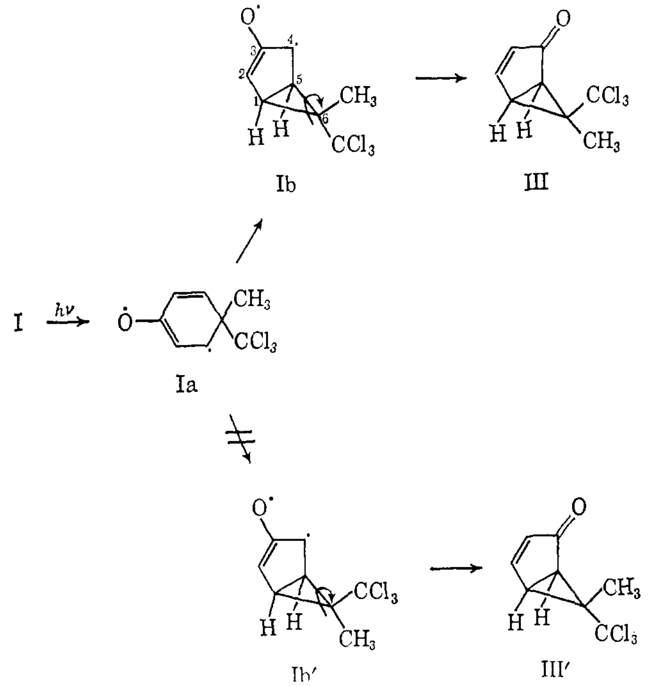
is formed exclusively by a nonpivot bond-shift mechanism[4b] *via* Ib′, seems much less reasonable.[6]



A summary of photolyses of I in a variety of solvents is given in Table I. The yields of I, II, and III are determined by quantitative gas-liquid partition chromatography, calibrated with known mixtures. Higher yields of *p*-cresol (II) are associated with solvents which are good hydrogen donors (ethyl ether, dioxane, cyclohexane, isopropyl alcohol). The formation of III and absence of II was noted from photolyses of I in toluene and carbon tetrachloride, as well as in benzene. A possible explanation is that radical fragmentation follows hydrogen abstraction, *i.e.*

$$\text{Ia} \xrightarrow{\text{RH}} \text{IV} \longrightarrow \text{II} + \text{CCl}_3\cdot$$

In the absence of a good hydrogen donor, Ia instead reacts by 3,5-bond formation to give Ib and ultimately III.[7]

The results in Table I also indicate that both reactions are sensitized by benzophenone (30-fold excess; 95% of incident light absorbed by benzophenone) and both are approximately equally quenched by piperylene.[8] Thus, a triplet state with E_T = 60–70 kcal/mole[9] is implicated as a reactive intermediate in the formation of II and III, respectively. Moreover, it is consistent with the entire set of results to suggest that there is only one triplet state involved, which we picture as Ia. The fact that the rate of reaction of I is about the same in the direct as well as the sensitized photolyses indicates that singlet-triplet intersystem crossing in excited I is a relatively efficient process.

Table I. Products of 20-Min Irradiation of Dienone I[a]

Solvent	Sensitizer or quencher	% yields I	II	III
Ethyl ether	None	11	65	0
Ethyl ether	Benzophenone (0.47 *M*)	2	68	0
Ethyl ether	Piperylene (1.6 *M*)	72	15	0
Benzene	None	34	0	31
Benzene	Benzophenone (0.47 *M*)	24	0	32
Benzene	Piperylene (1.6 *M*)	84	0	5
Cyclohexane	None	22	30	2
Isooctane	None	26	13	15
Isooctane[b]	Piperylene (1.6 *M*)	86	1	0

[a] Irradiation with a 450-w high-pressure mercury arc surrounded by a Pyrex filter in a quartz immersion well. Solutions of 0.01 mole of I + sensitizer or quencher diluted to a total volume of 640 ml. Yields determined by quantitative gas-liquid partition chromatography; estimated error ±2%. [b] Irradiation time 45 min.

Yet another pathway is available for photolysis of I in methanol or aqueous dioxane, as shown independently by other workers,[10] with further relevance to the characterization of the reactive intermediates in these systems. Our experiments in methanol will be reported shortly.

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(6) The pivoting mechanism postulated for Ib → III is in contrast to the more complex route required in cases (*e.g.*, α-santonin → lumisantonin) for which a pivot mechanism is stereochemically prohibited.[4b] We are assuming at this time that only one mechanism, pivot or nonpivot, operates exclusively in a given system.

(7) It is also possible that radical fragmentation occurs in benzene and the other poor hydrogen donor solvents, but leads exclusively to the observed polymer.

(8) The quenching may be due to chemical reaction with, as well as triplet energy transfer to, piperylene.

(9) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. C. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964).

(10) J. King and D. Leaver, *Chem. Commun.*, 539 (1965).

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Stereochemistry of Nucleophilic Substitution of Optically Active Trityl Derivatives. Carbonium Ion Asymmetry Due to Restricted Rotation

Sir:

We demonstrated earlier that the two stereospecific nucleophilic substitution reactions (1 and 2) of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid[1] (*l*-RSCH$_2$CO$_2$H) take the same stereochemical course, and evidence suggested that the reactions proceed with net retention of configuration.[2] We now report the first stereochemical study of the solvolysis of an optically active trityl benzoate, *l*-phenylbiphenyl-α-naphthylmethyl benzoate[3] (*l*-ROBz), an example of a nucleophilic substitution reaction (3) that occurs with high net retention of configuration (Table I). Evidence is presented that the observed stereospecificity results from solvent capture of a free, asymmetric carbonium

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgNO}_3 \xrightarrow[\text{acetone}]{66\%} d\text{-ROH} \qquad (1)$$

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgNO}_3 \xrightarrow[\text{ethanol}]{\text{absolute}} l\text{-ROEt} \qquad (2)$$

$$l\text{-ROBz} \xrightarrow[\text{acetone}]{95\%} d\text{-ROH} \qquad (3)$$

$$l\text{-ROBz} \xrightarrow[\text{ethanol}]{\text{absolute}} l\text{-ROEt} \qquad (4)$$

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgClO}_4 \xrightarrow[\text{dioxane}]{66\%} d\text{-ROH} \qquad (5)$$

(1) E. S. Wallis and F. H. Adams, *J. Am. Chem. Soc.*, 55, 3838 (1933).

(2) B. L. Murr, *ibid.*, 85, 2866 (1963).

(3) Prepared by the method of W. von E. Doering, K. Okamoto, and H. Krauch, *ibid.*, 82, 3579 (1960). Thus *l*-ROBz, *l*-ROEt, and *d*-ROH are correlated.

Table I. Stereochemistry of Some Substitution Reactions of Phenylbiphenyl-α-naphthylmethyl Derivatives

Compound	Medium	Product	% net retention[a]
l-$RSCH_2CO_2H$	66% acetone[b]	*d*-ROH[c]	50–70
l-$RSCH_2CO_2H$	Abs ethanol[d]	*l*-ROEt[c]	*e*
l-ROBz	95% acetone	*d*-ROH[f]	50
l-ROBz	Abs ethanol	*l*-ROEt[c]	*e*
l-$RSCH_2CO_2H$	66% dioxane	*d*-ROH[c]	60–70

[a] Difference from 100% is racemization. [b] Carried out as described in ref 1 and by mixing separate solutions of thioacid and silver perchlorate in 66% acetone. [c] Product not optically stable to final reaction conditions. Results are minimum optical yield. [d] Data from ref 1. [e] Optical yield not known. [f] Product stable to final reaction conditions.

ion. This example is quite different from the case of net retention found by Goering and Levy.[4]

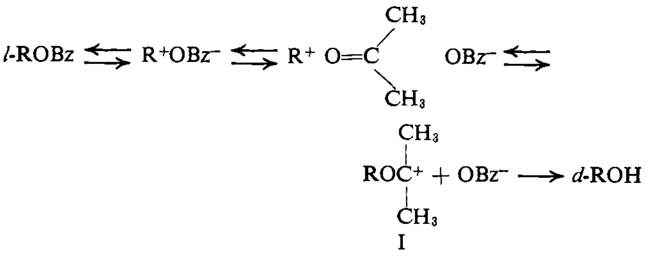
Our kinetic experiments (Table II) reveal a large mass-law effect in 95% acetone and in 80% dioxane indicating that the product is formed from dissociated trityl species that are free of the benzoate gegenion.[5] Common ion rate depression does not exclude a mechanism (Scheme I) involving acetone attack at the solvent-separated ion-pair stage because data in the literature suggest that I may be of comparable stability to R^+.[8,9] Although an anion could control attack by a hydroxylic nucleophile (by hydrogen bonding)[15] and even attack by acetone,[11] a mechanism similar to Scheme I involving dioxane is difficult to reconcile.[16] We conclude that the stereochemical outcome cannot be determined at an ion-pair stage of ethanolysis and hydrolysis in aqueous dioxane and probably not in moist acetone.

Table II. Solvolysis Rates of Phenylbiphenyl-α-naphthylmethyl Benzoate[a]

Salt	$10^4 \times$ [salt], *M*	$10^5 k_t$, sec^{-1}	$10^{-3}\alpha$, M^{-1}[b]
	95% Acetone at 54°		
None		36.2[c]	
NaOBz	1.00	12.4	19
Bu_4NOBz	7.22	2.56	18
Bu_4NOBz	7.61	2.59	17
Bu_4NOBz	142	1.25	2.0
Bu_4NOBz	167	1.14	1.8
	80% Dioxane at 35°		
None		29.9[c]	
Bu_4NOBz	2.81	11.5	5.7
Bu_4NOBz	4.32	10.2	4.5

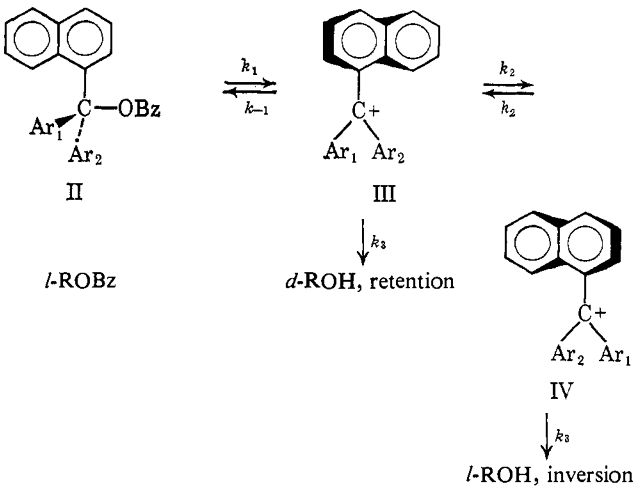
[a] $[ROBz] \approx 5 \times 10^{-3}$ *M*. [b] $\alpha = [k_t(\text{no salt})/k_t(\text{salt}) - 1]/[\text{salt}]$. [c] Average of three runs.

Scheme I



A plausible explanation of our results is a mechanism common to all of the reactions involving a carbonium ion that is asymmetric. Because all the atoms of the cation in solid trityl perchlorate are known not to lie in the same plane,[17] it follows that phenylbiphenyl-α-naphthylcarbonium ion can be asymmetric because the other two aromatic groups do not lie in the same plane as the naphthalene nucleus.[18] We assume that the carbonium carbon and the three atoms attached are in a common plane. The enantiomeric forms of the cation are III and IV in Scheme II. The results show: (1) the rate of conversion of III to IV is slower than the rate of product formation; (2) the rates of attack on the two faces of III are different; and (3) equal amounts of III and IV do not result from ionization–dissociation of II. These restrictions and the Curtin–Hammett principle still allow some flexibility of interpretation. The optical yield reflects the relative magnitudes of k_2 and k_3 (Scheme II) if *l*-ROBz has conformation II, dissociation produces III only, and capture occurs on the face of the cation that is more remote from the unsubstituted ring of the naphthalene nucleus. Alternatively, if only III is produced and the conversion of III to IV is

Scheme II



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

(5) This conclusion was reached by Winstein and Appel in their study of trityl benzoate.[6] A mass-law effect was observed in the methanolysis of trityl acetate.[7] Common ion rate depression in the ethanolysis of *l*-ROBz (reaction 4) seems assured.

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

(7) C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955).

(8) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 97.

(9) Data are very sparse concerning α-alkoxycarbonium ions. Application of Taft's σ* correlation to the rate data on α-alkoxyalkyl chlorides of de la Mare, *et al.*,[10] suggests that I is more stable than R^+. Parenthetically, these data provide insight into the nucleophilic behavior of acetone.[11] However, α-alkoxyalkyl benzoates[12,13] and acetates[14] are not as reactive as would be expected from de la Mare's data. We are investigating the solvolytic behavior of α-alkoxyalkyl derivatives to resolve these difficulties.

(10) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

(11) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 287, 292 (1965).

(12) P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953).

(13) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(14) P. Salomaa, *Acta Chem. Scand.*, **11**, 141 (1957).

(15) E. H. White and C. A. Aufdermarsh, *J. Am. Chem. Soc.*, **83**, 1179 (1961).

(16) The path analogous to formation of ROH from I is not available in the case of dioxane.

(17) A. H. Gomes de Misquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

(18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 174.

much slower than solvent capture, the optical yield measures the relative rates of attack on the two faces of III. Finally the optical yield might be a measure of the amounts of III and IV resulting from dissociation. More complicated mechanisms could of course be operative.

In support of the idea that a torsional barrier in cation III controls the stereochemistry of substitution other results of Wallis and Adams may be mentioned. Treatment of *l*-1,2-benzo-9-phenylxanthyl-9-thioglycolic acid according to reactions 1 and 2 gives products showing no detectable optical activity.[1,19]

Our results indicate that substitution processes involving phenylbiphenyl-α-naphthylmethyl radical and anion, as well as similar systems, might be stereospecific. Furthermore, with suitably substituted compounds, the likelihood of isolating an optically active carbonium ion, radical, and carbanion is clear. These expectations are being investigated.

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, through a Type G grant, and by the National Science Foundation, Grant GP 3537.

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[19] G. Wittig, F. Vidal, and E. Bohnert, *Chem. Ber.*, 83, 359 (1950).

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The Cleavage of Silanes by Oxides of Nitrogen

Sir:

As an extension of our studies on the interaction of organosilanes with ozone,[1] we wish to report the observation that the oxides of nitrogen, generally called[2] "nitrogen dioxide,"[3] "nitrogen trioxide,"[4] nitric oxide (NO), and nitrous oxide (N_2O), also individually react cleanly with Si–X bonds, where X = H, OH, OR, Si, alkyl, and aryl, to give cleavage products at room temperature.

Triethylsilane reacts exothermally with nitrogen dioxide to yield triethylsilanol and hexaethyldisiloxane. In a separate experiment, under similar conditions, triethylsilanol readily gave the dehydration product, hexaethyldisiloxane.

The silicon–silicon bond in hexamethyldisilane is also cleanly cleaved by nitrogen dioxide to hexamethyldisiloxane in 95% yield.

Rupture of the silicon–alkyl bond was observed when tetraethylsilane was allowed to react with nitrogen dioxide. The principal products obtained were hexaethyldisiloxane and acetic acid. Under similar conditions, hexaethyldisiloxane yielded hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane, based on vapor phase chromatographic analysis and comparison with authentic samples. A number of smaller unidentified peaks were observed, but the three mentioned siloxanes accounted for about 95% of the reaction product.

The silicon–aryl bond was also cleaved in trimethylphenylsilane by nitrogen dioxide to produce hexamethyldisiloxane and nitrobenzene. When all of the phenyl group had been removed from silicon, the vapor phase chromatogram of the crude reaction product did not show the presence of any polysiloxane components other than the disiloxane.

The rate of cleavage of an ethyl group from hexaethyldisiloxane by nitrogen dioxide was slow compared to that from tetraethylsilane. This indication of some stabilization effect of oxygen on silicon was observed also with ozone.[1] However, all other cleavage reactions proceeded readily and with exothermicity at room temperature to give reaction products in good (90%) yields.

Nitrogen trioxide cleaved triethylsilane to triethylsilanol at room temperature. Nitric oxide also produced the silanol with complete reaction in less than 6 hr, whereas nitrous oxide gave only 10% conversion after 6 hr.

It appears that the oxides of nitrogen behave similarly toward organosilanes, but with differing degrees of activity. In decreasing order of reactivity, we find nitrogen dioxide, nitrogen trioxide, nitric oxide, and, much slower, nitrous oxide. Which of the components in the equilibrium mixtures[3,4] is the principal reactive species is not known, although NO_2 or N_2O_4 appears to be the most powerful. Nitric acid, which can form from the nitrogen oxides and water,[5] does not appear to be responsible for the observed cleavage reaction.

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[1] L. Spialter and J. D. Austin, *J. Am. Chem. Soc.*, 87, 4406 (1965).

[2] "Matheson Gas Data Book," The Matheson Co., Inc., East Rutherford, N. J., 1961.

[3] An equilibrium mixture of about 80% N_2O_4 and 20% NO_2 at 27° (ref 2).

[4] Largely dissociated into NO and NO_2 in the vapor state at room temperature (ref 2).

[5] N. V. Sidgwick, "The Chemical Elements and Their Compounds," University Press, Oxford, 1951, p 689.

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A Facile Synthesis of β-Alkoxy Mercaptans and β-Thioalkoxy Mercaptans

Sir:

The reduction of sulfides RSR′ to mercaptans by sodium in liquid ammonia is a well-known reaction,[1] of great importance in the removal of S-protective groups, especially in peptide synthesis. The reaction is not of great value in the synthesis of mercaptans as such, however, since the needed sulfides are generally made from mercaptans in the first instance.

Among the readily accessible compounds containing an RSR′ function are mono- and dithioketals and -acetals. It occurred to us[2,2a] that, if reduction in these com-

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[1] F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, 53, 352 (1931); R. H. Sifferd and V. du Vigneaud, *J. Biol. Chem.*, 108, 753 (1935); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, 49, 1 (1951).

[2] See L. A. Pilato, Ph.D. Dissertation, Notre Dame University, 1962, p 59. We are grateful to Professor J. P. Danehy for his encouragement of this idea. Subsequent to inception of this work we found an isolated instance of the reaction in the literature, *viz.*, the reduction of the acetone ketal of 1,2-dithioglycerol to 2-thioisopropoxy-3-hydroxypropyl mercaptan: L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2938 (1950); other, similar reductions described in the literature lead to complete desulfurization—*e.g.*, N. S. Crossley and H. B. Henbest, *ibid.*, 4413 (1960); R. D. Stolow and M. M. Bonaventura, *Tetrahedron Letters*, 95 (1964)—or to more complicated reaction courses—*e.g.*, Q. F. Soper, W. E. Buting, J. E. Cochran, and A. Pohland, *J. Am. Chem. Soc.*, 76, 4109 (1954); A. Schönberg, E. Petersen, and H. Kalt-