of theoretical first-order rate constants for carbinolamine formation which have been calculated from the results and are given in Table I. The first set has been calculated neglecting the Cu(II) pathways, and the second set included them. In experiments 1-6 of Table I, it is seen that the difference between these two sets is small being within the experimental error. Under the conditions employed in experiments 7-9, however, the Cu(II) dependent pathways become important. In all cases good agreement has been achieved between the theoretical and observed values.

In the Cu(II) independent pathways I is formed by the rate limiting reaction of protonated or unprotonated PLP with ala^-, followed by rapid reaction (trapping) of the carbinolamine with Cu(II),

$$H_iPLP^{i-3} + ala^- \underset{k_{-a,i}}{\overset{k_{a,i}}{\rightleftarrows}} H_iPLP \cdot ala^{i-4}{}_{carb} \underset{fast}{\overset{+Cu^{2+}}{\rightleftarrows}} Cu(H_iPLP \cdot ala)^{i-2}{}_{carb}$$

Cu(II) ligand exchange reactions involved in the second step are considerably faster than those studied here,[11-13] as is borne out by the results. The Cu(II) dependent pathways, no doubt, involve the attack of ala^- on Cu(II) bound PLP.

In the absence of Cu(II), or other suitable trapping agent, carbinolamine rapidly dehydrates,

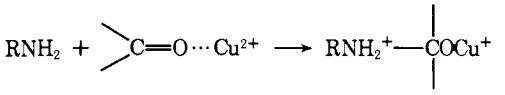
$$H_iPLP \cdot ala^{i-4} \underset{k_{-b,i}}{\overset{k_{b,i}}{\rightleftarrows}} H_iPLP \cdot ala^{i-4}{}_{aldimine} + H_2O$$

and is formed in only a low steady state concentration. In this context, the overall forward rate constant for aldimine formation along a given path is related to the microscopic rate constants by the expression,

$$k_{f,i} = \frac{k_{a,i}}{1 + k_{-a,i}/k_{b,i}} \quad (3)$$

From the measured values of $k_{f,i}$ and $k_{a,i}$ in Table II, the ratios $k_{-a,k}/k_{b,i}$ are found to be sufficiently greater than unity that eq 3 takes the form, $k_{fi} = (k_{ai}/k_{-ai})k_{bi}$; i.e., amine addition comprises a preequilibrium step to rate limiting dehydration. The rate of PLP carbinolamine formation is found here to be similar to that reported for pyridine-4-carboxaldehyde (PC)[4] but in agreement with the postulated catalytic effect of the aromatic phenolate group,[5] dehydration of the PLP carbinolamine is considerably faster than that of PC.[3,4]

It is also seen in Table II that the equilibrium constant for the reaction I ⇄ II lies far to the right. In spite of this, the rate of formation of I is considerably faster than its dehydration. The hydration of II is very slow. The CuH_iPLP^{i-1} complexes react significantly faster with ala^- than does uncomplexed PLP. Activation possibly arises from polarization of PLP, or from stabilization of the zwitterion that is the immediate reaction product of amine addition.[14]



References and Notes

(1) Support by the National Science Foundation is gratefully acknowledged.
(2) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1969, p 490 ff.
(3) T. C. French and T. C. Bruice, *Biochemistry*, **3**, 1589 (1964).
(4) R. N. F. Thorneley and H. Diebler, *J. Am. Chem. Soc.*, **96**, 1072 (1974).
(5) T. C. French, D. S. Auld, and T. C. Bruice, *Biochemistry*, **4**, 77 (1965).
(6) K. S. Bai and D. L. Leussing, *J. Am. Chem. Soc.*, **89**, 6126 (1967).
(7) D. Hopgood and D. L. Leussing, *J. Am. Chem. Soc.*, **91**, 3740 (1969).
(8) C. V. McDonnell, Jr., M. S. Michailidis, and R. B. Martin, *J. Phys. Chem.*, **74**, 26 (1970).
(9) M. E. Farago and T. Matthews, *J. Chem. Soc. A*, 609 (1969).
(10) Transamination of the aldimine to give pyridoxamine is observed in a third, much slower, step.
(11) A. F. Pearlmutter and J. Stuehr, *J. Am. Chem. Soc.*, **90**, 858 (1968).
(12) L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970).
(13) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 1955 (1972).
(14) J. M. Sayer, B. Pinsky, A. Schonbrunn, and W. Washtien, *J. Am. Chem. Soc.*, **96**, 7998 (1974).

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Stereospecific Synthesis of Heteroatom-Substituted Olefins from α,β-Epoxysilanes. Preparation of Vinyl Bromides, Enol Acetates, Enol Ethers, and Enamides[1]

Sir:

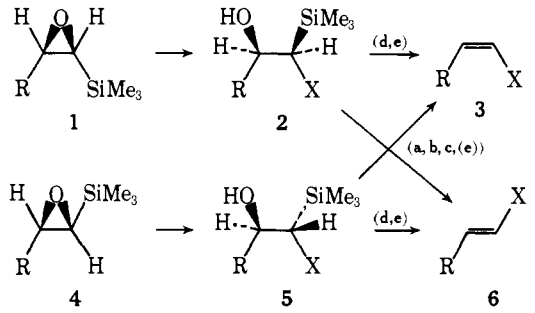
Considerable research effort has been devoted to the development of methods for the stereospecific synthesis of olefins in which only carbon or hydrogen atoms are directly attached to the carbon-carbon double bond.[2] Many methods for the stereospecific synthesis of vinyl halides have also been developed.[3] However, no general methods for the stereospecific synthesis of other heteroatom-substituted olefins exist. We report here the first general stereospecific method for preparing a variety of heteroatom-substituted olefins, and show its applicability to the synthesis of vinyl bromides, enol acetates, enol

Table I. Conversion of α,β-Epoxysilanes to Heteroatom-Substituted Olefins

Epoxide	Reaction conditions	Product	X	Isomeric purity[a]	Overall yield from epoxide (%)[b]
1a	*c, d*	**6a**	Br	>99% trans	95[e]
1b	*c, d*	**6b**	Br	98% trans	90
4a	*c, f*	**3a**	Br	>99% cis	80[e]
4b	*c, f*	**3b**	Br	>99% cis	85
1b	*g*	**6c**	OAc	97% trans	84
4b	*h*	**3c**	OAc	97% cis	81
1b	*i, j*	**3d**	OMe	86% cis	85
4b	*k, j*	**6d**	OMe	97% trans	81
1b	*l, m, n*	**3e**[o]	NHAc	>99% cis	80
4b	*l, m, n*	**6e**[p]	NHAc	>99% trans	62
7	*q, r*	**9**	(Br)		90[e]
10	*c, d*	**12a**	Br		82
10	*s, j*	**12b**	OMe		77

[a] Determined by VPC. [b] Isolated yield unless otherwise noted. [c] HBr, Et_2O, −25 °C, 30 min. [d] BF_3·Et_2O, CH_2Cl_2, 0 °C, 8–10 h. [e] Yield determined by NMR. [f] BF_3·Et_2O, CH_2Cl_2, 0 °C, 15 min. [g] BF_3·Et_2O, Ac_2O, AcOH, room temp, 2 h. [h] BF_3·Et_2O, Ac_2O, AcOH, room temp, 18 h. [i] CF_3CO_2H, MeOH, 0 °C, 5 h. [j] KH, THF, 0 °C, 45–60 min. [k] BF_3·Et_2O, MeOH, 0 °C, 30 h. [l] BF_3·Et_2O, CH_3CN, −25 °C, 11–20 min. [m] H_2SO_4, H_2O, THF, room temp, 10–12 h. [n] KH, THF, room temp, 45–50 min. [o] NMR (CCl_4) δ 8.8 (NH, d, J = 10 Hz), 6.60 (d, J = 9 Hz, of d, J = 10 Hz), 4.58 (t, J = 7.5 Hz, of d, J = 9 Hz). [p] NMR (CCl_4) δ 9.7 (NH, d, J = 10 Hz), 6.73 (d, J = 10 Hz, of d, J = 14 Hz), 5.25 (t, J = 7 Hz, of d, J = 14 Hz). [q] $MgBr_2$, Et_2O, room temp, 12 h (or HBr, Et_2O, −78 °C, 1 h). [r] BF_3·Et_2O, CCl_4, 0 °C, 1 h. [s] CF_3CO_2H, MeOH, room temp, 3 h.

Scheme I



1: a, R = n-C_3H_7; b, R = n-C_6H_{13}

2: a, R = n-C_3H_7; X = Br; b, R = n-C_6H_{13}; X = Br; c, R = n-C_6H_{13}; X = OAc; d, R = n-C_6H_{13}; X = OMe; e, R = n-C_6H_{13}; X = NHAc

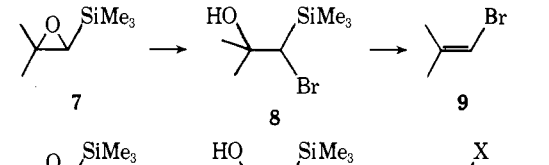
3: a, R = n-C_3H_7; X = Br; b, R = n-C_6H_{13}; X = Br; c, R = n-C_6H_{13}; X = OAc; d, R = n-C_6H_{13}; X = OMe; e, R = n-C_6H_{13}; X = NHAc

4: a, R = n-C_3H_7; b, R = n-C_6H_{13}

5: a, R = n-C_3H_7; X = Br; b, R = n-C_6H_{13}; X = Br; c, R = n-C_6H_{13}; X = OAc; d, R = n-C_6H_{13}; X = OMe; e, R = n-C_6H_{13}; X = NHAc

6: a, R = n-C_3H_7; X = Br; b, R = n-C_6H_{13}; X = Br; c, R = n-C_6H_{13}; X = OAc; d, R = n-C_6H_{13}; X = OMe; e, R = n-C_6H_{13}; X = NHAc

Scheme II



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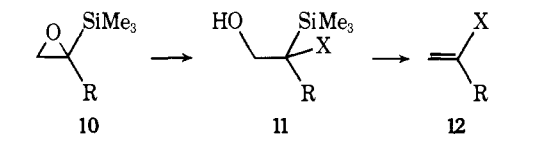


10

11

12

R = n-C_6H_{13}

a, R = n-C_6H_{13}; X = Br
b, R = n-C_6H_{13}; X = OMe
c, R = n-C_6H_{13}; X = $OCH_2CH{=}CH_2$

ethers, and enamides, compounds of demonstrated synthetic utility.[4-7]

Our synthetic approach, shown in Scheme I, involves the regio- and stereospecific acid-catalyzed ring-opening reactions of α,β-epoxysilanes, followed by stereospecific β-elimination reactions of the resulting β-hydroxysilanes. We have previously shown that the olefin-forming elimination reactions of β-hydroxysilanes are highly stereospecific and that a syn process takes place under basic conditions and an anti process under acidic conditions, thus either a cis or trans olefin can be obtained from a single precursor.[8,9] We have also recently shown that α,β-epoxysilanes undergo regio- and stereospecific ring opening by organocuprate reagents[9] (in contrast to some other organometallic reagents[9,10]) to give diastereomerically pure β-hydroxysilanes.[9] Because of the well-known stability of cations β to silicon,[11] acid-catalyzed reactions of α,β-epoxysilanes might be expected to proceed with ring opening at the β carbon. Remarkably, we observe only α ring opening by nucleophiles (HBr, AcOH, MeOH, CH_3CN) under a variety of experimental conditions.[12,14]

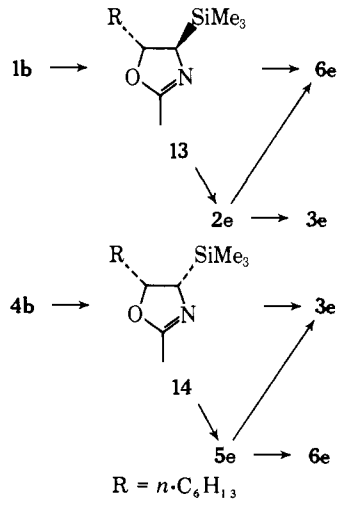
Thus, α,β-epoxysilanes[15] react with HBr in ether to give excellent yields of α-bromo-β-hydroxysilanes,[16] which are readily converted to vinyl bromides in high yields and in very high stereochemical purity by treatment with BF_3·Et_2O[17] (see Table I and Schemes I and II). The overall stereochemistry is consistent with a highly stereospecific epoxide opening (with inversion of configuration) followed by an anti β-elimination process.[9]

Treatment of epoxysilanes **1b** and **4b** with acetic acid containing 10–20% acetic anhydride and 0.2% BF_3·Et_2O at room temperature produced directly the enol acetates **6c** and **3c**, respectively, in high yields and isomeric purities (see Table I and Scheme I).[18,19] (When the epoxides were treated with acetic acid in the absence of BF_3·Et_2O, acetoxy alcohols were observed.)

α,β-Epoxysilanes react with methanol in the presence of acid to give methoxy alcohols.[21] Although further treatment with acid, to effect anti elimination,[9] has not yet been successful, treatment with KH, to effect syn elimination,[9] yields enol ethers (see Table I and Schemes I and II).

Enamides can be prepared in high stereochemical purity via the reactions of α,β-epoxysilanes with acetonitrile. When the epoxides **1b** and **4b** were treated with CH_3CN in the presence of BF_3·Et_2O, the initial products were the oxazolines **13** and **14**, respectively.[22] Hydrolysis of the oxazolines yielded hydroxyamides **2e** and **5e**, respectively; treatment of these hydroxyamides with KH in THF gave the enamides **3e** and **6e**, respectively, in isomeric purities over 99% (see Table I and Scheme I).[23]

The regiospecificity of the ring-opening reactions is dramatically illustrated by the reactions of the epoxides **7** and **10** with HBr and with MeOH. With epoxide **7**, cationic processes should strongly favor β-opening since the resulting carbonium ion would be tertiary as well as β to silicon.[24] With epoxide **10**, S_N2-type processes might be expected to favor β-opening on



the basis of steric hindrance. However, both epoxides (as well as all other α,β-epoxysilanes we have studied) yielded only products of α-opening under acidic conditions. The preference for α-opening (together with the high stereospecificity of these reactions) suggests that trimethylsilyl groups considerably facilitate nucleophilic displacements α to silicon.[13b]

Since general methods for the synthesis of geometrically defined heteroatom-substituted olefins have not been available, the potential applications of such compounds in organic chemistry (apart from those of vinyl halides[4]) have not been explored. Enol acetates can be converted to lithium enolates with preservation of double bond configuration.[5b] Although enolates have found considerable use in organic synthesis,[5,25] the effect of double bond configuration on their reactions has been little studied.[26] Applications of geometrically defined heteroatom-substituted olefins in a variety of pericyclic reactions can be envisioned. For example, allyl enol ethers of known configuration would be expected to undergo Claisen rearrangements with the formation of two new asymmetric centers having a known relationship.[27] In preliminary experiments, we have found that epoxide **10** can be converted (via the allyloxy alcohol **11c**) to the allyl enol ether **12c** which appears to undergo a normal Claisen rearrangement.

Previously known methods for the preparation of enol acetates, enol ethers, and enamides generally give mixtures of isomeric products.[28] The method described here promises to be valuable for the stereospecific synthesis of these compounds. This work, combined with our previously reported stereospecific synthesis of alkyl-substituted olefins,[9] demonstrates that α,β-epoxysilanes can be viewed as the first "stereospecific vinyl cation equivalents". Extensions to the synthesis of other heteroatom-substituted olefins and new synthetic applications of heteroatom-substituted olefins are under investigation in our laboratories.

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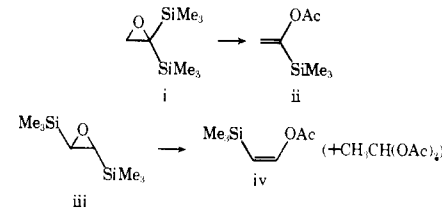
References and Notes

(1) Presented in part at the 7th Central Regional Meeting of the American Chemical Society, Morgantown, West Virginia, May 1975, paper no. 11, and at the 171st National Meeting of the American Chemical Society, New York, N.Y., April 1976, Abstracts INOR 70.
(2) Reviews: J. Reucroft and P. G. Sammes, *Q. Rev., Chem. Soc.*, **25**, 135–169 (1971); D. J. Faulkner, *Synthesis*, 175–189 (1971).
(3) For some recent methods, see (a) F. Näf and P. Degen, *Helv. Chim. Acta*, **54**, 1939–1949 (1971); (b) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, **94**, 9256–9258 (1972); (c) H. C. Brown, T. Hamaoka, and N. Ravindran, *ibid.*, **95**, 5786–5788 (1973); (d) H. C. Brown, T. Hamaoka, and N. Ravindran, *ibid.*, **95**, 6456–6457 (1973); (e) J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, **77**, 269–279 (1974); (f) J. F. Normant, C. Chuit, G. Cahiez, and J. Villieras, *Synthesis*, 803–805 (1974); (g) R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543–546 (1974); (h) D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 679–680 (1975).
(4) For synthetic applications of vinyl halides, see ref 3a, 3b, and the following: (a) H. Normant, *Adv. Org. Chem.*, **2**, 1–65 (1960); (b) G. Linstrumelle, *Tetrahedron Lett.*, 3809–3812 (1974); (c) M. Tamura and J. Kochi, *Synthesis*, 303–305 (1971); (d) S. M. Neumann and J. K. Kochi, *J. Org. Chem.*, **40**, 599–606 (1975); (e) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, **94**, 7210–7211 (1972); (f) C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *ibid.*, **97**, 857–865 (1975); (g) G. Stork and M. Isobe, *ibid.*, **97**, 6260–6261 (1975), and references cited in each of the above.
(5) Enol acetates: (a) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 467–468, 565–568. See also (b) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502–2512 (1965); (c) H. O. House, R. A. Auerbach, M. Gall, and N. P. Peet, *ibid.*, **38**, 514–522 (1973); (d) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310–3324 (1973).
(6) Enol ethers: F. Effenberger, *Angew. Chem., Int. Ed. Engl.*, **8**, 295–312 (1969); S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1–252 (1975).
(7) Enamides: R. B. Boar, J. F. McGhie, M. Robinson, D. H. R. Barton, D. C. Horwell, and R. V. Stick, *J. Chem. Soc., Perkin Trans. 1*, 1237–1241 (1975); R. B. Boar, J. F. McGhie, M. Robinson, and D. H. R. Barton, *ibid.*, 1242–1244 (1975); see also R. B. Boar, F. K. Jetuah, J. F. McGhie, M. S. Robinson, and D. H. R. Barton, *J. Chem. Soc., Chem. Commun.*, 748 (1975).
(8) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1133–1136 (1974); *J. Am. Chem. Soc.*, **97**, 1464–1468 (1975).
(9) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263–2264 (1975).
(10) (a) J. J. Eisch and J. E. Galle, *J. Org. Chem.*, **41**, 2615–2621 (1976); (b) *J. Am. Chem. Soc.*, **98**, 4646–4648 (1976).
(11) A. W. P. Jarvie, *Organomet. Chem. Rev., Sect. A*, **6**, 153–207 (1970); see also G. D. Hartman and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 6147–6151 (1975).
(12) α,β-Epoxysilanes were first shown to undergo regioselective α ring-opening with $LiAlH_4$ by J. J. Eisch and J. T. Trainor (*J. Org. Chem.*, **28**, 2870–2876 (1963)). In our studies of the rearrangements of α,β-epoxysilanes,[13] we observed bromohydrins resulting from clean α ring-opening by $MgBr_2$ in several cases.[13b] Products resulting from both α and β ring-opening were formed in the reactions of triphenylsilylethylene oxide with HCl, with $MgBr_2$, and with amines.[10a]
(13) (a) P. F. Hudrlik, C.-N. Wan, and G. P. Withers, *Tetrahedron Lett.*, 1449–1452 (1976); (b) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, *ibid.*, 1453–1456 (1976).
(14) Since the original submission of this manuscript, regio- and stereospecific α ring-opening of an α,β-epoxysilane by H_2O, MeOH, and HBr was reported: C. M. Robbins and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 697–698 (1976). See also P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra, and R. J. Rona, *Tetrahedron Lett.*, in press.
(15) Epoxides **1a**[9] and **1b** were prepared from 1-pentynyltrimethylsilane and 1-octynyltrimethylsilane, respectively, as previously described.[9] Epoxides **4a**[9] and **4b** were prepared from 1-pentyne and 1-octyne, respectively, by chloroplatinic acid-catalyzed hydrosilylation with $MeCl_2SiH$ or Me_2ClSiH, reaction with MeMgX, and epoxidation. Epoxides **4a** and **4b** thus obtained were each contaminated with about 10% of a regioisomer (e.g., **10**). Epoxide **4b** was purified by flash-vacuum pyrolysis at 500 °C (to destroy the minor regioisomer): P. F. Hudrlik and C.-N. Wan, to be submitted for publication (see also ref 13a). Epoxide 7 was prepared as previously reported.[9] Epoxide **10** was prepared from 1-octynyltrimethylsilane by a method analogous to that described for the preparation of **10** (R = *n*-Pr) in ref 13, and also by a new method to be described in a future report: P. F. Hudrlik, R. H. Schwartz, and J. C. Hogan, unpublished work.
(16) We have previously prepared the bromohydrins **2a**, **5a**, and **8** by treating the epoxides **1a**, **4a**, and 7 with $MgBr_2$ in ether (see ref 13b). For several epoxides, rearrangement accompanied bromohydrin formation, and in some cases only rearranged products could be isolated. The HBr method described here gave pure bromohydrins in every case so far examined.
(17) When bromohydrin **2a** was treated with KH in THF (room temp, 15 min), only the starting epoxide **1a** was formed, rather than the vinyl bromide **3a** which might have resulted from a syn β-elimination process. Similarly, bromohydrin **8** was converted to epoxide 7 on treatment with either KH in THF or with LiH in THF.
(18) In a similar way the bis(trimethylsilyl)epoxides i[13] and iii[13] were converted to the enol acetates ii and iv, respectively.



(19) In the conversions of **1b** and **4b** to **6c** and **3c**, respectively, no *gem*-diacetate (a common by-product when aldehydes are converted to enol acetates[20]) was observed.
(20) For example, see P. Z. Bedoukian, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, pp 127–129.
(21) Methoxy alcohols were also prepared by epoxide opening with MeONa in

MeOH, but this was generally less satisfactory than the acid-catalyzed reactions.
(22) Oxazolines from epoxides: R. A. Wohl and J. Cannie, *J. Org. Chem.*, **38**, 1787–1790 (1973); J. R. L. Smith, R. O. C. Norman, and M. R. Stillings, *J. Chem. Soc., Perkin Trans. 1*, 1200–1202 (1975).
(23) Enamides could also be obtained in good yields when the epoxysilanes were treated with BF_3-Et_2O for longer periods of time, or when the oxazolines or the hydroxyamides were treated with BF_3-Et_2O, but these reactions were accompanied by some cis–trans isomerization when carried out on a preparative scale.
(24) However, the relative orientation of the C–Si bond and the β C–O bond greatly deviate from the parallel alignment favorable for the stabilization of a developing positive charge by the silicon (see ref 13b).
(25) Enolates are useful precursors to other enol derivatives, e.g., silyl enol ethers (G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462–4464 (1968); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324–2336 (1969)) and vinyl triflates (P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562–4569 (1974); T. C. Clarke and R. G. Bergman, *ibid.*, **96**, 7934–7944 (1974)).
(26) Enolate configuration appears to influence the ratio of C/O acylation[5c] and the stereochemistry of the aldol condensation.[5d]
(27) Compare R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Am. Chem. Soc.*, **98**, 2868–2877 (1976).
(28) One method for the stereospecific conversion of cis or trans olefins to enol ethers is known: P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, **91**, 7131–7137 (1969); P. J. Stang and M. G. Mangum, *ibid.*, **97**, 1459–1464 (1975). A few reactions are known in which predominantly one geometrical isomer of an enol ether is formed: S. I. Miller, *J. Am. Chem. Soc.*, **78**, 6091–6095 (1956); E. N. Marvell and T. Li, *Synthesis*, 457–468 (1973); D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, **96**, 5560–5561 (1974); W. C. Still and T. L. Macdonald, *ibid.*, **98**, 5561–5563 (1974); J.-F. Normant, A. Alexakis, A. Commerçon, G. Cahiez, and J. Villieras, *C.R. Acad. Sci., Ser. C*, **279**, 763–765 (1974); J. J. Eisch, H. Gopal, and S.-G. Rhee, *J. Org. Chem.*, **40**, 2064–2069 (1975).
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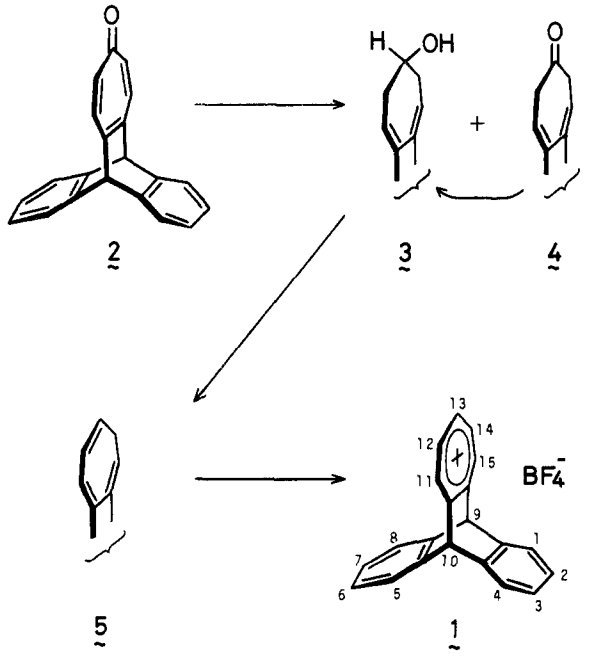
The 9,10-Dihydro-9,10-(1,2-tropylio)anthracene Tetrafluoroborate. Transannular π–π Interaction between Tropylium Ion and Remote Benzene Rings

Sir:

In the time since the 1942 publication by Bartlett and coworkers of their first synthesis of triptycene,[1] the question of transannular π–π interaction between the remote (nonconjugated) benzene rings in triptycene still remains a subject of controversy.[2] Previous UV[3] and CD[4] spectroscopy measurements of some heterocyclic triptycenes have revealed that π–π interaction between all three rings in triptycene systems exists. On the other hand, intermolecular charge-transfer complex formation has been found between various stable carbonium ions and aromatic hydrocarbons.[5,6] Quite recently, intramolecular charge-transfer interaction was observed in the [2.2](1,4)tropylioparacyclophane tetrafluoroborate independently by two research groups.[7,8]

In view of these precedents, the 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate (**1**), which consists of the tropylium ion and two benzene rings with rigid spacial arrangement identical with triptycene, would be a pertinent model for the intramolecular remote π–π interaction. In this communication we wish to describe the synthesis and properties of **1**.

Our synthetic approach to **1** is outlined in the following scheme. The requisite tropone (**2**) was accessible conveniently by the reaction of 4,5-dehydrotropone with anthracene.[9] Reaction of **2** with a threefold excess of lithium aluminum hydride[10] in a mixture of benzene and ether for 2 h at ambient temperature gave the dienol (**3**). Chromatographic (Al_2O_3, CH_2Cl_2) purification afforded a 35% yield of **3**,[11] pale yellow prisms, mp 184–186 °C (IR 3300 cm^{-1} OH; NMR δ (in $CDCl_3$, 100 MHz) 1.57 (d, J = 6 Hz, OH), 2.43 (dd, J = 5 and 4 Hz, $-CH_2-$), 3.99 (dq, J = 6 and 5 Hz, >CHO–), 4.71 (s, >CH), 5.75 (t, J = 4 Hz, –CH=), 7.00–7.38 (AA′BB′, aromatic)), along with 9% yield of the dienone (**4**). When the reduction was carried out at −70 to −65 °C with 3 molar equiv of lithium aluminum hydride, the dienone (**4**),[11] colorless prisms, mp 230 °C dec (IR 1699 cm^{-1} C=O; NMR δ (in $CDCl_3$, 60 MHz) 3.04 (d, J = 5 Hz, $-CH_2CO-$), 4.88 (s, >CH), 5.74 (t, J = 5 Hz, –CH=), 7.02–7.45 (AA′BB′, aromatic)), was obtained as a major product which afforded the dienol (**3**) as the sole product (70% yield) through further reduction with lithium aluminum hydride.



Attempts to prepare the cycloheptatriene (**5**) from **3** by direct dehydration failed. Instead conversion of **3** to its mesylate (CH_3SO_2Cl, Et_3N, CH_2Cl_2) which, without purification, was subjected to elimination with 1,8-diazabicyclo[5.4.0]undec-7-ene[12] in CH_2Cl_2 gave the cycloheptatriene (**5**)[11] in 33% yield, colorless prisms, mp 196–199 °C (NMR δ (in $CDCl_3$, 100 MHz) 2.24 (t, J = 6.5 Hz, 2 H), 4.92 (s, 1 H), 4.95 (s, 1 H), 5.17 (dt, J = 9.8 and 6.5 Hz, 1 H), 5.40 (t, J = 6.5 Hz, 1 H), 5.96 (dd, J = 9.8 and 6.0 Hz, 1 H), 6.54 (d, J = 6.0 Hz, 1 H), 6.95–7.40 (m, aromatic)).[13]

Completion of the synthesis requires a hydride ion abstraction from **5** and was achieved by use of trityl tetrafluoroborate in CH_2Cl_2. The cation, **1** (as tetrafluoroborate), which was obtained in ~70% yield as greenish yellow prisms, decomposed at around 110 °C. The structure of **1** was supported by its spectroscopic data (IR 1030–1125 cm^{-1} (broad strong, BF_4^-); NMR δ (in CD_2Cl_2, 100 MHz) 6.26 (s, 2 H, H-9 and -10), 7.18 (AA′ part) and 7.69 (BB′ part of AA′BB′ system, 8 H, aromatic), 8.60–8.94 (m, 3 H, H-12, -13, and -14), 9.14–9.32 (m, 2 H, H-11 and -15); δ (in CF_3COOH, 100 MHz) 6.15 (s, 2 H, H-9 and -10), 7.22 (AA′ part) and 7.66 (BB′ part of AA′BB′ system, 8 H, aromatic), 8.74–8.92 (m, 3 H, H-12, -13, and -14), 9.04–9.24 (m, 2 H, H-11 and -15)). Although the NMR data obtained for the cation, **1** (slight downfield chemical shifts of the aromatic protons of **1** compared with those of **5** and triptycene[14]), suggested a certain degree of the positive charge delocalization over the two benzene rings, because of the complexity of the factors affecting the chemical shifts, no definite conclusion concerning the intramolecular π–π interaction could be made.