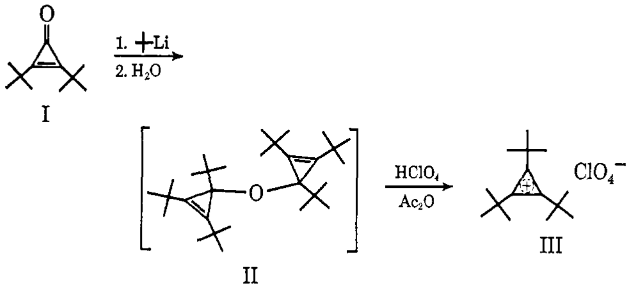
Nmr spectra of I (in CDCl$_3$) show a sharp singlet at δ 1.34.[6] Catalytic hydrogenation (Pt, dioxane) afforded dineopentyl ketone.[1] The remarkable stability of I can be demonstrated by its recovery in 86% yield (after sublimation) from treatment with a solution of 25% aqueous sodium hydroxide at reflux for 2 hr! Dipropylcyclopropenone, however, is completely destroyed under identical conditions.



I

II

III

Reaction of I with *t*-butyllithium in benzene afforded, after work-up with cold aqueous KH$_2$PO$_4$, an oil exhibiting characteristic cyclopropene absorption at 1820 cm^{-1} in the infrared, presumably due to bis(tri-*t*-butylcyclopropenyl) ether (II).[1a] Treatment of an ether solution of II with a 10% solution of perchloric acid in acetic anhydride resulted in the immediate precipitation of III as a white solid in 36–57% yield. Recrystallization from acetone gave white needles which decompose explosively at 248–250°. *Anal.* Calcd for C$_{15}$H$_{27}$ClO$_4$: C, 58.73; H, 8.87; Cl, 11.56. Found: C, 58.65; H, 8.74; Cl, 11.54. Compound III has infrared absorption (KBr) at 2980 (s), 2950 (m), 2920 (m), 2880 (m), 1485 (s), 1465 (s), 1425 (m), 1370 (s), 1225 (s), 1198 (s), 1090 (vs), 941 (w), 860 (m), and 626 cm^{-1} (s). Cation III (in CH$_3$CN) exhibits only end absorption in the ultraviolet as expected for alkyl-substituted cyclopropenyl cations.[4,7] The nmr spectrum (in CDCl$_3$) shows only a sharp singlet at δ 1.58 with the anticipated downfield shift of the *t*-butyl signal relative to the signal of I.

Potentiometric titration of cation III in 50% aqueous acetonitrile with 0.104 *N* NaOH gives a classical titration curve from which an apparent pK_{R^+} value of 6.6 is obtained. We have observed a pK_{R^+} of 7.0 for the tri-*n*-propylcyclopropenyl cation (IV) under identical conditions.[8]

In view of the greater electron-releasing inductive effect of *t*-butyl relative to the *n*-propyl substituent,[9] greater stability would be expected for cation III relative to IV.[7] Furthermore, steric considerations predict greater destabilization of the tri-*t*-butylcyclopropenyl alcohol relative to the tripropylcyclopropenyl alcohol. These two factors would predict a greater pK_{R^+} for III relative to IV, contrary to the observed results. On the other hand, solvation of charge would be more difficult in the hindered cation III relative to IV and may well be playing an important role.[10]

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(11) National Aeronautics and Space Administration Trainee.

Joseph Ciabattoni, Edward C. Nathan, III[11]
Metcalf Research Laboratories
Brown University, Providence, Rhode Island 02912
Received June 3, 1968

Synthesis and Reactivity of Chloromethyl Phenyl Sulfoxide[1]

Sir:

We communicate in this report a new synthesis of chloromethyl phenyl sulfoxide,[2] PhSOCH$_2$Cl, and its resistance to bimolecular nucleophilic displacement reactions.

Although it is known that acylating reagents such as acyl anhydrides[3a] or acyl chlorides[3b] react with methyl sulfoxides, RSOCH$_3$, to give α-substituted methyl sulfides such as RSCH$_2$OCOR or RSCH$_2$Cl, respectively, we have found that in the presence of pyridine *p*-toluenesulfonyl chloride reacts with methyl phenyl sulfoxide to yield chloromethyl phenyl sulfoxide without cleavage of the S–O bond. In the absence of pyridine this reaction gives almost exclusively chloromethyl phenyl sulfide. Attempted synthesis of chloromethyl phenyl sulfoxide by oxidation of chloromethyl phenyl sulfide failed.

In a typical experiment 28 g (0.2 mol) of methyl phenyl sulfoxide was added dropwise into a solution of *p*-toluenesulfonyl chloride (0.18 mol) in pyridine (0.4 mol) during 1 hr at 40–45°. After being acidified with cold dilute hydrochloric acid, the mixture was extracted thoroughly with *n*-hexane from which some chloromethyl phenyl sulfide and methyl phenyl sulfide was obtained. The aqueous layer was extracted thrice with chloroform; the combined extracts were washed once with water, dried with sodium sulfate, and fractionally distilled yielding 8.1 g (23%) of chloromethyl phenyl sulfoxide as a colorless viscous oil, bp 120–121° (4 mm). *Anal.* Calcd for C$_7$H$_7$SOCl: C, 48.14; H, 4.04; S, 18.36; Cl, 20.30. Found: C, 48.09; H, 4.11; S, 18.30; Cl, 20.42. The proton nmr spectrum of this compound shows a multiplet centered at τ 2.45 (aromatic protons) and a singlet at τ 5.61 (methylene protons), relative peak areas being 5:2. The infrared spectrum showed strong absorption at 1047 cm^{-1}, characteristic of sulfoxides. This compound is readily soluble in water and can be converted quantitatively by potassium permanganate into chloromethyl phenyl sulfone, mp 52°, lit.[4] mp 52–53°.

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(1) Presented at the 21st National Meeting of the Chemical Society of Japan, Osaka, Japan, March 31, 1968, Abstracts III, p 2037.

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Chloromethyl phenyl sulfoxide is highly resistant to the reaction with potassium iodide in acetone at 50°; even after 60 hr no potassium iodide was consumed, and the sulfoxide was recovered quantitatively. Comparison of this result with those reported[5,6] for some chlorides in the same condition led us to conclude that chloromethyl phenyl sulfoxide is less reactive than *n*-butyl chloride by a factor of at least 10^2, this factor being as high as 10^7 when compared with phenacyl chloride (Table I). Preliminary experiments showed that chloromethyl phenyl sulfoxide is less reactive than *n*-butyl chloride toward piperidine in boiling benzene, too.

Table I. Relative Rates of Alkyl Chlorides in the Reaction with Potassium Iodide in Acetone at 50°

RCl	Relative rates
$CH_3CH_2CH_2CH_2Cl$	1^a
$PhCOCH_2Cl$	$105{,}000^b$
$PhSOCH_2Cl$	$<0.01^c$
$PhSO_2CH_2Cl$	$<0.01^{c,d}$

[a] $k = 0.0933$ l. mol^{-1} hr^{-1} (0.0955^5); the value reported by Conant[5] is for $0.4343k$. [b] See ref 5. [c] No reaction occurred in 60 hr at 60°. [d] No reaction was observed in 12 hr at 56° or after 10 weeks at 0°.[6] With chloromethyl *p*-tolyl sulfone the relative rate was estimated to be <0.02.[6]

The present results appear quite interesting. The inertness of chloromethyl phenyl sulfone was successfully shown by Bordwell and Cooper[6] to be due to a steric blocking of the attacking reagent by the sulfonyl group; *i.e.*, this molecule has a structural resemblance to neopentyl chloride. The inertness of chloromethyl phenyl sulfoxide, however, is hardly rationalized in terms of this kind of steric blocking. On the other hand, electronic effects of carbonyl, sulfinyl, and sulfonyl groups are known to be almost the same. Thus the marked retarding effect of the sulfinyl group[7] seems quite interesting but remains unexplained.

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(7) Even if the lack of enhanced reactivity may be explained according to the postulate of Bartlett and Trachtenberg,[8] the retarding effect, taking *n*-butyl chloride as standard, cannot be explained.

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Masaru Hojo, Zen-ichi Yoshida
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan

Received May 28, 1968

Secondary Isotope Effects for Solvolyses Leading to Classical Norbornyl Cations

Sir:

During a recent study of the solvolysis of *exo*-norbornyl-3,3-d_2 bromide and its *endo* counterpart, it was found that the secondary isotope effect for the former was significantly smaller than that of the latter (k_H/k_D = 1.04 *vs.* 1.16 per D).[1] The magnitude of a secondary isotope effect is a sensitive function of the characteristics of the transition state, and it is diminished by such factors as participation by solvent[2] or strong resonance interactions in the transition state.[3] Since a neighboring group that provides assistance during a solvolysis reaction functions as an "internal solvent," a similar perturbation of the secondary isotope effect would be expected. By applying this criterion we concluded[1] that *exo*-norbornyl bromide solvolyzes with assistance and that the transition state that leads to the norbornyl cation is best formulated as one that is delocalized and nonclassical.[4]

To expand the experimental foundation upon which these conclusions are based, we have now measured the secondary isotope effects that arise during the solvolysis of the *exo*- and *endo*-*p*-nitrobenzoates of 2-phenylnorbornan-2-ol. The labeled compounds were prepared by exchanging norcamphor in deuteriotrifluoroacetic acid, allowing the dideuterio ketone to react with phenylmagnesium bromide to give the *endo* alcohol, and inverting the configuration of the alcohol with hydrochloric acid to produce the *exo* alcohol.[5,6] The *p*-nitrobenzoates, which contained 1.87 atoms of deuterium, were solvolyzed in 60% dioxane, and the rate constants are summarized in Table I.

Table I. Solvolysis of the *exo*- and *endo*-*p*-Nitrobenzoates of the 2-Phenylnorbornan-2-ols[a]

Compound	Temp, °C	$k \times 10^4$, sec^{-1}	k_H/k_D
endo-*p*-Nitrobenzoate	62.50	0.288 ± 0.002	1.15 ± 0.02
endo-*p*-Nitrobenzoate-3,3-d_2		0.250 ± 0.002	
exo-*p*-Nitrobenzoate	39.50	3.47 ± 0.02	1.18 ± 0.02
exo-*p*-Nitrobenzoate		2.94 ± 0.02	

[a] Rate constants were measured in duplicate or triplicate, and the errors represent the deviations from the mean value of a series of constants. The observed constants are in excellent agreement with the values calculated from Brown's data.[6]

Several important conclusions can be drawn from these results. From a comparison of the values of these isotope effects with those that have been reported for the α-phenylethyl system,[3] it is apparent that the electronic characteristics of the solvolysis transition states in both of these diverse systems must be similar; *i.e.*, the transition state that leads to the phenylnorbornyl cation must be classical regardless of whether the exiphile (leaving group) departs from an *exo* or an *endo* position.[7] Therefore, the magnitude of the secondary isotope effect is not a property of the geometry of the exiphile but is rather a reflection of the electronic nature of the transition state that leads to the cation.

Since the transition states for the solvolysis of the *p*-nitrobenzoates of *exo*- and *endo*-2-phenylnorbornanols and *endo*-norbornyl bromide are classical, *the dramatic contrast in secondary isotope effects that is observed during the ionization of exo- and endo-norbornyl bro-*

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