essentially complete within 30 min.[16] However the exchange rate is not so high that phosphorus coupling with α hydrogens of phosphorane 5 is suppressed.[17] The limit of proton donor concentration for transylidation is thus even below that necessary to prohibit P–C–H coupling. This realization explains the variable results reported earlier concerning coupling as a function of solvent. Solvent source is a serious determinant as regards the extent of observed phosphorus–hydrogen coupling.

Removal of acid altogether eliminates the P–C–H temperature effect. Carbomethoxyphosphorane 1 (L = C_6H_5; R = H; R' = CO_2CH_3)[10] at 23° in carbon tetrachloride (distilled from aluminum oxide) displays the static spectrum expected for a pair of rotamers free from proton exchange.[1a] Acid exclusion thus not only prevents reversible proton transfer by eliminating traces of phosphonium salt but also raises the barrier to hindered internal rotation for carbalkoxyphosphoranes.[1a,13]

As a practical matter, the chemical shifts and coupling constants of protons α and β to hetero atoms in ylide systems can be reliably determined by the successive addition of milligram portions of basic aluminum oxide to the nmr tube at room temperature. The effect of lowering the temperature, i.e., suppressing the rate of proton exchange, is simulated until clean sharp peaks are obtained.[18] This technique has been utilized to demonstrate the nature of the broadened methine proton for dimethylsulforanes[19] 9 and 10 as identical with that described above for phosphorus ylides.[20]

9   **10**
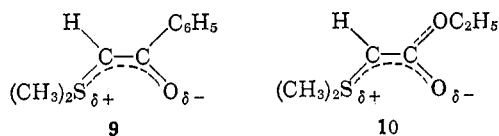
Acknowledgment. We are grateful to the Deutsche Forschungs-Gemeinschaft, Farbwerke Hoechst, and the American Philosophical Society for financial assistance.

(16) Time lapse between admixture and taking of spectrum.

(17) At high temperature the methyl quartet of pure methyl ylide 4 collapses to a doublet; the PCCH coupling retained even under conditions of very rapid transylidation.[6b]

(18) Neutral aluminum oxide and powdered KOH suffice as well. Dr. Crews[2b] has utilized n-butyllithium.

(19) (a) Dimethylsulforane 9, mp 48–52° (lit.[19b] 50–55°); dimethylsulforane 10, oil (lit.[19b] oil),nmr as reported; (b) K. W. Ratts and A. N. Yao, J. Org. Chem., 31, 1185 (1966).

(20) Ratts and Yao[19b] were unable to locate the methine proton of sulforane 10 in the nmr due to serious band broadening. Treatment of betaine 10 with basic alumina results in a sharp singlet for the appropriate hydrogen at τ 7.10 (CDCl₃). Likewise the broadened proton α to sulfur in betaine 9 appears at τ 5.70 as a sharp spike (CDCl₃). The presence of a fine suspension of Al₂O₃ does not prevent sharp bands with excellent ringing.

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Stereochemistry of Trityl Compounds. III. Ionization–Dissociation of Phenylbiphenyl-α-naphthylmethyl Benzoate and Cation Conformational Changes[1]

Sir:

The three mechanisms proposed earlier[2] to account for stereoselective solvolysis of phenylbiphenyl-α-naphthylmethyl benzoate (ROBz) have now been distinguished in a study of the racemization of D-ROBz.

Mechanism 1 entails formation of one cation (D-R⁺) by ionization–dissociation. The substituting agent attacks only one face of D-R⁺ at a rate comparable to formation of L-R⁺ (k_r[D-R⁺]) by rotation of the naphthyl group.
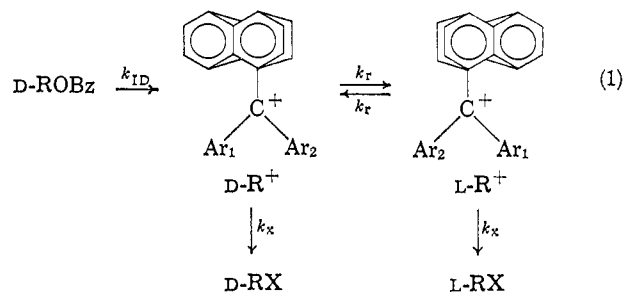
Alternatively, ionization–dissociation might produce only D-R⁺, but the reagent could attack *both* faces of D-R⁺ (mechanism 2) much faster than naphthyl group rotation.
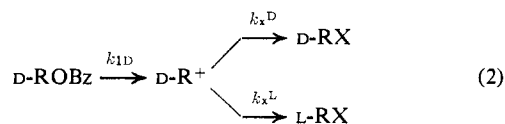
Finally, both cations might be produced with subsequent attack by reagent on only one face of each enantiomeric cation (mechanism 3).
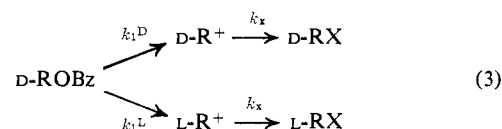
Mechanism 1 can be distinguished from the other two by comparing the racemization rate (k_{rac}) of D-ROBz in the presence of n-Bu₄NOBz to the ionization–dissociation rate[3] (k_{ID}). In racemization, the entering and leaving groups are identical, and mechanisms 2 and 3 are indistinguishable as a result of microscopic reversibility and the requirement of equal energies of enantiomeric ion pairs. Thus, if benzoate ion attacks both faces of D-R⁺, ionization–dissociation must produce both D-R⁺ and L-R⁺.

Qualitatively, if solvolysis proceeds by mechanism 1, the rates of solvent capture of D-R⁺ (k_x) and naphthyl group rotation (k_r) must be about equal ($k_x/k_r = 0.98$) to satisfy the observed optical yield at 54° (Table I). Mass-law data require that at 1.67 × 10⁻² M n-Bu₄NOBz the dissociated cation must be formed an average of 30 times before solvent capture and, therefore, before

(1) This work was supported by National Science Foundation Grants GP 3537 and GP 6406.

(2) B. L. Murr and C. Santiago, J. Am. Chem. Soc., 88, 1826 (1966).

(3) This rate was taken as the solvolysis rate in the absence of benzoate ion corrected for salt effects.[4] The correction was 5%. In mechanisms 3 and 4, $k_{ID} = k_1^D + k_1^L$.

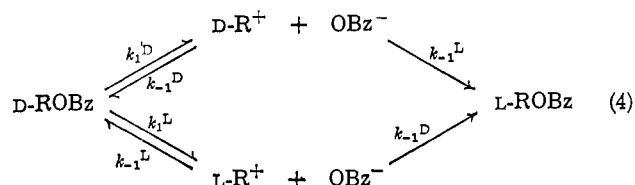(4) S. Winstein and B. R. Appel, J. Am. Chem. Soc., 86, 2720 (1964).

Table I. Solvolysis, Racemization, and Mass-Law
Data for Phenylbiphenyl-α-naphthylmethyl
Benzoate in 95% Acetone

Temp, °C	[Bu₄NOBz], $10^2 M$	$10^5 k$, sec^{-1}	$10^{-3}\alpha^a$	Optical yield, $\%^b$
	Solvolysis Rates (k_t)			
25	0	1.29 (1.35)^c		46.5
	1.67	0.081^d	0.9^d	
35	0	3.83		
	1.65	0.192	1.14	
54	0	39.2 (41.1)^c		32.8
	1.67	1.14	1.80	
	Racemization Rates (k_{rac})			
25	0	0		
	1.67	0.564 (0.103)^e		
	1.67	0.564 (0.103)^e		
54	1.67	22.0 (2.9)^e		
	1.67	24.3 (2.9)^e		

^{a} $\alpha = [k_t(\text{no salt})/(k_t(\text{with salt}) - 1]/[\text{salt}]$. ^{b} Difference from 100% is racemization. ^{c} Values in parentheses are the number after small salt effect correction.^{4} ^{d} Calculated from data at 35 and 54° using the Arrhenius equation. ^{e} The numbers in parentheses are the steady-state k_{rac} if mechanism 1 obtained.

naphthyl group rotation. If benzoate ion attacks only one face of D-R$^+$, k_{ID}^{3} must be about 30 times the rate of formation of L-ROBz or 15 times k_{rac}. The more nucleophilic benzoate ion captures D-R$^+$ before as much naphthyl group rotation as with the less nucleophilic water molecule. By mechanism 1 the optical yield of ionization and capture is higher the better the nucleophile. These qualitative conclusions have been corroborated by quantitative steady-state equations.^{5}

The solvolysis (k_{ID}) rates at 54 and 25° (Table I) are only *twice* the experimental racemization rates (k_{rac}) and not 15 times as required by mechanism 1. We conclude that benzoate ion attacks both faces of R$^+$ and that ionization–dissociation produces both D-R$^+$ and L-R$^+$. To our knowledge, the racemization mechanism summarized in eq 4^3 is without precedent.

$$\text{D-ROBz} \underset{k_{-1}^L}{\overset{k_1^D}{\rightleftharpoons}} \begin{array}{c} \text{D-R}^+ + \text{OBz}^- \\ \\ \text{L-R}^+ + \text{OBz}^- \end{array} \overset{k_{-1}^L}{\underset{k_{-1}^D}{\rightleftharpoons}} \text{L-ROBz} \quad (4)$$

The conformations of D-ROBz and the transition states for ionization–dissociation must satisfy the Curtin–Hammett principle^7 so that [D-R$^+$]:[L-R$^+$] = $k_1^D:k_1^L = k_{-1}^D:k_{-1}^L$. The difference in transition-state energies ($F_L{}^{\ddagger} - F_D{}^{\ddagger}$, Chart I) determines the optical yield of ionization–dissociation and its reverse. The relative rates of ionization–dissociation ($k_1^D:k_1^L$) by the two pathways are 7.5 at 25° and 5.5 at 54° with a $\Delta\Delta H^{\ddagger}$ of 2.0 kcal/mole. Analysis shows that at most

(5) The absence of a special salt effect in solvolysis of trityl benzoate and the equality of the rates of trityl alcohol and trityl azide formation demonstrate that n-Bu₄NOBz does not intervene at an ion-pair stage of dissociation.^{4} Internal return, if important, must be stereospecific because D-ROBz isolated after one solvolysis half-life showed no decrease in specific rotation (k_{rac} = 0, Table I). Internal return is stereospecific for p-chlorobenzhydryl p-nitrobenzoate.^{6}

(6) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

(7) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 237. Although it is not obvious, this statement is justified by good first-order kinetics for solvolysis and racemization. The ester would not so racemize if the conformations were not rapidly interconvertible.

2% racemization could have occurred by direct interconversion of cations assuming water attacks one face of R$^+$, but far less than 2% if water attacks both faces.

Chart I. Curtin–Hammett Diagram for Mechanism 4

anti-D-ROBz   syn-D-ROBz
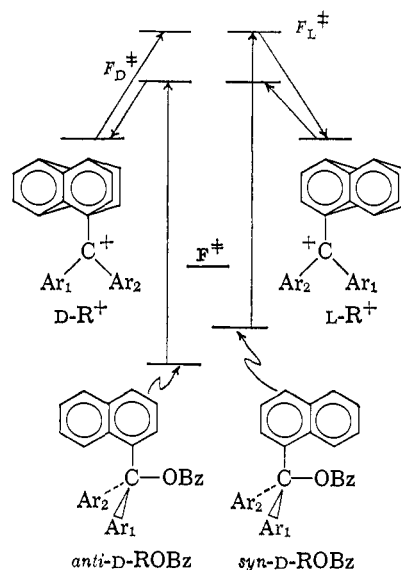
Water probably attacks both faces of R$^+$. If so, the relative rates for the two faces are 4.1 at 25° and 2.8 at 54°, with a $\Delta\Delta H^{\ddagger}$ of 2.6 kcal/mole. If water attacks only one face, $\Delta\Delta H^{\ddagger}$ between naphthyl group rotation and water capture is only 3.6 kcal/mole. If Taft's^8 $\Delta H^{\ddagger}$ for water capture of bis(p-methoxy)trityl cation (5.4 kcal/mole) is used as the upper limit for $\Delta H^{\ddagger}$ for water capture of R$^+$, the maximum for $\Delta H^{\ddagger}$ for naphthyl group rotation is 9.0 kcal/mole, or about the same as that found by Kurland, Schuster, and Colter^9 for conformational inversion of tris(m-fluoro)trityl cation. Because $\Delta H^{\ddagger}$ for naphthyl group inversion in R$^+$ should be much greater than that for aryl flipping in the tris(m-fluoro)trityl cation we conclude that water attacks both faces of R$^+$ without naphthyl group inversion.

Our results have implications for other systems of current mechanistic interest. According to eq 4 the lowest energy path for the conformational inversion D-R$^+$ to L-R$^+$ involves a nucleophile. This conformational change is analogous to that of tris(m-fluoro)trityl cation.^{9} Our results strongly suggest the possibility of nucleophilic involvement in the ring inversion of this cation.^{10} Covalent alkyl fluoride could behave in a manner analogous to the flexible form in interconversion of two chair forms of cyclohexane.

Collins^{11} has established in elegant fashion that the stereochemistry of substitution in 1,2,2-triphenylethyl systems is independent of phenyl group migration. He has interpreted his results in terms of mechanism 1 in the absence of specific information requiring more complex mechanisms (2 or 3). From models, 1,2,2-

(8) R. A. Diffenback, K. Sano, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 4747 (1966).

(9) R. J. Kurland, I. Schuster, and A. K. Colter, *ibid.*, **87**, 2279 (1965).

(10) Professor Colter has considered the necessity of nucleophile in his inversion reactions and, although there are arguments against nucleophilic participation, the data do not exclude the possibility (private communication, A. K. Colter).

(11) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.*, **81**, 466 (1959); C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

triphenylethyl cation appears more susceptible to nucleophilic attack at both faces than does R⁺. The probe employed in our work, i.e., the dependence or independence of optical yield on the steady-state cation (product precursor) concentration, could provide additional mechanistic details. The particular form of the probe would depend on the nature of the product precursor(s), whether ion pair or dissociated ion, which is not yet determined.

The principles involved in our work together with data already available[12] make it clear that 1-substituted homotropylium ions are capable of sustaining optical activity and giving stereoselective substitution reactions.

(12) J. L. von Rosenberg, J. E. Mahler, and R. Petit, J. Am. Chem. Soc., 84, 2842 (1962); S. Winstein, H. D. Kaesz, G. C. Kreiter, and E. C. Friedrich, ibid., 87, 3267 (1965); C. E. Keller and R. Petit, ibid., 88, 604 (1966); R. Huisgen, G. Boche, and H. Huber, ibid., 89, 3345 (1967).

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Stereochemistry of Trityl Compounds. IV.
The Optical Rotation of an Asymmetric Carbonium Ion and Microscopic Reversibility in Carbonium Ion Reactions

Sir:

Stereochemical control in the solvolysis of phenylbiphenyl-α-naphthylmethyl benzoate results from (1) a hindrance to rotation of the α-naphthyl group that prevents interconversion of the enantiomeric cations d-I and l-I, and (2) unequal rates of attack on the two faces of the asymmetric cation.[1] It appeared that intro-

d-I, X = H
d-II, X = CH₃

l-I
l-II
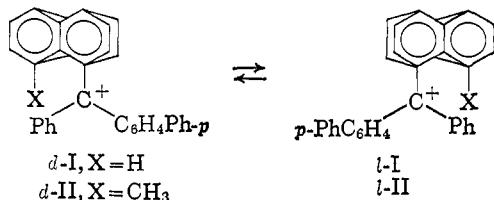
duction of a methyl group into the 8 position of the naphthalene nucleus might increase the barrier to interconversion (d-II → l-II) sufficiently to allow observation of an asymmetric cation.

A precursor of ion II, phenylbiphenylyl-1-(8-methylnaphthyl)carbinol (III), was synthesized by the reaction of 8-methylnaphthyllithium with phenyl biphenyl ketone.[2,3] The alcohol (Anal. Calcd for C₃₀H₂₄O: C, 89.96; H, 6.04. Found: C, 90.63; H, 6.33) was resolved by the method of Powell[4] (so-called spontaneous resolution). The first crystals from ether had a specific rotation[5] [α]D +76° (c 2.0); mp 188°. A second crop from cyclohexane had [α]D −76° (c 0.300); mp 188° after one recrystallization from ether.

The infrared and ultraviolet spectra of d- and l-III were identical. The nmr spectrum is of interest because there are two possible conformations of the

(1) B. L. Murr and C. Santiago, J. Am. Chem. Soc., 88, 1826 (1966); 90, 2964 (1968).
(2) R. L. Gray and C. R. Hauser, ibid., 89, 2297 (1967).
(3) L. Fieser and A. M. Seligman, ibid., 61, 136 (1939).
(4) H. M. Powell, Nature, 170, 155 (1952).
(5) Rotations were taken in chloroform unless otherwise stated using a Perkin-Elmer Model 141 automatic polarimeter. The precision was ±0.002°.

alcohol: the syn and anti conformations. The nmr spectra of d- and l-III exhibited an aromatic multiplet

syn-III   anti-III
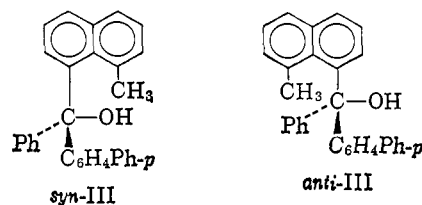
centered at δ 7.35 (20 protons), a singlet at 3.28 (1 proton, OH), and a singlet at 2.38 (3 protons, CH₃). The methyl singlet did not differ significantly in spectra taken at 118, 30, and −40°. The syn and anti conformations should have different methyl group chemical shifts, melting points, and optical rotations.

The rotations of d-II and l-II have been measured in sulfuric acid[6] in a 0.1-dm cell (Table I). d-III (2 mg) was dissolved in 20 ml of sulfuric acid at −20°. The solution was stirred 15–20 min before the measurements. The cation (blue green) undergoes rapid sulfonation at room temperature, and the solution becomes red after 10 min in the cell.[7] The readings before 10 min are for the unsubstituted ion. d-III gave a dextrorotatory ion at 365 mμ (2 min, blue green). The sulfonated ion is levorotatory at 365 mμ (29 min, red) but dextrorotatory at 436 mμ (43 min). The signs of rotation were opposite using l-III. Rotations determined after keeping the cation 2 hr at −20° were essentially the same. Visible spectra and the quenching product (carbinol) establish that the optically active species is the carbonium ion.

Table I. Rotations of Enantiomeric Phenylbiphenylyl-1-(8-methylnaphthyl)carbonium Ions in Sulfuric Acid

ROH	t,[a] min	λ, mμ	$\alpha \times 10^3$, deg	$[\alpha]$, deg
d-III	2	365	24	1940
(1.24 × 10⁻⁵ M)	6	436	39	3160
	29	365	−3	−243
	43	436	23	1860
l-III	2	365	−21	−1780
(1.17 × 10⁻⁵ M)	4	436	−32	−2720
	26	365	4	340
	31	436	−17	−1445

[a] Time after transfer to polarimeter cell.

d-III, [α]D +76°, was dissolved in sulfuric acid[6] at −20° and the solution was quenched by pouring it into ether and ice–water or ice–water containing sodium hydroxide.[8] The product was l-III, [α]D −69° (Table II). This rotation is the minimum value based on initial d-III (30 mg) assuming no losses in dissolution and recovery. The infrared, ultraviolet, and nmr spectra of recovered l-III were identical with those of starting d-III. The recovered alcohol (27 mg, [α]D −69°) was redissolved in acid and quenched. The isolated alcohol exhibited the same spectra but had [α]D +58°. Similar experiments were carried out with l-III.

(6) H₂SO₄ (98%, 50 ml) containing 2 g of water.
(7) W. Dilthey, J. Prakt. Chem., [2] 109, 286 (1925).
(8) Omission of hydroxide does not alter the results provided sufficient ice–water is used. We assume that quenching involves simply a cation reaction in water, but it could involve an ion pair in ether or an interfacial process.