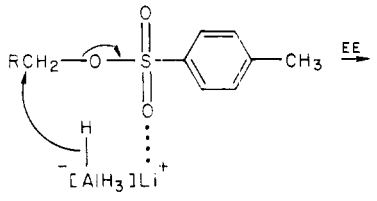
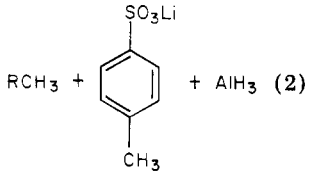
Table II. Relative Reactivities of *n*-Octyl Tosylate and Alkyl Halides toward Lithium Aluminum Hydride at 0 °C[a]

compds used	products[b]	% yield EE[c]	% yield DG[d]
n-octyl tosylate and *n*-heptyl iodide	*n*-octane	100	1
	n-octyl tosylate[e]	0	99
	n-heptane	2	100
	n-heptyl iodide	98	0
n-octyl tosylate and *n*-heptyl bromide	*n*-octane	99	13[f]
	n-octyl tosylate[e]	1	87[f]
	n-heptane	<1	85[f]
	n-heptyl bromide	>99	15[f]

[a] Solutions of $LiAlH_4$ in ethereal solvents were added to equimolar mixtures of tosylate and halide and stirred for 1 h. [b] Determined by GLC. [c] $LiAlH_4/RX = 1.5$. [d] $LiAlH_4/RX = 1.0$. [e] Not determined directly; estimated by difference. [f] Lowering the temperature to −23 °C increased the selectivity of ROTs/RX to 8/92.

ethyl ether, the lithium ion of $LiAlH_4$ is poorly solvated. However, in solvents such as tetrahydrofuran, monoglyme, and diglyme, lithium ion is strongly solvated, forming solvent-separated ions, thereby dramatically enhancing the nucleophilicity of tetrahydroaluminate, resulting in rapid reduction of alkyl halides. The high reactivity of $LiAlH_4$ toward alkyl tosylates in weakly solvating media such as ethyl ether can be attributed to the complexation of the lithium ion with the tosylate group, which increases the leaving-group ability[7] of that group (eq 2).

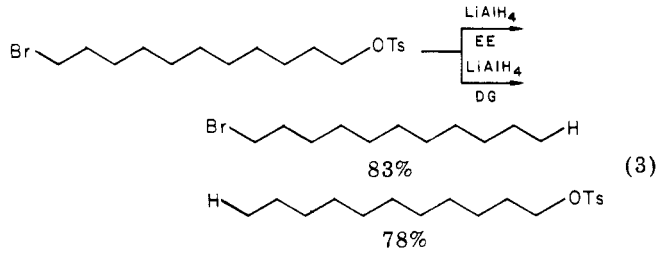




(2)

The relative reactivity of alkyl tosylates vs. alkyl iodides and bromides toward $LiAlH_4$ was determined by competition experiments in EE and DG. Results summarized in Table II clearly indicate that in ethyl ether alkyl tosylates can be rapidly and selectively (>99%) reduced in the presence of alkyl iodides and bromides (≤2% attack). In diglyme it is possible to selectively reduce alkyl iodides and bromides without significant attack on alkyl tosylates.

It was desirable to test the applicability of these observations in organic synthetic transformations. Reduction of 11-bromoundecyl tosylate, a difunctional molecule, was examined in EE and DG. In EE, the tosylate group was selectively reduced, yielding *n*-undecyl bromide in 83% isolated yield (95% by GLC). In DG, the reagent selectively reduced the bromo substituent, yielding *n*-undecyl tosylate in 78% yield (eq 3).



(3)

In conclusion, this work provides the first clear documentation that the solvent can be used as an effective tool to modify chemoselectivity and reactivity of the complex metal hydride. Further, by judiciously changing the solvents, it should be possible to use the same reagent to selectively reduce various different functional groups. Recently, a number of complex borohydrides and aluminohydrides with various substituents in the complex ion have been synthesized. Some of these are soluble in a wide variety of solvents. We plan to explore the effectiveness of solvents to control the functional group selectivity of these new reagents.

Acknowledgment. I thank Professor Herbert C. Brown for his stimulating discussions. Financial support of this study by the U.S. Army Research Office through Grants DA31-124 ARO(D) and DAAG-29-76-G-0218 is gratefully acknowledged.

Registry No. *n*-Octyl iodide, 629-27-6; lithium aluminum hydride, 16853-85-3; 11-bromoundecyl tosylate, 66605-81-0; *n*-undecyl bromide, 693-67-4; *n*-undecyl tosylate, 41240-51-1; *n*-octyl tosylate, 3386-35-4; *n*-octyl bromide, 111-83-1; *n*-octyl chloride, 111-85-3; *n*-heptyl iodide, 4282-40-0; *n*-heptyl bromide, 629-04-9; *n*-octane, 111-65-9; *n*-heptane, 142-82-5.

(7) (a) Kraus, W.; Chassin, C.; Chassin, R. *Tetrahedron* **1969**, *25*, 3681–3692. (b) Kraus, W.; Chassin, C. *Tetrahedron Lett.* **1970**, 1113–1116.

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Synthetic Applications of Phenylselenenyl Chloride Additions. A Simple 1,3-Enone Transposition Sequence

Summary: The regiospecific addition of phenylselenenyl chloride to allylic alcohols is used as the key step in a simple 1,3-enone transposition sequence.

Sir: In a previous study we examined the scope and limitations of phenylselenenyl chloride additions to simple olefins.[1] During the course of our investigations we observed that additions of PhSeCl to allylic alcohols generally proceed with high regio- and stereoselectivity. For example, cyclohexenol (**2**, R = R′ = H) reacts with PhSeCl to form only one of four possible regio- and stereoisomers[2] (vide infra). In this communication we wish to report that (a) the regiospecificity of this addition appears to be quite general and that (b) this reaction can be used as the key step in the general 1,3-enone transposition sequence shown in eq 1.[3] The results of our study are illustrated in Scheme I.

(1) Liotta, D.; Zima, G. *Tetrahedron Lett.* **1978**, 4977.
(2) PhSCl additions to allylic ethers apparently proceed in a similar fashion. See: Masaki, Y.; Sakuma, K.; Kaji, K. *Chem. Lett.* **1979**, 1235.
(3) For some examples of 1,3-enone transpositions as well as 1,3-alkylative enone transpositions, see: (a) Wharton, P. S.; Bohlen, D. H. *J. Org. Chem.* **1961**, *26*, 3615; (b) Wharton, P. S. *Ibid.* **1961**, *26*, 4781; (c) Trost, B. M.; Stanton, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4018; (d) Trost, B. M.; Hiroi, K.; Holy, N. *Ibid.* **1975**, *97*, 5873; (e) Still, W. C. *J. Am. Chem. Soc. 1977*, *99*, 4836; (f) Buchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021; (g) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623.

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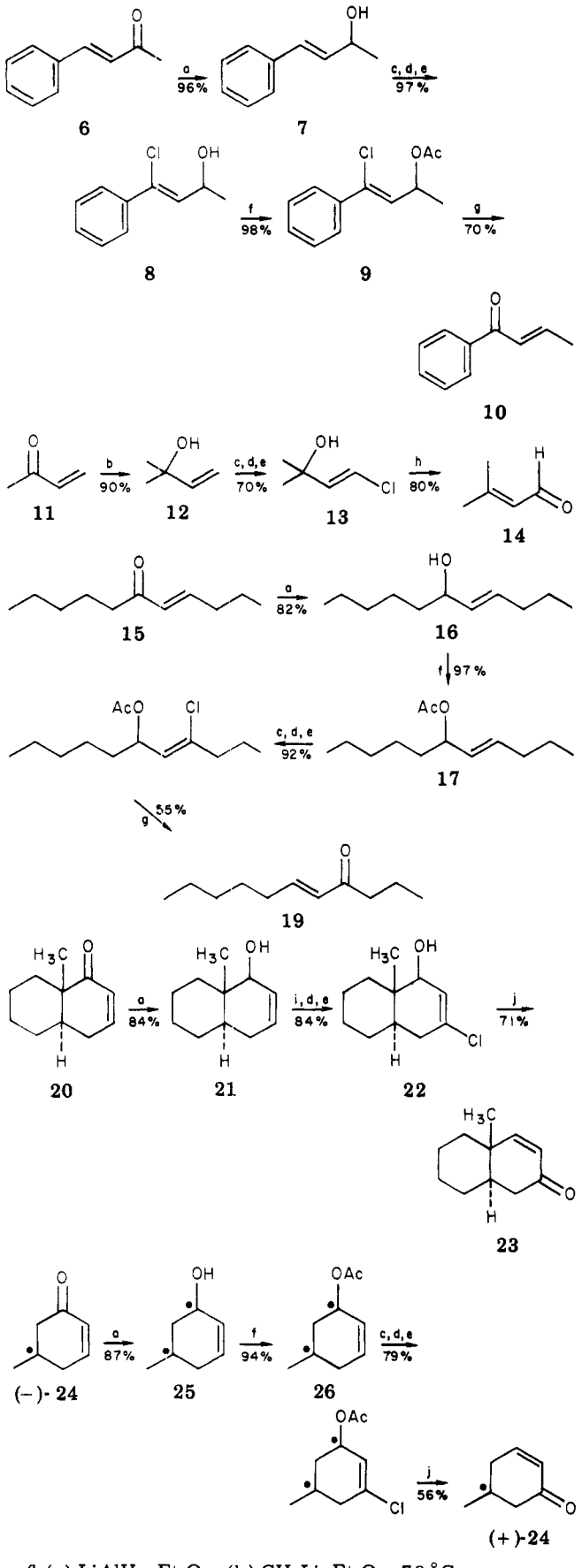
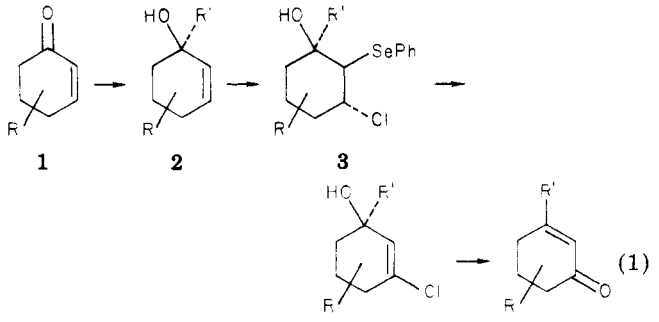
Scheme I[a]



[a] (a) $LiAlH_4$, Et_2O. (b) CH_3Li, Et_2O, −78 °C. (c) PhSeCl, CH_2Cl_2, −78 °C. (d) O_3, CH_2Cl_2. (e) Et_2NH, CH_2Cl_2, Δ. (f) CH_3COCl, py, Et_2O. (g) $Hg(OAc)_2$, CF_3COOH. (h) 10% HCl/$CHCl_3$. (i) PhSeCl, CH_2Cl_2, 25 °C. (j) 90% HCOOH, Δ.



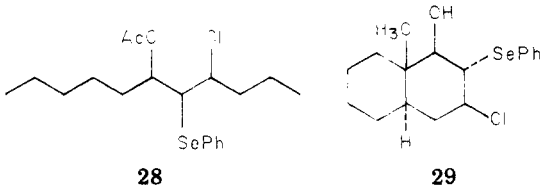
R = alkyl; R′ = H or alkyl

Conversion of the starting enones to their corresponding allylic alcohols can be achieved either reductively with lithium aluminum hydride (**6** → **7**, **15** → **16**, **20** → **21**, and **24** → **25**) or alkylatively with an alkyllithium reagent (**11** → **12**). The hydride reductions of **20** and **24** proceed stereospecifically to produce **21** and **25**, respectively; none of the corresponding epimeric alcohols are observed.

Addition of PhSeCl to allylic alcohol **7** proceeds rapidly and regiospecifically (Markovnikov addition at −78 °C. The regiochemistry of the adduct is easily established by NMR, since in 3-(phenylselenenyl)-4-chloro-4-phenylbutan-2-ol the **CH**SePh must appear as a clean doublet of doublets. Although the phenylselenenyl adduct can be isolated, it is more convenient to oxidize and eliminate the resulting selenoxide in situ.[4a] Consistent with the previous findings of Sharpless,[5] the elimination reaction proceeds in a completely regiospecific fashion away from the hydroxyl group to yield **8**. Acetylation[6] and subsequent hydrolysis[7] yields the transposed enone **10** in 65% overall yield from **6**.

Addition of PhSeCl to **12** initially yields the anti-Markovinkov adduct, which isomerizes on standing to the Markovnikov adduct.[1,8] If the addition is done at −78 °C in CH_2Cl_2, no isomerization occurs. Oxidation/elimination in situ yields **13**, which is easily hydrolyzed to **14** by using a two-phase system (10% HCl/$CHCl_3$). It is important to note that this method of hydrolysis is only suitable for tertiary chloroallylic alcohols; less substituted chloroallylic alcohols are recovered unchanged under these conditions.

Reaction of **16** with PhSeCl yields a mixture of regioisomers. However, if **16** is first converted to its corresponding acetate, **17**, and then allowed to react with PhSeCl, the desired regioisomer, **28**, is produced almost exclusively.[9] Further elaboration to transposed enone **19** is accomplished in a straightforward fashion by using the approach discussed above.[3b]



When **20** is allowed to react with PhSeCl at room tem-

(4) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697. (b) Consistent with ref 4a, selenoxide eliminations involving unactivated cyclohexane rings may take up to 3 days to completely eliminate in refluxing CH_2Cl_2.

(5) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

(6) Under the experimental conditions, hydrolysis of acetate **9** gave higher yields than with alcohol **8**.

(7) Martin, S. F.; Chow, T. *Tetrahedron Lett.* **1978**, 1943.

(8) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950.

(9) At present, it is not clear whether the increased regioselectivity is the result of steric or electronic factors (or both).

perature, a complex mixture of isomers is initially produced. Upon being allowed to stand, however, the mixture slowly isomerizes (2 days) to the thermodynamically more stable, diequatorial adduct, **29**. Oxidation of **29** with ozone (−78 °C), followed by regiospecific elimination in refluxing CH_2Cl_2, yields **22**,[4b] which is conveniently hydrolyzed to octalone **23** in refluxing 90% formic acid.[10]

A more subtle application of this enone transposition sequence involves the conversion of certain chiral 5-substituted cyclohexenones into their optical antipodes. Thus, by performing the sequence of reactions indicated in Scheme I, (−)-**24** is converted to (+)-**24** in at least 92% optical purity.

On examination of Scheme I, it is important to realize that each of these transpositions can be accomplished by using just two or three flasks, with little or no purification of intermediates being necessary. Moreover, even in its current, nonoptimized state, we are able to use this methodology to effect both simple and alkylative 1,3-enone transpositions on a variety of structurally diverse enones in approximately 40–60% overall yields. Further studies involving the synthetic and mechanistic aspects of this work are currently in progress and will be the subject of future reports.

Acknowledgment. We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, Research Corp., and the National Institutes of Health for financial support.

Registry No. **6**, 1896-62-4; **7**, 36004-04-3; **8**, 73587-62-9; **9**, 73587-63-0; **10**, 35845-66-0; **11**, 78-94-4; **12**, 115-18-4; **13**, 62493-31-6; **14**, 107-86-8; **15**, 73587-64-1; **16**, 73587-65-2; **17**, 73587-66-3; **18**, 73587-67-4; **19**, 73587-68-5; **20**, 73587-69-6; **21**, 73587-70-9; **22**, 73587-71-0; **23**, 22844-34-4; (−)-**24**, 54307-74-3; (+)-**24**, 15466-88-3; **25**, 73610-84-1; **26**, 73610-85-2; **27**, 73587-72-1; **28**, 73587-73-2; **29**, 73587-74-3; PhSeCl, 5707-04-0.

Supplementary Material Available: Experimental Section describing details of a representative 1,3-enone transposition sequence (15 → **19**) (3 pages). Ordering information is given on any current masthead page.

(10) Lansbury, P. T. *Acc. Chem. Res.* **1972**, *5*, 311.
(11) Fellow of the Alfred P. Sloan Foundation, 1980–1984.

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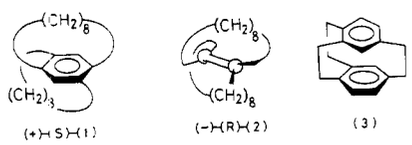
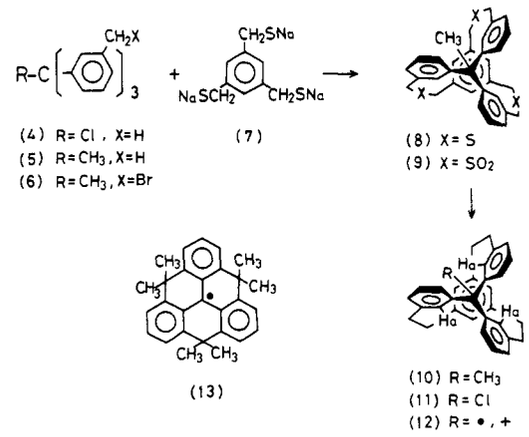
Synthesis of a C_3-Symmetric Tris-Bridged [2.2.2]Cyclophane with a Triphenylmethyl Component

Summary: High-dilution coupling of **6** and **7** afforded the trithia derivative **8** which was converted, via the trisulfone **9**, into 17-methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (**10**) with C_3 symmetry.

Sir: We have been interested in gyrochiral twisted π-electron systems, and the preparations and chiroptical properties of (+)-(*S*)-[8.8]paracyclophane (**1**)[1] (D_2 symmetry) and (−)-(*R*)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**2**)[2] (D_2 symmetry) were reported from our laboratory. An extension of our recent study on the twisted [2.2.2] tris-bridged cyclophane derivative **3**[3] with C_2 symmetry led us to investigate a novel [2.2.2] tris-bridged cyclophane system (**10**, Scheme I) with C_3 symmetry which is composed of the mesitylene and the *m*-substituted triphenylmethane components, and this communication describes its preparation as well as its conformational mobility.



Scheme I



The Grignard reaction of the *m*-substituted triphenylmethyl chloride **4**[4] with methylmagnesium iodide afforded the higher homologue **5** (mp 73–74 °C, 82% yield) whose NBS photobromination in CCl_4 gave a 41% yield of the tribromide **6**, mp 111–112 °C. High-dilution coupling of **6** and the sodium salt of 1,3,5-tris(mercaptomethyl)benzene (**7**) was carried out in a benzene–ethanol (1:1) solution, and the product was purified through SiO_2 column chromatography to provide the trithia derivative **8**[5] (17% yield), melting at 220–221 °C after recrystallization from ethyl acetate. The trisulfone **9** (mp >350 °C), secured from **8** by conventional hydroperoxide oxidation with a quantitative yield, was vacuum sublimed (0.1 mmHg) and slowly passed through an evacuated Pyrex pyrolysis tube heated at 540 °C. Column chromatography (SiO_2) of the product followed by recrystallization from hexane gave a 55% yield of 17-methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (**10**):[6] mp 213–214 °C, UV (isooctane) λ_{max} nm (log ϵ) 223 sh (4.49), 256 sh (2.94), 263 (2.99), 271 sh (2.69). Anal. Found: C, 92.70; H, 7.26.

Inspection of a molecular model reveals that **10** has a chiral strain-free rigid conformation with C_3 symmetry which can convert into the enantiomer via various labile

(1) (a) Synthesis of the racemic modification: M. Nakazaki, K. Yamamoto, and S. Tanaka, *Tetrahedron Lett.*, 341 (1971); M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Org. Chem.*, **41**, 4081 (1976). (b) Preparation of the optically active modification and chiroptical properties: M. Nakazaki, K. Yamamoto, and M. Itho, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki and K. Yamamoto, *Chem. Lett.*, 1051 (1974); M. Nakazaki, K. Yamamoto, M. Itho, and S. Tanaka, *J. Org. Chem.*, **42**, 3468 (1977).
(2) (a) Synthesis of the racemic modification: M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Chem. Soc., Chem. Commun.*, 346 (1977); M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Am. Chem. Soc.*, **101**, 147 (1979). (b) A paper on asymmetric synthesis and chiroptical properties is to be submitted for publication.
(3) M. Nakazaki, K. Yamamoto, and Y. Miura, *J. Chem. Soc., Chem. Commun.*, 206 (1977); M. Nakazaki, K. Yamamoto, and Y. Miura, *J. Org. Chem.*, **43**, 1041 (1978).
(4) J. H. Brown and C. S. Marrel, *J. Am. Chem. Soc.*, **59**, 1175 (1937).
(5) Satisfactory spectroscopic data and elemental or exact mass analyses were obtained for all new compounds.
(6) Following the nomenclature proposed by Vogtle: F. Vogtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970); F. Vogtle and G. Hohner, *Angew. Chem., Int. Ed. Engl.*, **14**, 497 (1975).

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