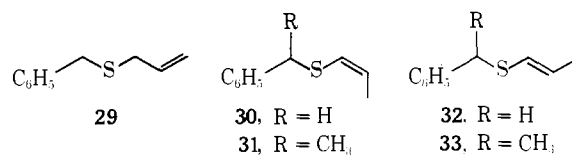


geometric isomers, but preparative vapor phase chromatography afforded pure isomers. Vinylic coupling constants were used to assign double bond geometries. Lithiation of both isomers **16** and **19** under standard conditions proved to be slow even at room temperature. As a result, uncharacterized substances with high molecular weight accompanied the anticipated products **17** and **20**. Rearrangement of the *E* isomer **16** afforded only the *E* carbinol **17** by [1,2] shift with retention of stereochemistry within the migrating group. Similarly, rearrangement of the *Z* isomer **19** produced the *Z* carbinol **20** stereospecifically in addition to not fully characterized products seemingly produced by addition of butyllithium⁶ to the alcoholate **20** followed by elimination of lithium oxide. The structures of the two unsaturated alcohols **17** and **20** were deduced again by proton spectroscopy after complexation with $\text{Eu}(\text{fod})_3$. Vapor-phase chromatography was capable of separating the four substances **16**, **17**, **19**, and **20** and was used to monitor the over-all as well as the stereochemical course of the rearrangement. Of mechanistic interest is the complete absence of aldehyde **18** whose enolate would be the result of a [1,4] shift. No attempt was made to trap the organolithium intermediates because lithiation is probably the rate-limiting step in these slow transformations, nor did we try to speed up lithiation by using the more basic *sec*-*tert*-butyllithium.

Two additional vinyl ethers **21** and **23** were prepared and subjected to lithiation. Neither one underwent the anticipated rearrangement. β -Phenylallyl vinyl ether **21** yielded olefin **22** by either $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}2'$ substitution by *n*-butyllithium. The β -cyclogeranyl vinyl ether **23** gave a mixture of ketone **27** and β -cyclogeraniol (**28**). Steric crowding undoubtedly prevents lithiation at the allylic carbon atom causing metallation to yield the two vinylolithium derivatives **24** and **25**. The latter suffers the well known cleavage to the alcoholate of **28** and presumably acetylene while the former, **24**,⁷ produces the enolate **26** by yet another seemingly unrecorded [1,2] shift.

To study the behavior of sulfur analogs we prepared the two benzyl propenyl sulfides **30** and **32** by base-

catalyzed isomerization⁸ of allyl benzyl sulfide **29**. Lithiations were fast; the resulting organolithium reagents were stable and could be methylated to the two sulfides **31** and **33**.⁹



Mechanism. Vinyl migration within an organolithium compound derived from allyl or benzyl vinyl ethers could in principle proceed by any of four mechanisms: (1) a concerted rearrangement, (2) an addition-elimination sequence, and (3) a dissociation-recombination process. A concerted rearrangement represents a highly unlikely event because the [1s,2s] shift is symmetry forbidden¹⁰ while the allowed [1a,2s] and [1s,2a] shifts with inversion at the migrating sp^2 carbon atom or antarafacial migration, respectively, are geometrically unfeasible. The stereospecificity of the rearrangement may exclude the "oxacyclopentyl carbinyl anion" intermediate demanded by the second mechanism. In the last two mechanisms both a geminate radical-radical anion pair and a geminate vinyl-lithium-carbonyl compound pair need to be considered. The stereospecificity of the rearrangement seems to be inconsistent with a radical pathway.¹¹ Furthermore, such recombinations seem to proceed with little structural discrimination and should furnish products reflecting both [1,2] and [1,4] shifts.^{12,13} An ionic dissociation-recombination emerges as the most reasonable mechanism. It convincingly accounts for the stereo-

(8) D. S. Tarbell and M. A. McCall, *J. Amer. Chem. Soc.*, **74**, 48 (1952); D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

(9) For similar alkylations, see P. L. Stotter and R. E. Hornish, *J. Amer. Chem. Soc.*, **95**, 4444 (1973); K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 4446 (1973).

(10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(11) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971), and references cited.

(12) H. Felkin and A. Tambuté, *Tetrahedron Lett.*, 821 (1969).

(13) V. Rautenstrauch, *Chem. Commun.*, 4 (1970); J. E. Baldwin, J. deBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970); S. H. Pine, *J. Chem. Educ.*, **48**, 99 (1971).

(6) J. K. Crandall and A. C. Clark, *J. Org. Chem.*, **37**, 4236 (1972); H. Felkin, G. Swierczewski, and A. Tambuté, *Tetrahedron Lett.*, 707 (1969).

(7) Such lithiations represent known transformations: V. Rautenstrauch, *Helv. Chim. Acta*, **55**, 594 (1972); U. Schöllkopf and P. Hänsle, *Justus Liebig's Ann. Chem.*, **763**, 208 (1972); J. E. Baldwin, M.I.T., private communication and unpublished observations in these laboratories by P. Masi and H. Wüest.

specificity as well as the structural change associated with the rearrangements. Finally, the thermal stability displayed by the thioether anions is explained because the thioaldehydes that would result from analogous cleavage are high-energy species.

Conclusion

The stereospecific [1,2] rearrangement of benzyl vinyl and certain allyl vinyl ethers induced by *n*-butyllithium is a preparatively useful method for the synthesis of phenylvinyl- and divinylcarbinols with predictable double bond configurations. High yields can be anticipated whenever lithiation is fast. A low over-all rate of reaction may call for the use of more basic lithium reagents.

Experimental Section

Reactions with organolithium compounds were carried out in Schlenk tubes¹⁴ under nitrogen, with magnetic stirring. Solvents were distilled off through an efficient glass spiral column; a small short-path distillation apparatus was used for distillations. Infra-red (ir) spectra of neat films were taken on a Perkin-Elmer 125 instrument. Nuclear magnetic resonance (nmr) spectra were measured in CCl₄ (unless otherwise stated) on Hitachi Perkin-Elmer R-20B and Bruker HFX90 instruments and are given in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were determined on an Atlas CH 4 instrument (*ca.* 70 eV); the molecular ion and the three most intense fragments are reported. Gas chromatography (gc) was performed on F and M 500 and Carlo Erba GT instruments, using regular and capillary Carbowax 20M15 and silicon Fluid XF 1105 columns. Abbreviations: *n*-butyllithium, BuLi; tetramethylethylenediamine, TMEDA; tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadecano)europium(III), Eu(fod)₃ (Sievers' reagent).

Reaction of Methallyl Vinyl Ether (1)¹⁵ with BuLi. To a mixture of 1.96 g (20 mmol) of 1, 4 ml of TMEDA, and 25 ml of hexane was added at -30° 12.5 ml (25 mmol) of 2 *M* BuLi-hexane. After 1 hr of stirring at 5° the mixture was poured into water and extracted with ether. The organic layer was washed with water, dried (Na₂SO₄), concentrated, and distilled giving 634 mg (32%) of alcohol 4, bp 45–48° (18 mm). A sample was purified by gc collection: ir (CHCl₃) 3630, 3460, 1650, 1635, 980, 920, 900 cm⁻¹; nmr δ 6.1–4.7 (m, 5), 4.4 (d, 1, *J* = 5 Hz), 2.9 (br s, 1, disappears on exchange with D₂O), 1.7 (s, 3); mass spectrum *m/e* (rel intensity) 98 (11), 83 (100), 56 (73), 41 (81).

Reaction of Benzyl Vinyl Ether (7)¹⁶ with BuLi. To a stirred mixture of 134 mg (1 mmol) of 7, 0.25 ml of TMEDA, and 1.5 ml of ether was added at -75° 0.85 ml (1.5 mmol) of 1.75 *M* BuLi in hexane. After 16 hr of standing at -27° the mixture was hydrolyzed and extracted with ether. The organic layer was washed with water, dried (MgSO₄), concentrated, and distilled giving 119 mg (89%) of 8: bp 92–93° (12 mm); ir 3350, 1640, 1600, 990, 930 cm⁻¹; nmr δ 7.12 (s, 5), 5.45–6.25 (m, 1), 5.12 (br, d, 1), 4.90 (m, 2); mass spectrum *m/e* (rel intensity) 134 (5), 133 (85), 132 (100), 105 (85), 79 (85).

Trapping Experiments. No reaction occurred at -75° (1.5 hr, otherwise as above). Quenching with excess deuterium oxide after 4.5 hr (-27° , same conditions as above) gave a *ca.* 4:1 mixture of 8 and 7. According to mass spectrum and nmr, 7 isolated from this mixture contained no deuterium.

Allylic Rearrangement of Alcohol 8. A solution of 208 mg of 8 in 2 ml of dioxane and 0.5 ml of water was treated with 100 mg of *p*-toluenesulfonic acid hydrate and left for 7 days at room temperature. The mixture was diluted with ether, washed with water and sodium bicarbonate solution, dried (MgSO₄), and concentrated. Gc analysis showed cinnamyl alcohol as the main component. It was isolated by preparative gc and identified by its spectra (ir, nmr, mass spectrum).

(14) U. Schöllkopf in "Houben-Weyl," Vol. XIII/1, Georg Thieme Verlag, Stuttgart, 1970, chapters 1 and 3.

(15) Om. P. Vig, B. Vig, and R. C. Anand, *Ind. J. Chem.*, 7 (11), 1111 (1969).

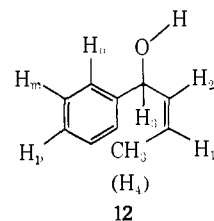
(16) Prepared by B. Egger, according to the general method given by S. Julia, H. Linares, and J.-C. Blondel, *Bull. Soc. Chim. Fr.*, 1947, 1952 (1962).

(Z)-Propenyl Benzyl Ether (10). A solution of 5.17 g (35 mmol) of allyl benzyl ether and 621 mg (5.5 mmol) of potassium *tert*-butoxide in 11 ml of DMSO was left for 3 days at 37° . The mixture was poured into saturated NaCl solution and extracted with ether. The organic layer was washed with water, dried (MgSO₄), concentrated, and distilled giving 4.35 g (84%) of 10: bp 75–80° (12 mm); ir 1665, 695 cm⁻¹; nmr δ 7.25 (s, 5), 5.92 (d of m, 1, *J* = 6.0 Hz), 4.70 (s, 2), 4.35 (apparent q, 1), 1.60 (d of d, 3, *J* = 7, 1.5 Hz); mass spectrum *m/e* (rel intensity) 148 (3), 91 (100), 65 (10).

Allyl benzyl ether and 10 could not be separated on gc. According to nmr the product contained none of the allylic isomer and only a trace of E isomer 11.

(E)-Propenyl Benzyl Ether (11). Ether 10 (592 mg, 4 mmol) in the presence of 20 mg (0.06 mmol) of mercuric acetate was heated for 1 hr at *ca.* 120°. Analysis by gc indicated that equilibration with formation of a *ca.* 2:1 mixture of 10 and 11 had occurred (further heating did not change the composition of the mixture). Direct distillation afforded 531 mg (90%) of 10 and 11: bp 75–80° (12 mm). Isomer 11 was isolated by preparative gc (1.6 m Carbowax, 130°, two passages through the column): ir 1670, 1650, 980 cm⁻¹; nmr δ 7.25 (s, 5), 6.24 (d of m, 1, *J* = 12.5 Hz), 4.4–5.0 (m, 1), 4.62 (s, 2), 1.53 (d of d, 3, *J* = 6.5, 1.5 Hz); mass spectrum *m/e* (rel intensity) 148 (2), 91 (100), 65 (10).

Reaction of (Z)-Propenyl Benzyl Ether (10) with BuLi. A solution of 2.19 g (14.8 mmol) of 10 (containing *ca.* 2% of 11, as determined by gc) in 20 ml of ether and 3.5 ml of TMEDA was treated at -65° with 12.7 ml (22.2 mmol) of 1.75 *M* BuLi-hexane. After 16 hr of standing at -27° water was added, and the mixture was extracted with ether. The ethereal layer was washed with water, dried (MgSO₄), concentrated, and distilled giving 1.91 g (87%) of 12: bp 108–113° (12 mm); ir 3460, 1660, 1600, 700 cm⁻¹; mass



spectrum *m/e* (rel intensity) 148 (85), 133 (84), 105 (100), 77 (78); nmr (90 MHz, CDCl₃) δ 7.40 (m, 5), 5.70 (m, 3), 1.80 (m, 3). On complexation with Eu(fod)₃ a first-order spectrum was obtained which could easily be interpreted. Only one of the series of spectra is given (20 mg of 12, 70 mg of Eu(fod)₃, 0.5 ml of CDCl₃): δ 10.5 (br, d, *J*₂₃ = 9 Hz, H₃), 9.85 (d with further small coupling, *J* = 7 Hz, 2 H₀), 9.0 (d of d with further small coupling, *J*₁₂ = 10, *J*₂₃ = 9 Hz, H₂), 7.6–8.2 (m, 2 H_m, H_p), 6.85 (d of q, *J*₁₂ = 10, *J*₁₄ = 7 Hz, H₁), 2.65 (d of d, *J*₁₄ = 7, *J*₂₄ = 2 Hz, 3 H₄). On irradiation of H₂, H₁ appeared as a quartet (*J*₁₄ = 7 Hz).

Degree of Stereospecificity. The Eu(fod)₃ complexed nmr of a *ca.* 2:1 mixture of alcohols 12 and 13 (34 mg of 12 + 13, 80 mg of Eu(fod)₃, 0.5 ml of CDCl₃) showed the methyl groups as distinct, clearly separated signals: 12, δ 2.47 (d of d, *J*₁₄ = 7, *J*₂₄ = 2 Hz, 3 H₄); 13, δ 2.31 (br d, *J*₂₄ = 6.5 Hz, 3 H₄). The Eu(fod)₃ complexed nmr of reaction product 12 (20 mg of 12, 70 mg of Eu(fod)₃, 0.5 ml of CDCl₃) exhibited a small signal (*ca.* 2%) at δ 2.44, which could be attributed to the methyl group of E isomer 13. Since starting material 10 contained a similar amount of E isomer 11, the rearrangement is stereospecific within experimental error.

Trapping Experiments. With Deuterium Oxide. Ether 10 (296 mg, 2 mmol) was treated with BuLi as before. After 5 hr at -27° deuterium oxide (1 ml) was added at -75° , and stirring was continued for 5 min at room temperature. Work-up gave 280 mg (95%) of a *ca.* 1:3 mixture of 10 and 12, from which compound 10 was isolated by gc collection: ir similar to that of undeuterated material, except for the region of 1200–1400, 1350, 1340, 1250 cm⁻¹; nmr shows the presence of 0.8 D in the benzylic position (signal at δ 4.70); mass spectrum *m/e* (rel intensity) 149 (4), 148 (1), 92 (100), 91 (58).

With Trimethylsilyl Chloride. Ether 10 (296 mg, 2 mmol) was lithiated as before (4 hr at -27°), then 470 mg (4.3 mmol) of trimethylsilyl chloride was added at -75° . After stirring for 30 min at -75° and 30 min at 5° pentane was added. The solution was washed with 2% sulfuric acid and 3% sodium bicarbonate, dried (molecular sieve), evaporated, and concentrated giving 266 mg of product, bp 78–80° (12 mm). Gc analysis showed two peaks

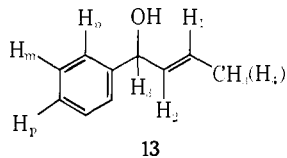
A and B, which were collected. According to nmr, peak A consisted of a *ca.* 1:2 mixture of **10** and **14**; the signals of **14** were discerned: δ 7.12 (m, 5), 5.79 (d of m, 1, $J = 6.0$ Hz), 4.43 (s, 1), 4.35 (m, 1), 1.60 (m, 3), 0.01 (s, 9); mass spectrum m/e 220 (M^+). Peak B consisted of **15**: ir 1660, 1600, 695 cm^{-1} ; nmr δ 7.21 (s, 5), 4.48 (s, 3), 1.75 (m, 3), 0.10 (s, 9); mass spectrum m/e (rel intensity) 220 (62), 205 (60), 75 (90), 73 (100).

Oxidation of Alcohol 12. To a stirred mixture of 2.54 g (26 mmol) of chromic acid, 2.6 ml of water, and 2 ml of ether was added at 5° a solution of 750 mg (5.06 mmol) of **12** in 5 ml of ether. After 23 hr of stirring at room temperature water was added and the mixture extracted with ether. The ethereal layer was washed, dried (MgSO_4), concentrated, and distilled giving 155 mg of benzaldehyde (identification by spectra), bp 58–61° (12 mm). Further distillation gave 315 mg of a mixture of benzylidene acetone (main component) and (*E*)-1-phenylbut-2-en-1-one (minor component), bp 117–119° (12 mm). Separation was achieved by gc collection. Benzylidene acetone: ir 1690, 1665, 1620, 1610, 970 cm^{-1} ; nmr δ 7.42 (d, 1, $J = 16.5$ Hz), 7.3 (m, 5), 6.58 (d, 1, $J = 16.5$ Hz), 2.24 (s, 3); mass spectrum m/e (rel intensity) 146 (74), 131 (100), 103 (88), 77 (48). (*E*)-1-Phenylbut-2-en-1-one: ir 1675, 1640, 1620, 1595, 960 cm^{-1} ; nmr δ 7.8 (m, 2), 7.0–7.6 (m, 4), 6.85 (m, 1), 1.84 (d, 3, $J = 5$ Hz); mass spectrum m/e (rel intensity) 146 (64), 105 (100), 77 (79), 69 (59).

Rearrangement of Alcohol 12. A mixture of 740 mg (5 mmol) of **12**, 6 ml of dioxane, 1.5 ml of water, and 85 mg (0.45 mmol) of *p*-toluenesulfonic acid was left overnight at room temperature. The mixture was diluted with ether, washed with water, dried (MgSO_4), concentrated, and distilled giving 612 mg (83%) of (*E*)-1-phenylbut-1-en-3-ol: bp 57–60° (12 mm); ir 3350, 1595, 960 cm^{-1} ; nmr δ 7.19 (s, 5), 5.9–7.2 (m, 2), 4.37 (m, 1), 1.27 (d, 3, $J = 6.5$ Hz); mass spectrum m/e (rel intensity) 148 (59), 105 (100), 91 (71), 43 (82).

Reaction of (*E*)-Propenyl Benzyl Ether 11 with BuLi. The ether (90 mg, 0.61 mmol) (containing *ca.* 2% of *Z* isomer **10**, as determined by gc) was treated with BuLi and worked up as described for **10** to give 95 mg of crude material. Purification by gc collection afforded **13**: ir 3350, 1680, 1600, 960 cm^{-1} ; nmr (90 MHz, CDCl_3) δ 7.35 (s, 5), 5.75 (m, 2), 5.17 (m, 1), 1.72 (m, 3); mass spectrum identical with that of **12**.

Eu(fod)₃ Complexation Spectra. A (32 mg of **13**, 100 mg of

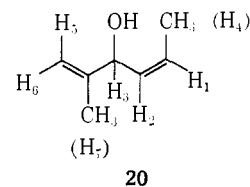


Eu(fod)_3 , 0.5 ml of CDCl_3): 10.45 (br d, $J_{23} = 6$ Hz, H_3), 10.12 (d with further small coupling, $J = 8$ Hz, 2 H_6), 8.95 (d of d with further small coupling, $J_{23} = 6$, $J_{12} = 15$ Hz, H_2), 7.75–8.50 (m, 2 H_m , H_p , H_1), 2.42 (br d, $J_{14} = 6$ Hz, 3 H_4). B (32 mg of **13**, 50 mg of Eu(fod)_3 , 0.5 ml of CDCl_3): at this lower Eu(fod)_3 concentration H_1 can be observed, while H_2 shifts into the aromatic region (H_m , H_p), and the signals of H_6 and H_3 change places; δ 9.0 (d with further small coupling, $J = 8$ Hz, 2 H_6), 8.30 (br d, $J_{23} = 6$ Hz, H_3), 7.35–8.0 (m, 2 H_m , H_p , H_2), 7.23 (q of q, $J_{12} = 15$, $J_{14} = 6$ Hz, H_1), 2.13 (br d, $J_{14} = 6$ Hz, 3 H_4). On irradiation of H_4 , H_1 appeared as a doublet ($J = 15$ Hz). The Eu(fod)_3 complexed nmr of **13** (A) indicated the presence of *ca.* 2% of the *Z* isomer **12** (br d at δ 2.50). This corresponds to the amount of *Z* isomer **10** present in the starting material.

(*E*)- and (*Z*)-Methallyl Propenyl Ether 16 and 19. A solution of 28.8 g (0.4 mol) of methallyl alcohol in 250 ml of ethyl propenyl ether (mixture of *E* and *Z* isomers) containing 20 g of mercuric acetate was heated at reflux for 3 days. The mixture was left for 11 days at room temperature and then filtered through a dry column containing 200 ml of alumina (Woelm, neutral). The column was washed with 400 ml of pentane. The combined eluates were concentrated and fractionated on a short glass spiral column to give 10.2 g of a *ca.* 1:4 mixture of **16** and **19** and *ca.* 20% of an unknown substance, bp 113–118° (730 mm). Separation was achieved by preparative gc. Ether **16**: nmr (90 MHz, benzene- d_6) δ 6.31 (d of q, 1, $J_1 = 12.5$, $J_2 = 2$ Hz), 5.14 (br s, 1), 4.97 (6 lines, 1, $J_1 = 12.5$, $J_3 = 6.5$ Hz), 4.45 (br s, 1), 4.00 (br s, 2), 1.72 (br s, 3), 1.57 (d of d, 3, $J_2 = 2$, $J_3 = 6.5$ Hz). Ether **19**: ir 1665, 900 cm^{-1} ; nmr (90 MHz, benzene- d_6) δ 5.97 (d of q, 1, $J_1 = 6.5$, $J_2 = 2$ Hz), 5.07 (br s, 1), 4.54 (br s, 1), 4.53 (quintet, 1, $J_1 = J_3 = 6.5$ Hz), 3.98

(br s, 2), 1.85 (d of d, 3, $J_2 = 2$, $J_3 = 6.5$ Hz); 1.67 (br s, 3); mass spectrum m/e (rel intensity) 112 (7), 55 (189), 44 (100), 39 (26).

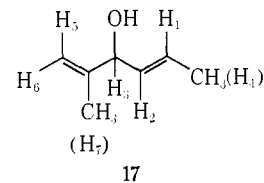
Reaction of (*Z*)-Propenyl Methallyl Ether 19 with BuLi. To a stirred mixture of 434 mg (3.87 mmol) of **19** (no detectable impurity of **16**, as determined by gc), 3.9 ml of ether, and 0.78 ml of TMEDA was added at 5° 4.65 ml (8.1 mmol) of 1.75 *M* BuLi-hexane. After 16 hr of standing at 25° the mixture was hydrolyzed, worked up as usual, and distilled giving 216 mg of *ca.* 80% pure alcohol **20**:



bp ~55° (12 mm). Separation from three unidentified by-products by gc collection afforded pure **20**: ir 3350, 1650, 900, 690 cm^{-1} ; mass spectrum m/e (rel intensity) 112 (10), 97 (93), 43 (99), 41 (100); nmr (90 MHz, CDCl_3) δ 5.25–5.90 (m, H_1 , H_2), 5.07, 4.88 (br s, H_5 , H_6), 4.90 (br d, $J = \sim 8$ Hz, H_3), 1.65–1.80 (m, 3 H_4 , 3 H_7); nmr (15 mg of **20**, 30 mg of Eu(fod)_3 , 0.3 ml of CDCl_3) δ 9.11 (br d, $J_{23} = 8.5$ Hz, H_3), 8.32 (d of d, $J_{23} = 8.5$, $J_{12} = 11$ Hz, H_2), 7.49 (br s, H_5), 6.75 (d of q, $J_{12} = 11$, $J_{14} = 7$ Hz, H_1), 6.0 (br s, H_6), 3.23 (br s, 3 H_7), 2.47 (d of d, $J_{14} = 7$, $J_{24} = 2$ Hz, 3 H_4).

Alcohols **17** and **20** are separable by gc. Since gc analysis of the crude reaction mixture did not reveal any **17** (within experimental error), the rearrangement was stereospecific.

Reaction of (*E*)-Propenyl Methallyl Ether 16 with BuLi. Ether **16** (80 mg) (containing *ca.* 2% of **19**, as determined by gc) was treated with BuLi as described for **19** giving *ca.* 27 mg (*ca.* 34%) of alcohol **17**, bp 50–60° (12 mm). An analytical sample was ob-



tained by gc collection: mass spectrum m/e (rel intensity) 112 (17), 97 (86), 43 (100), 41 (87); nmr (90 MHz, CDCl_3) δ 5.35–6.0 (m, H_1 , H_2), 5.05, 4.87 (br s, H_5 , H_6), 4.51 (br d, $J_{23} = 7$ Hz, H_3), 1.65–1.85 (m, 3 H_4 , 3 H_7); nmr (9 mg of **17**, 18 mg of Eu(fod)_3 , 0.3 ml of CDCl_3) δ 9.14 (br d, $J_{23} = 6$ Hz, H_3), 8.35 (d of d with *t* fine structure, $J_{12} = 15$, $J_{23} = 6$, $J_{24} = 1.5$ Hz, H_2), 7.94 (d of q, $J_{12} = 15$, $J_{14} = 6$ Hz, H_1), 7.78 (br s, H_5), 6.22 (br s, H_6), 3.43 (br s, 3 H_7), 2.31 (d of d, $J_{14} = 6$, $J_{24} = 1.5$ Hz, 3 H_4). On irradiation of H_4 , H_2 appeared as a d of d ($J_{12} = 15$, $J_{23} = 6$ Hz), and H_1 changed to a doublet ($J_{12} = 15$ Hz).

Gc analysis of crude reaction product **17** indicated the presence of *ca.* 2% of *Z* isomer **20**. This corresponds to the amount of *Z* isomer **19** present in the starting material **16**.

2-Phenylprop-1-en-3-yl Vinyl Ether (21). A solution of 6.7 g (50 mmol) of 2-phenyl-2-propen-1-ol¹⁷ and 415 mg (1.2 mmol) of mercuric acetate in 250 ml of ethyl vinyl ether was heated at reflux for 6 days. The mixture was filtered through a dry column filled with 100 ml of alumina (Woelm, neutral). The column was washed with ether, and the combined eluates were concentrated. Further purification by chromatography and distillation proved to be difficult; an almost pure sample of **21** was obtained by low-temperature gc collection: ir 1630, 1610, 905 cm^{-1} ; nmr δ 6.9–7.5 (m, 5), 6.38 (q, 1, $J = 7$, 14 Hz), 5.42 (br s, 1), 5.28 (br s, 1), 4.45 (br s, 2), 3.80–4.40 (m, 2); mass spectrum m/e 160 (M^+).

Reaction of 2-Phenylprop-1-en-3-yl Vinyl Ether (21) with BuLi. To a mixture of 160 mg (1 mmol) of **21**, 0.25 ml of TMEDA, and 1.5 ml of ether was added at –75° 0.85 ml (1.5 mmol) of 1.75 *M* BuLi-hexane. After 2 hr at –75° water was added and the mixture worked up as usual to give 154 mg (89%) of **22**: bp ~100° (12 mm); ir 1625, 1600, 890 cm^{-1} ; nmr δ 7.0–7.5 (m, 5), 5.17 (m, 1), 4.97 (m, 1), 2.45 (br t, 2), 1.1–1.6 (m, 4), 0.86 (br t, 3); mass spectrum m/e (rel intensity) 174 (4), 118 (100), 103 (12), 91 (12).

Reaction of β -Cyclogeranyl Vinyl Ether (23)¹⁸ with BuLi. A

(17) L. F. Hatch and T. L. Patton, *J. Amer. Chem. Soc.*, **76**, 2705 (1954).

(18) G. Buchi and J. D. White, *J. Amer. Chem. Soc.*, **86**, 2884 (1964).

solution of 180 mg (1 mmol) of **23** and 0.2 ml of TMEDA in 1 ml of ether was treated at 5° with 1.2 ml (2.1 mmol) of 1.75 M BuLi-hexane. The mixture was left for 16 hr at room temperature then hydrolyzed and worked up as usual to give 165 mg of crude product. Gc analysis indicated the presence of ca. 45% of **23**, 25% of **28**, and 30% of **27**. Separation was achieved by gc collection. Starting material **23** and β -cyclogeraniol (**28**) were identified by comparison of their spectra with authentic ones; ketone **27**: ir 1720 cm⁻¹; nmr (90 MHz, CDCl₃) δ 3.17 (br s, 2), 2.16 (s, 3), 2.02 (br t, 2), 1.53 (br s, 3), 1.35–1.80 (m, 4), 0.93 (s, 6); mass spectrum *m/e* (rel intensity) 180 (26), 95 (73), 81 (59), 43 (100).

(*Z*)- and (*E*)-Propenyl Benzyl Sulfides (**30**) and (**32**). A solution of 5.0 g (30 mmol) of allyl benzyl sulfide and 1.08 g (9.6 mmol) of potassium *tert*-butoxide in 11 ml of DMSO was left for 11 days at 39°. The mixture was poured into water and extracted with ether. The organic layer was washed with water, dried (MgSO₄), and concentrated. The residue was applied to a dry column containing 50 ml of alumina (Woelm, neutral). The column was washed with 400 ml of pentane. The eluate was concentrated and distilled to give 4.39 g (88%) of a mixture of **30** and **32**: bp 111–114° (12 mm); nmr δ 7.18 (s, 5), 5.0–5.9 (m, 2), 3.70 (s, 2), 1.64 (d with fur-

ther fine structure, 3); ir 1600, 700 cm⁻¹; mass spectrum *m/e* (rel intensity) 164 (20), 91 (100).

Reaction of (*Z*)- and (*E*)-Propenyl Benzyl Sulfides (**30**) and (**32**) with BuLi. A solution of 253 mg (1.54 mmol) of a mixture of **30** and **32** in 3 ml of THF was treated at -75° with 1.1 ml (1.7 mmol) of 1.75 M BuLi-hexane. After 15 hr of standing at 23°, the mixture was treated at -75° with 1.52 g (10.8 mmol) of methyl iodide then stirred at -75° for 10 min and at 25° for 5 min. Water was added, and the mixture was extracted with ether. The ether layer was washed with water, dried (MgSO₄), and concentrated. Distillation afforded 110 mg (40%) of a mixture of **31** and **33**, bp ca. 115° (12 mm). A sample of **31** + **33** was isolated by gc collection: ir 1600, 700 cm⁻¹; nmr δ 7.20 (s, 5), 5.6–6.0 (m, 2), 3.95 (q, *J* = 7 Hz, 1), 1.4–1.8 (m, 6); mass spectrum *m/e* (rel intensity) 178 (9), 105 (100), 91 (13).

Lithiation as described above, but at -75° for 1.5 hr, followed by methylation as described, gave a mixture of **31** and **33** in 85% yield.

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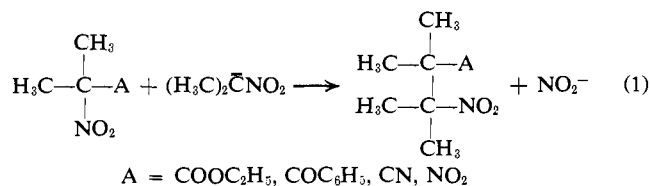
Displacement of the Sulfone Group from α -Nitro Sulfones¹

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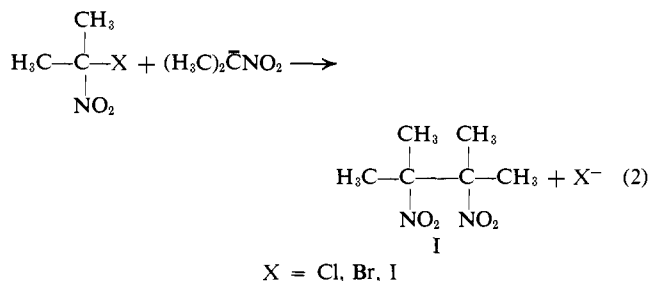
Abstract: At room temperature the sulfone group of α -nitro sulfones is readily displaced by a variety of nucleophiles. These new reactions all appear to be radical anion-free radical chain processes.

In 1970 a new reaction, the displacement of a nitro group from α -nitro esters, α -nitro ketones, α -nitro nitriles, and α,α -dinitro compounds by nitroparaffin salts, was described.² These displacements, which are exemplified by the reactions of eq 1, take place at room

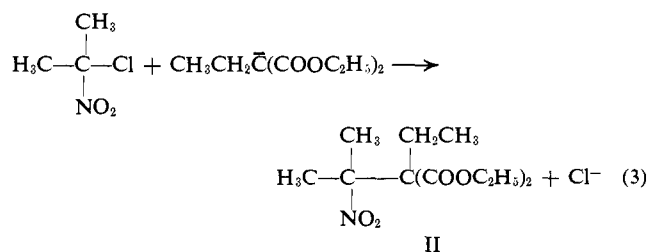


temperature and give excellent yields of pure products.

It has been known for some time, however, that the closely related α -halo nitro compounds undergo an alternative type of displacement in which the halogen atom, rather than the nitro group, is displaced. The first report of such a reaction appears to have been made by Seigle and Hass in 1940; they found that 2-chloro-2-nitropropane, 2-bromo-2-nitropropane, and 2-iodo-2-nitropropane react with the sodium salt of 2-nitropropane according to eq 2; *i.e.*, the vicinal



dinitro compound (I) is produced.^{3,4} Another early example is the reaction of 2-chloro-2-nitropropane with the anion of diethyl ethylmalonate which gives a 68% yield of II (eq 3).⁵ In 1971 further instances of re-



actions in which the halogen atom rather than the nitro group is displaced were described.^{4b} These in-

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