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).

B. L. Murr, Cielo Santiago

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
Received March 18, 1968

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   *l*-I
d-II, X=CH₃   *l*-II
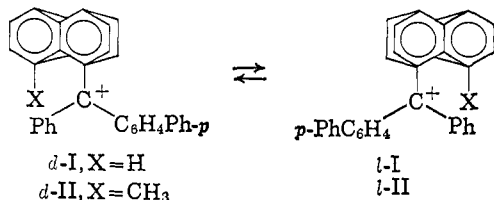
duction of a methyl group into the 8 position of the naphthalene nucleus might increase the barrier to interconversion (*d*-II → *l*-II) sufficiently to allow observation of an asymmetric cation.

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 $C_{30}H_{24}O$: 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
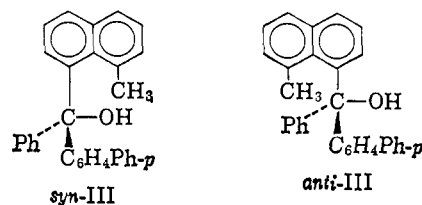
centered at δ 7.35 (20 protons), a singlet at 3.28 (1 proton, OH), and a singlet at 2.38 (3 protons, CH₃). The methyl singlet did not differ significantly in spectra taken at 118, 30, and −40°. The *syn* and *anti* conformations should have different methyl group chemical shifts, melting points, and 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	[α], 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) H_2SO_4 (98%, 50 ml) containing 2 g of water.
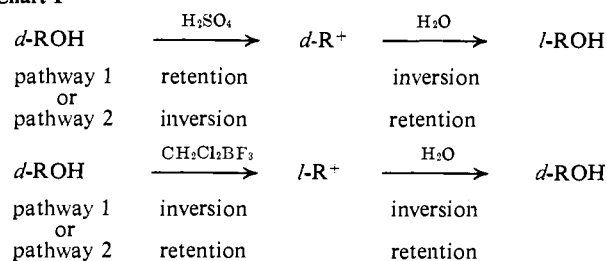(7) W. Dilthey, *J. Prakt. Chem.*, [2] 109, 286 (1925).
(8) Omission of hydroxide does not alter the results provided sufficient ice–water is used. We assume that quenching involves simply a cation reaction in water, but it could involve an ion pair in ether or an interfacial process.

Table II. Stereochemistry of Formation and Capture of Phenylbiphenyl-1-(8-methylnaphthyl)carbonium Ion

| Reagent	Initial $[\alpha]_D$, deg	Final $[\alpha]_D$, deg	Net optical[a] yield, %
H₂SO₄	−76	+58	77 inv
	+76	−69	91 inv
	−69	+58	84 inv
	−24	+20	84 inv
CH₂Cl₂–BF₃Et₂O	+74	+50	68 ret
	−23	−15	66 ret

[a] Difference from 100% is % racemic material.

The stereochemical outcome was different when d-III was ionized in methylene chloride–boron trifluoride ether and quenched.[8] The recovered alcohol had $[\alpha]_D$ +50° corresponding to 68% net retention (Table II). The methylene chloride solution showed no detectable rotation. However, a sulfuric acid solution obtained by extraction of the methylene chloride solution showed $[\alpha]_{365}$ −1120°. The same result was achieved when the methylene chloride was removed *in vacuo* and the residue was dissolved in sulfuric acid. The results establish: (1) removal of water from ROH_2^+ in sulfuric acid has the opposite stereochemistry from R^+ capture by water in quenching; (2) naphthyl group rotation (inversion) through the plane of the central carbon and the two attached aryl groups must accompany *either* ionization in sulfuric acid *or* capture by water in quenching; (3) ionization in sulfuric acid has the opposite stereochemistry from ionization in methylene chloride; and (4) water capture of carbonium bisulfate and fluoroborate has the same stereochemistry. The allowed stereochemical pathways are summarized in Chart I. If

Chart I

$$d\text{-ROH} \xrightarrow{\text{H}_2\text{SO}_4} d\text{-R}^+ \xrightarrow{\text{H}_2\text{O}} l\text{-ROH}$$

pathway 1   retention   inversion
or
pathway 2   inversion   retention

$$d\text{-ROH} \xrightarrow{\text{CH}_2\text{Cl}_2\text{BF}_3} l\text{-R}^+ \xrightarrow{\text{H}_2\text{O}} d\text{-ROH}$$

pathway 1   inversion   inversion
or
pathway 2   retention   retention

pathway 1 is followed in sulfuric acid, pathway 1 must be followed in methylene chloride.

Our current working hypothesis is that pathway 1 is followed in sulfuric acid and methylene chloride (Chart II). Alcohol ionization is exothermic in sulfuric acid but endothermic in dilute acid (the reverse of quenching). Hammond's postulate[9] allows that the ionization transition state in sulfuric acid is more like the protonated alcohol (less cation character) than the transition state for quenching (more cation character). This reasoning suggests that water would attack the cation from the least hindered face (*anti* to methyl). Inversion of the naphthyl group occurs subsequently, affording the presumably more stable *syn*-III (Fisher–Hirshfelder models). Ionization in sulfuric acid involves loss of water from *syn*-III *without* naphthyl group inversion. Naphthyl group inversion accompanying ionization in methylene chloride may be forced by the steric requirements of the leaving group. Experiments

(9) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

Chart II
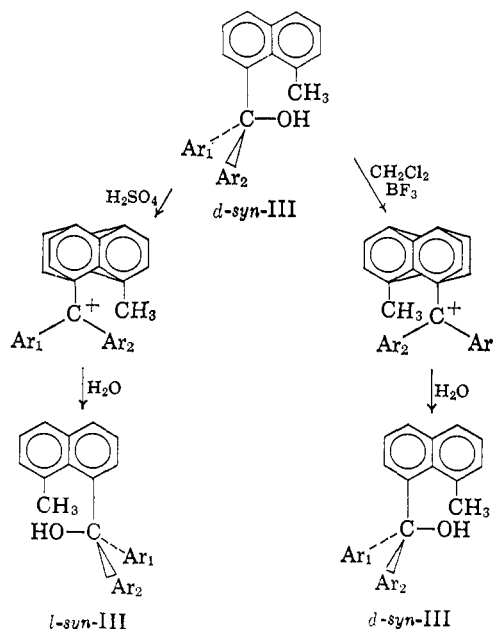
are in progress to further specify the mechanistic details of these intriguing transformations.

There is a parallel between the ionizations of III in sulfuric acid and methylene chloride–boron trifluoride and the ionizations of *cis*-7,8-dichlorocyclooctatriene-1,3,5 in fluorosulfonic and in methylene chloride–antimony pentafluoride.[10]

(10) R. Huisgen, C. Boche, and H. Huber, *ibid.*, 89, 3345 (1967).

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

B. L. Murr,[11] L. W. Feller

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
Received March 18, 1968

Tosylate Oxygen Scrambling Associated with Ion-Pair Return[1]

Sir:

The relationship between structure and rates of ionization is of considerable importance in mechanistic investigations of carbonium ion processes. Unfortunately, in most cases, ionization rates cannot be determined from rates of solvolysis because the amount of ion-pair return is unknown.

In earlier investigations[2,3] it was found that ion-pair return associated with solvolysis of carboxylic esters results in randomization of the carboxyl oxygen atoms. Thus oxygen equilibration of ¹⁸O-labeled esters (eq 1) is a method for measuring re-formation of substrate by ion-pair return.[3] A unique feature of this method is that it is applicable in systems in which the alkyl group does not racemize or rearrange; however, it is limited to reactive systems that undergo alkyl-oxygen cleavage

(2) (a) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Am. Chem. Soc.*, 85, 3059 (1963); (b) H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965); (c) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, 84, 3853 (1962); (d) A. F. Diaz and S. Winstein, *ibid.*, 88, 1318 (1966).

(3) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, 86, 1951 (1964).