Table I. Structures for Photoadducts and Their Thermal Rearrangement Products

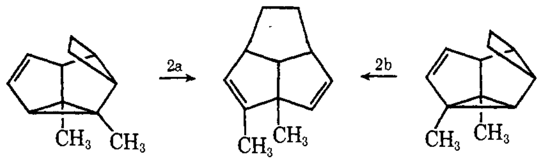
		Photoadduct I nmr spectrum		Pyroproduct II nmr spectrum		Possible CH_3 positions		
Aromatic compd	No. of adducts obsd	No. of olefinic protons obsd	Methyl group at δ	No. of olefinic protons obsd	Methyl group at δ	Photoadduct[a] I	Pyroproduct[b] II	Final[d] structure for photoadduct I
o-Xylene	1	2	1.08, 1.23	3	1.12, 1.58	7,1; 1,2; 2,10	3,4	1,2
m-Xylene	2	2	1.20, 1.30	3	1.12, 1.58	7,2; 1,10	3,4	1,10
		1	1.40, 1.80	3	1.12, 1.58	1,8; 7,9; 8,10; 9,2		1,8[c]
p-Xylene	1	1	1.36, 1.86	3	1.13, 1.60	1,9; 2,8	2,4; 3,10	1,9[c]
Toluene	1	2	1.27	4	1.09	1; 2; 10; 7	4; 10	1[c]

[a] Only structures consistent with the number of olefinic protons are given. [b] Only structures consistent with the number of olefinic protons and condition a are given. [c] Final structure based on absence of nmr absorption due to proton at C_1 position in photoadduct (see text). [d] All new compounds gave satisfactory elemental analyses.

It suggested that one substituent position was common to all of these adducts. This corresponded to the C_1 position in the two adducts for which unique structures were assignable. The final structures for the other three were selected on this basis (Table I).[8]

A fortuitous extra check of the assignments came out of the observation that the dimethyltricyclo-[5.2.1.$0^{7,10}$]deca-2,5-diene derived from the adduct of *o*-xylene to cyclobutene was identical with the one from one of the adducts of *m*-xylene to cyclobutene.

This was interpreted according to reactions 2a and 2b.



Pyrolysis of the second adduct from *m*-xylene (one olefinic proton) gave exactly the same dimethyltricyclodecadiene as the first adduct. A possible explanation is that this compound first undergoes the vinylcyclopropane rearrangement to yield the first adduct which then rearranges as in reaction 2b. Hence the second adduct is most likely to be the 1,8-dimethyl derivative. The absence of the nmr absorption at δ 3.1 as described before supports this.[9]

The most remarkable feature of these reactions is the limited number of adducts that are actually formed compared to the number that are theoretically possible. The selectivity seems to depend on the requirement that position 1 in the adduct must be substituted. Since no major adduct was unexamined, there are no negative exceptions to this statement, and the only positive exception (*i.e.*, a possible product that is not formed in significant quantity) is the 1,9-dimethyl derivative of I when the reactants are *o*-xylene and cyclobutene. The explanation may be simply that in a rigid structure such as I, it is impractical, on steric grounds, to have methyl groups at both positions 1 and 7.[10]

The preferential orientation of a methyl group at the C_1 position may be viewed as being due to either a strong directive influence from the CH_3 group or the intermediacy of an excited state in which one substituent will always be in this position. The latter hypothesis suggests that the excited state may have a high order of symmetry.[11] It is at present obscure whether or not a unique structure would satisfy this and the other observations (concertedness; constant ratio of 1,2, 1,3, 1,4 addition) concerning the 1,3-addition reaction.

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(8) A complication that can exist in all but one of these systems is that a vinylcyclopropane rearrangement in structure I may precede the (2'-vinylcyclopropyl)cyclobutane rearrangement. The exception is the adduct from *p*-xylene for which the photoadduct is degenerate with respect to the first transformation. In the other cases, the complication will arise only if the photoadduct can give one dimethyltricyclo[5.2.1.$0^{4,10}$]deca-2,5-diene while its valence isomer (formed by a vinylcyclopropane rearrangement) can give a different dimethyltricyclo[5.2.1.$0^{4,10}$]-deca-2,5-diene with the same number of olefinic protons. Fortunately, this complication did not come up although evidence for the occurrence of the vinylcyclopropane rearrangement was uncovered in one instance.

(9) It is possible that the methyl group at the C_8 position impedes the pyrolytic rearrangement to the expected 1,7-dimethyltricyclo[5.2.1.$0^{4,10}$]-deca-2,5-diene.

(10) Molecular models show that the 1,2-dimethyl derivative of I is not similarly crowded.

(11) It may at first sight seem as if an excited prismane structure would be an appropriate choice as the reactive state. In addition to possessing a high symmetry it can account for the formation of 1,2, 1,3, and 1,4 adducts from a single intermediate. But on closer scrutiny it can be realized that it would have no better chance (on a statistical basis) of giving a limited number of products in the 1,3 addition than the substituted Kekulé benzene structure.

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The Stereochemistry of [2,3]-Sigmatropic Reactions. The Wittig Rearrangement

Sir:

The [2,3]-sigmatropic rearrangement of ylides and related anionic species, **1** to **2**, is now recognized as a process of great facility and widespread occurrence.[1] This reaction is accompanied by a second pathway of higher activation energy, shown to be a radical dissociation–recombination route, **1** to **3**, whose importance depends on the structural environment and temperature.[1c,i,j,2]

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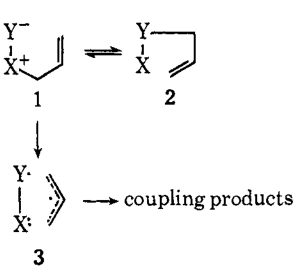
(1) (a) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, **90**, 4758 (1968); (c) J. E. Baldwin and R. E. Hackler, *ibid.*, **91**, 3646 (1969); (d) R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969); (e) J. E. Baldwin, J. E. Brown, and R. W. Corddell, *ibid.*, 32 (1970); (f) J. E. Baldwin and F. J. Urban, *ibid.*, 165 (1970); (g) J. E. Baldwin and C. H. Armstrong, *ibid.*, 659 (1970); (h) J. E. Baldwin J. E. Brown, and G. Höfle, *J. Amer. Chem. Soc.*, **93**, 788 (1971); (i) V. Rautenstrauch, *Chem. Commun.*, 4 (1970); (j) U. Schollkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(2) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).



Analysis of the [2,3]-sigmatropic transition state as the overlap of the lowest unoccupied molecular orbital [LUMO] of a double bond with the highest occupied orbital [HOMO] of an allyl anion suggests that it may proceed with retention of orbital symmetry in two distinct fashions, suprafacially with respect to both fragments, as **4**, or through the geometrically less appealing mode **5**, which is doubly antarafacial.[3] Although there have been several suggestions that such reactions proceed in the former manner,[4] through **4**, there has been no definite proof of this point. We now present stereochemical evidence for the case of the concerted Wittig rearrangement.

The substrate used in this study was the chiral ether (**6**, R = H)[5] from (*S*)-(+)-*trans*-3-penten-2-ol (acid phthalate, $[\alpha]\mathrm{D}^{25}$ +30.4° (ether)).[6] As we, and others, have previously shown, the contribution from the nonconcerted process,[1i,4a,7] **1** to **3**, is small in these rearrangements, and to obtain limits for this pathway we rearranged the racemic ether (**6**, R = ^{2}H) with *n*-butyllithium in tetrahydrofuran to the alcohol **7**, as a mixture of cis and trans isomers.[8] Assay of the vinyl hydrogen content of these (nmr spectroscopy) showed that the trans product **7** contained 14 ± 5% deuterium at the double bond, when the reaction was conducted at 0°. At −80° this value fell to essentially 0%, indicating complete domination of the [2,3]-sigmatropic process at the low temperature.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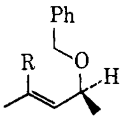

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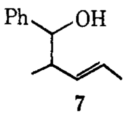

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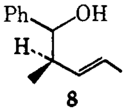
Similar rearrangement of ether **6** (R = H), $[\alpha]^{25}\mathrm{D}$ −46.0° (ether), at 0° gave the trans alcohol **8**, 83%, and cis alcohol **9**, 17%, whose geometrical configurations were determined by the presence of strong infrared absorptions at 970 and 720 cm^{-1}, respectively, characteristic of trans- and cis-disubstituted double bonds.[9] That each of these alcohols was formed as a pair of diastereomers, differing in configuration at the alcoholic function, was shown by their nmr spectra (superimposition of resonances) and by oxidation (Jones reagent) to the homogeneous trans and cis β,γ-unsaturated ketones, $\nu_{\max}$ 1685 cm^{-1} (neat), respectively. The configuration of this newly created tetrahedral center in the trans and cis series was established by sequential reduction (PtO$_2$, ethyl acetate) and Jones oxidation to a pair of enantiomeric ketones, respectively, **10** ($[\alpha]^{25}\mathrm{D}$ −15.8° (ethanol)), and **11** ($[\alpha]^{25}\mathrm{D}$ +13.2° (ethanol)), followed by Baeyer–Villiger cleavage[10] (peroxytrifluoroacetic acid) of **10** to (*R*)-(−)-2-pentyl benzoate ($[\alpha]^{25}\mathrm{D}$ −23° (ethanol)), identical with a sample ($[\alpha]^{25}\mathrm{D}$ −20.4° (ethanol)) obtained by benzoylation of (*R*)-(−)-2-pentanol ($[\alpha]^{25}\mathrm{D}$ −6.65° (CHCl$_3$)).



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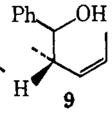

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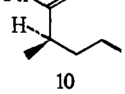

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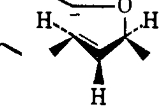

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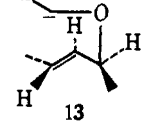

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The origin of the trans and cis series of rearrangement products is found in the two rotational forms of the precursor anion, **12** and **13**, respectively. Rearrangement of each of these by a [2,3]-sigmatropic process through the suprafacial transition state **4** provides the alcohols **8** and **9** whose configurations have been elucidated; *vide supra*. Therefore the antarafacial process depicted in **5** is excluded.

Since (*S*)-(+)-*trans*-3-penten-2-yl acid phthalate has been shown to possess a maximal rotatory power of $[\alpha]\mathrm{D}$ +38.75° (ether),[11] and (*R*)-(−)-2-pentanol has $[\alpha]\mathrm{D}$ −13.4°,[12] then it is possible to estimate the stereospecificity of the overall process as 72% for the trans series and 62% for the cis series.

The contribution from the classical Wittig 1,2 shift for the trans olefin is 14 ± 5% as measured from the deuterium experiments above. An examination of the radical pairs that precede the trans and cis products, *i.e.*, **14** and **15**, respectively, indicates that in the trans precursor **14** the ketyl radical is in juxtaposition to a symmetrical dimethyl allyl radical and hence recoupling may produce equal amounts of the two diastereoisomeric ions, **16** and **17**, even though the radical pair **14** is chiral.[13] Thus, assuming complete randomization in this pathway,[14] then 28 ± 5% of the derived ketone **10** would be racemized. Since we determined this material, **10**, is formed with a stereospecificity of 72% based on the optical purity of the starting material (**6**, R = H), then the [2,3]-sigmatropic pathway to the trans product is virtually 100% stereospecific. In summary the [2,3]-sigmatropic Wittig rearrangement pro-

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[3] R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969); K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

[4] (a) U. Schollkopf, V. Fellenberger, and M. Rizk, *Justus Liebigs Ann. Chem.*, 734, 106 (1970); (b) M. Moriwaki, S. Sawada, and Y. Inouye, *Chem. Commun.*, 419 (1970).

[5] All of the new compounds described in this study have given satisfactory combustion analyses and spectral data (nmr, infrared, and ultraviolet).

[6] H. W. J. Hills, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 576 (1936).

[7] J. E. Baldwin, J. DeBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970).

[8] The cis and trans diastereoisomers were separated by preparative glpc on the Varian Aerograph Model 700 using a 30% FEAP on Chromosorb W (45–60 mesh, 20 ft × 0.375 in.) column at 245°, although it was not possible to effect resolution of each pair of diastereoisomers. Analytical glpc was performed on a Varian Aerograph Model 1200 using a 5% Carbowax 20M on Chromosorb G (60–80 mesh, 10 ft × 0.125 in.) column at 190°.

[9] All of the products have been shown to be configurationally stable to reaction conditions and work-up procedures.

[10] C. H. Hassall, *Org. React.*, 9, 73 (1957).

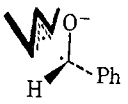
[11] H. L. Goering, M. M. Pombo, and K. D. McMichael, *J. Amer. Chem. Soc.*, **85**, 965 (1963).

[12] F. Barrow and R. G. Atkinson, *J. Chem. Soc.*, 638 (1939).

[13] This distribution of stereoisomers is of course maximal since there may be some stereochemical induction by the overall chirality existent in this radical pair, **14**, although mutual rotation of both fragments could readily produce a symmetric pair. The stereochemistry at the alkoxyl shown in **15** and **16** was chosen arbitrarily since it is destroyed in the configurational proof.

[14] U. Schollkopf and D. Walter, *Justus Liebigs Ann. Chem.*, **654**, 27 (1962).

ceeds *via* a doubly suprafacial transition state **4**, and it is likely that the other examples of this process[1] involve a similar geometry.



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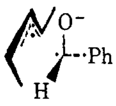

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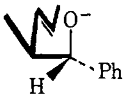

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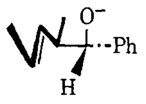

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(15) A. P. Sloan Fellow, 1969–1971.

(16) Public Health Service Predoctoral Fellow, 1969–1971.

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Stereoselective Attack at One Enantiotopic Face of a Carbonium Ion by Chiral Nucleophile

Sir:

Reactions in which the unsymmetrically substituted trigonal central atom of an achiral substrate (point group C_s) is transformed into a tetrahedral configuration are known to result in asymmetric syntheses when chiral reagents are employed.[1] The formation of optically active alcohols from the reaction of unsymmetrically substituted carbonyl compounds with chiral reducing agents has received particular attention.[2] Although symmetry considerations lead to the prediction that optically active products should also arise from the capture of suitably substituted carbonium ions by chiral nucleophiles, the high reactivity of such ions suggests that the necessary discrimination between enantiotopic faces of the cations by nucleophile might be too small to detect experimentally. We now report the formation of optically active 2-phenylbutane through capture of the 2-phenyl-2-butyl cation by a chiral organosilicon hydride.

Carbonium ions generated from a variety of sources are reduced by organosilicon hydrides.[3–11] Moreover, the transition states for these reactions are known to be sensitive to stereochemical features of the reactants.[6,11] We have found that either (*R*)-(+)- or (*S*)-(−)-1-naphthylphenylmethylsilane[12] smoothly captures the 2-phenyl-2-butyl cation generated from racemic 2-phenyl-2-butanol to give an enantiomeric excess (2–3%) of either (*R*)-(−)- or (*S*)-(+)-2-phenylbutane,[13] respectively.

In a typical experiment, 7.5 ml of trifluoroacetic acid was added dropwise with stirring over a 2.5-min interval to a methylene chloride (40 ml) solution of 30.7 mmol of (*R*)-(+)-1-naphthylphenylmethylsilane (88.8% optical purity) and 30.0 mmol of racemic 2-phenyl-2-butanol which was maintained at 0° under a dry nitrogen atmosphere. After 15 min, the reaction mixture was quenched with 20 g of anhydrous potassium carbonate, filtered, and carefully distilled through a 4-in. glass spiral-packed column. The 2-phenylbutane so obtained [82%, bp 77.0–77.5° (31 Torr)] was purified by preparative vpc (0.75 × 80 in. 20% diisodecyl phthalate on Chromosorb P, 120°) and its optical activity was measured. The data for three runs are summarized in Table I.[14]

Table I. Enantiomeric Compositions of 2-Phenylbutanes Obtained from the 2-Phenyl-2-butyl Cation

			2-Phenylbutane product	
Run	Silane	Temp, °C	α^{26}D (*l* 1 dm, neat), deg	Enantiomeric excess,[a] %
1	(*R*)-(+)[b]	0	-0.493 ± 0.010	2.3 ± 0.1, *R*
2	(*R*)-(+)[b]	−30[d]	-0.636 ± 0.011	3.0 ± 0.1, *R*
3	(*S*)-(−)[c]	−15[d]	$+0.539 \pm 0.016$	2.3 ± 0.1, *S*

[a] Corrected for optical purity of starting silane. Based on α^{23}D −24.2° (*l* 1 dm, neat) for maximum rotation of 2-phenylbutane.[13] [b] $[\alpha]^{26.5}$D +30.45 ± 0.11° (*c* 10.9, cyclohexane); optical purity 88.8%.[12a] [c] $[\alpha]^{26}$D −33.61 ± 0.08° (*c* 10.9, cyclohexane); optical purity 98.0%.[12a] [d] ±5°.

It is clear from these data that the (*R*)-(+)-silane preferentially attacks the *si* face of the 2-phenyl-2-butyl cation to give (*R*)-(−)-2-phenylbutane, whereas (*S*)-(−)-silane selectively attacks the *re* face to give (*S*)-(+)-2-phenylbutane.[15] The observed stereoselectivity requires a difference in activation (transition state) free energies of about 25 cal/mol for attack at

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(1) For recent discussions of terms, theory, and examples see: (a) K. R. Hanson, *J. Amer. Chem. Soc.*, **88**, 2731 (1966); (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965; (c) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967); (d) R. Bentley, "Molecular Asymmetry in Biology," Vol. 1, Academic Press, New York, N. Y., 1969; (e) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971; (f) E. L. Eliel, *J. Chem. Educ.*, 48, 163 (1971).

(2) See ref 1e, Chapter 5.

(3) D. N. Kursanov, Z. N. Parnes, G. I. Bossova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, 23, 2235 (1967).

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(5) D. N. Kursanov and Z. N. Parnes, *Russ. Chem. Rev.*, **38**, 812 (1969).

(6) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 90, 2578 (1968).

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(8) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **34**, 4 (1969).

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(10) F. A. Carey and C. L. W. Hsu, *J. Organometal. Chem.*, **19**, 29 (1969).

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(12) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(13) D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1954).

(14) The reaction is essentially complete and quantitative within 1 min after the acid is added. 2-Phenyl-1-butene and the two 2-phenyl-2-butene isomers also are reduced under these conditions to 2-phenylbutane. At higher reaction temperatures the acid-catalyzed cleavage of naphthalene from the silane becomes important; *cf.* R. A. Benkeser and H. R. Krysiak, *ibid.*, **76**, 6353 (1954).

(15) It has recently been reported that optically active 2-phenylbutane (7–8% enantiomeric excess) is produced by homogeneous hydrogenation of 2-phenyl-1-butene in the presence of various chiral rhodium catalysts: L. Horner, H. Siegel, and H. Büthe, *Angew. Chem.*, 80, 1034 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 942 (1968); J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, **93**, 1301 (1971).