yielding 6 g, bp 76–80° (2 mm), n^{20}D 1.4735. Vpc (20M column at 200°) showed the following composition: 6% *trans*-3-*p*-menthen-5-ol (2); 94% *cis*-3-*p*-menthen-5-ol (2a). For nmr and ir spectra see Table I.

***trans*-3-*p*-Menthen-5-ol (2) by Reduction of 3-*p*-Menthen-5-one with AlP (Meerwein–Pondorff–Verley).**[6]—3-*p*-Menthen-5-one (8 g) and 8 g of AlP were heated in a Claisen–Vigreux flask for 5 min at 130–140° while acetone distilled off. Analysis of the reaction product (vpc, 20M column at 200°) showed that 25% of the ketone was reduced, affording a mixture of 60% *trans*-3-*p*-menthen-5-ol (2) and 40% *cis*-3-*p*-menthen-5-ol (2a). The reaction mixture was quenched in 30% NaOH and separated. After boration with 1 g of B_2O_3 at 120–130°, the unreacted ketone (5 g) was recovered by distillation at 95° (5 mm). The borate ester residue was then decomposed with 30% NaOH and afforded 1 g of distillate, bp 80–85° (2 mm), n^{20}D 1.4650, which consisted of a mixture of 2 and 2a in a ratio of 60:40, respectively. The components of the mixture were identified by vpc with those obtained from the $LiAlH_4$ reduction and with pure samples obtained by Nester–Faust distillation of the rearrangement products of 3,4-epoxy-*cis*- and -*trans*-*p*-menthane (1 and 1a).

(6) D. Malcolm and J. Read, *J. Chem. Soc.*, 1037 (1939).

Pure *trans*-3-*p*-menthen-5-ol (2), bp 102–108° (14 mm), n^{20}D 1.4712, has been previously described by Malcolm and Read.[6]

Catalytic Reductions.—The catalytic reductions of the various samples of the allylic alcohols were carried out in a 10% ethanolic solution using 2 g of substance and 0.5 g of catalyst. The hydrogenation was carried out in a Parr shaker at 50 psi hydrogen pressure at 30° and continued until the hydrogen absorption ceased. The results are given below.

cis-Pulegol (5) gave 3% neoisomenthol, 90% menthol, and 8% menthone.

trans-3-*p*-Menthen-5-ol (2) gave 25% neomenthol, 15% menthol, and 60% isomenthol.

cis-3-*p*-Menthen-5-ol (2a) gave 88% menthol and 12% menthones. 3-*p*-Menthen-8-ol (6) gave 60% *trans*-*p*-menthan-8-ol and 40% *cis*-*p*-menthan-8-ol.

α-Terpineol gave 60% *trans*-*p*-menthan-8-ol and 40% *cis*-*p*-menthan-8-ol.

Registry No.—1, 23602-11-1; 1a, 23602-12-2; 2, 22472-77-1; 2a, 22472-78-2; 5, 22472-80-6; 6, 18479-65-7.

A New and Useful Sulfur Ylide. Thetin Anions

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A procedure for utilization of stabilized sulfur ylides in ketone condensations in good yields is described. The sodium salts of dimethylthetin anion and diphenylthetin anion condense with ketones to produce glycidic acids and with α,β-unsaturated ketones to produce cyclopropanecarboxylic acids. With 4-*t*-butylcyclohexanone, the formed glycidic acid was almost exclusively the *trans* isomer. Thermal decomposition of glycidic acids is known to give aldehydes with loss of CO_2. Thus this method allows easy chain extension by one or two carbon atoms.

The utilization of ylides in organic synthesis has exploded in the last few years. Although phosphorus ylides enjoy the most widespread use, interest into the applications of sulfur ylides to synthetic problems has been stimulated by the work of Corey and coworkers.[3] Utilization of all kinds of stabilized ylides has been hampered by the unreactivity of these synthetic intermediates. One solution to the problem with phosphorus ylides involves the use of a less electronegative phosphorus substituent. The decreased stabilization by phosphorus of the carbanionic center sufficiently enhanced the reactivity of the species to allow normal condensation with most carbonyl partners. A second approach involves reducing the ability of the substituent on carbon to stabilize an adjacent carbanionic center. We have explored this latter alternative to the solution of this problem in the area of sulfur ylides and wish to report our results at this time.

Dimethyl(carbomethoxymethylene)sulfuran (I) has been reported not to add to carbonyl groups of aldehydes and ketones, although its Michael condensation with α,β-unsaturated systems to produce cyclopropanes is well documented.[4,5] Conversion of the carbomethoxy group into a carboxy anion may sufficiently reduce the stabilization of the ylide to allow normal carbonyl condensations. To examine this possibility, the requisite betaines, IIIa[5a] and IIIb, were prepared from the corresponding sulfonium salts, IIa and IIb. Dimethylthetin (IIIa) was obtained by treatment of an aqueous solution of the sulfonium bromide with silver oxide at room temperature;[5a] diphenylthetin (IIIb) was obtained by treatment of the sulfonium fluoroborate with Amberlite resin at 25°. Other attempts to prepare IIIb led only to decomposition products.

Reaction of dimsylsodium with dimethylthetin generated a suspension of the anion in DMSO (see Scheme I). This suspension reacted with chalcone to produce two cyclopropanes in approximately equimolar amounts. Analysis of this mixture proceeded after conversion of the acids into their esters with diazomethane. Nmr allowed unambiguous assignment of stereochemistry to the two compounds. In cyclopropane V,[6] the cyclopropyl hydrogen adjacent to the benzoyl group had couplings to the adjacent protons of 5.0 and 10.0 Hz, the benzylic cyclopropyl hydrogen of 5.0 and 7.0 Hz, and the cyclopropyl hydrogen α to the ester of 7.0 and 10.0 Hz. In cyclopropane

$(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2CH_3$ (I) $\quad R_2\overset{+}{S}CH_2CO_2R^1\ X^-$ (II) $\quad R_2\overset{+}{S}CH_2CO_2^-$ (III) $\quad R_2\overset{+}{S}\overset{-}{C}HCO_2^-$ (IV)

a, R = CH_3

b, R = Ph

(1) NSF Undergraduate Research Participant, 1969.

(2) Alfred P. Sloan Foundation Fellow.

(3) E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967), and references cited therein.

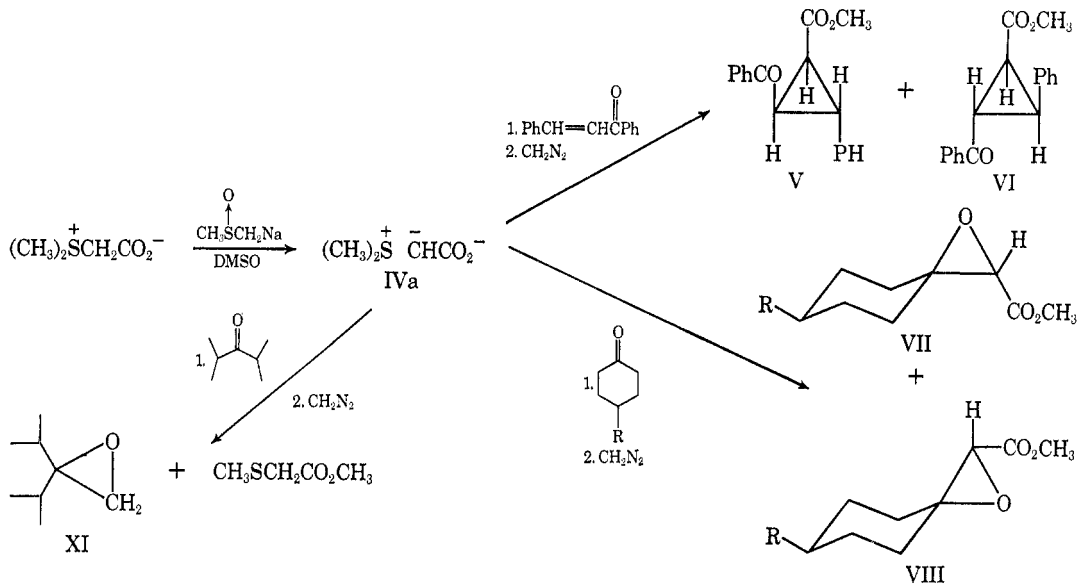
(4) (a) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969). (b) Similar reactivity has been reported for very closely related sulfuranylideneacetates. See H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

(5) For preparation and properties of very closely related sulfuranylideneacetates, see (a) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966); (b) J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *J. Amer. Chem. Soc.*, **89**, 6804 (1967); (c) J. Casanova and D. A. Rutolo, *Chem. Commun.*, 1224 (1967); (d) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967); (e) G. B. Payne, *ibid.*, **33**, 1284, 3517 (1968); (f) G. B. Payne and M. R. Johnson, *ibid.*, **33**, 1385 (1968); (g) H. Nozaki, M. Takaku, Y. Hayashi, and K. Kondo, *Tetrahedron*, **24**, 6536 (1968).

(6) In cyclopropanes, it has been established that *cis* couplings are larger than *trans*. See S. Sternhell, *Quart. Rev.* (London), **23**, 236 (1969); J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962).

Scheme I

Preparation and Reactions of Dimethylthetin Anion



VI,[6] the corresponding hydrogens had coupling constants of 4.5 and 6.5 Hz, 6.5 and 13.3 Hz, and 4.5 and 10.0 Hz. A similar reaction of I has been reported to yield cyclopropane(s) of undetermined stereochemistry.[4b]

Diphenylthetin anion (IVb) has been generated from the corresponding betaine either by treatment with dimsylsodium in DMSO or with *n*-butyllithium in hexamethylphosphoramide (HMPA). It reacted in identical fashion with chalcone to produce the cyclopropanes. Whereas, in the former reaction, the ratio of V to VI was *ca.* 1, in the latter it was *ca.* 1.5.

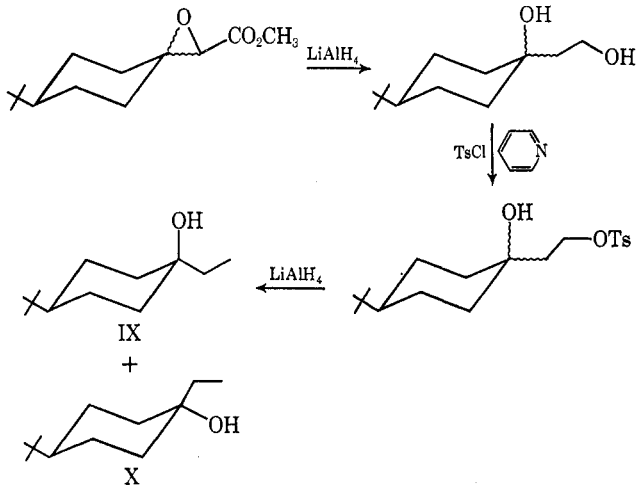
It is interesting to note the difference in reactions of chalcone with various sulfur ylides. Whereas the parent ylide, dimethylmethylenesulfurane, produces the epoxide exclusively,[7] less reactive ylides add in conjugative fashion exclusively. In this regard, we have found that dimethyl(phenacylene)sulfurane,[8] dimethyl(carbomethoxymethylene)sulfurane (I), sodium(dimethylsulfuranylidene)acetate (IVa), and dimethyl(vinylmethylene)sulfurane[9] produce only cyclopropane products with no detectable amounts of epoxides. There are two steps to this reaction—addition to the carbonyl or olefinic carbon followed by elimination to epoxide or cyclopropane. Since it is difficult to understand why elimination to epoxide would be very much slower than elimination to cyclopropane in each respective adduct, we attribute exclusive cyclopropane formation with the stabilized ylides to lack of carbonyl addition. With the most reactive ylide, the transition state of addition should more closely resemble reactant than product, leading ultimately *via* reaction at the most highly electron-deficient center to epoxide.[10] Stabilization of the carbanionic center even with a simple double bond moves the transition state sufficiently along the reaction coordinate so that the thermodynamically most favored adduct (Michael-type addition) is produced exclusively. Presumably, choice of an ylide intermediate in reactivity between dimethylmethylenesulfurane and dimethyl(vinylmethylene)sulfurane would yield mixtures of both types of products.

The condensation of dimethylthetin anion with cyclohexanone proceeded readily to produce after esterification a 60% yield of the glycidic ester (VII, R = H). Identification was made by comparison of its spectral properties with those reported in the literature.[11] Reaction of sulfonium ylides with cyclohexanones has been reported to proceed in a highly stereoselective fashion with production of the axial carbon–carbon bond.[7,12] For example, reaction of 4-*t*-butycyclohexanone with dimethylmethylenesulfurane produced 83% *cis* epoxide (axial C–C bond) and 17% *trans* epoxide (equatorial C–C bond).[7] On the other hand, the less reactive sulfoxonium ylides produce the opposite stereochemical preference. To determine if this difference is a function of the electronegativity of sulfur or the reactivity of the carbanionic center, the reaction of IV with 4-*t*-butylcyclohexanone was examined. The reaction gave a 56% isolated yield of glycidic esters after treatment with diazomethane. Vpc analysis showed essentially one isomer. Deduction of the stereochemistry proceeded as outlined in Scheme II. Lithium aluminum hydride reduction followed by tosylation and lithium aluminum hydride reduction produced a mixture of *cis*- (X) and *trans*-4-*t*-butyl-1-ethylcyclohexanol (IX) in 3 and 97% relative yields, respectively. The stereochemistries were established by comparison with authentic samples prepared by addition of ethylmagnesium bromide to 4-*t*-butylcyclohexanone.[13] In contradiction to the unstabilized sulfonium ylide, the thetin anion adds virtually exclusively *via* the least hindered route to produce an equatorial carbon–carbon bond, *i.e.*, VII.

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).
(8) B. M. Trost, *ibid.*, **89**, 138 (1967).
(9) R. W. LaRochelle, unpublished work in these laboratories.
(10) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).
(11) H. O. House and J. W. Blaker, *ibid.*, **80**, 6389 (1958).
(12) (a) R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967); (b) R. S. Bly, C. M. DuBose, Jr., and G. B. Konizer, *ibid.*, **33**, 2188 (1968); (c) C. E. Cook, R. C. Corley, and M. E. Wall, *ibid.*, **33**, 2789 (1968).
(13) G. F. Hennion and F. X. O'Shea, *J. Amer. Chem. Soc.*, **80**, 614 (1968).

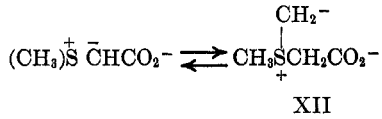
SCHEME II

DETERMINATION OF STEREOCHEMISTRY



The reasons for these stereochemical preferences remain unclear.

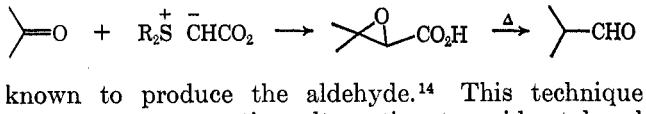
In an ancillary experiment, the extent to which the reactivity of the ylide IV has been increased was tested by examining the reaction of the anion with diisopropyl ketone. After the usual diazomethane work-up, vpc analysis revealed the presence of two materials. The first was identified as methyl methylthioacetate. The second product shows no carbonyl nor hydroxyl absorptions in the infrared spectrum. Its mass spectrum exhibits a parent peak at *m/e* 128 and its nmr spectrum exhibits absorptions at δ 2.45 (singlet, 2 H, epoxide methylene), 1.96 (multiplet, 2 H, isopropyl methines), 0.90 (doublet, 6 H, one set of isopropyl methyls), and 0.85 (doublet, 6 H, second set of isopropyl methyls). These data clearly indicate the structure to be 2-isopropyl-3-methyl-1-butene epoxide (XI). It appears that dimethylthetin anion IV is not reactive enough to add to the hindered carbonyl and that it equilibrates to the more reactive sulfoniummethylide XII before condensation. To



XII

obviate this reaction, we treated the diphenylthetin anion with diisopropyl ketone. However, no glycidic esters could be found. Thus, although the ylide IV is sufficiently more reactive than I to add to simple ketones, it remains unreactive enough not to add to hindered carbonyls.

The utilization of the thetin anion can also serve as a one carbon chain extension procedure, since the thermal decomposition of the initially formed glycidic acid is



known to produce the aldehyde.[14] This technique serves as an attractive alternative to acid-catalyzed rearrangement of epoxides formed from the methylenesulfonium ylides, to the Wittig procedure using the alkoxymethylene ylide, and to the normal Darzens procedure.

(14) M. S. Newmann and B. J. Magerlein, *Org. React.* **5**, 413 (1949). For a discussion of the problems encountered in the usual conversion of glycidic esters into aldehydes and a modification of that technique, see E. P. Blanchard, Jr., and G. Buchi, *J. Amer. Chem. Soc.*, **85**, 955 (1963).

Experimental Section[15]

Preparation of Dimethylthetin (IIIa).—The procedure of Ratts and Yao was employed.[6a] From 5.73 g (25 mmol) of dimethyl(carboethoxymethyl)sulfonium bromide was obtained 4.55 g (60%) of dimethylthetin, mp 138–140° dec (lit. mp 137–138°) after recrystallization from ethanol–ether and drying overnight *in vacuo* over phosphorus pentoxide. The nmr spectrum[16] showed singlets at δ 2.92 (6 H) and 4.15 (2 H). The latter signal slowly decreases and eventually disappears, indicating fairly facile H–D exchange.

Preparation of Diphenyl(carbomethoxymethyl)sulfonium Fluoroborate (IIb, R′ = CH₂).[17]—In a dry bag under a nitrogen atmosphere, a solution of 3.60 g (19.3 mmol) of diphenyl sulfide in 30 g (196 mmol) of methyl bromoacetate was prepared. With magnetic stirring, portionwise addition of 3.75 g (19.3 mmol) of anhydrous silver fluoroborate took place over a period of 0.5 hr. After having been stirred for an additional 2 hr and allowed to stand overnight, the mixture was diluted with methylene chloride and filtered by gravity. Concentration of the methylene chloride solution *in vacuo* produced an oil which crystallized after dissolving in ethanol and addition of ether. Recrystallization in similar fashion produced 3.13 g (47%) of colorless crystals, mp 87–88°. The infrared spectrum[18] showed absorptions at 1740 (carbonyl) and 1000–1100 cm^{-1} (fluoroborate anion). The nmr spectrum[19] showed multiplets at δ 7.80–8.15 (4 H) and 7.50–7.80 (6 H) and singlets at δ 5.23 (2 H) and 3.66 (3 H).

Anal. Calcd for $C_{15}H_{15}O_2SBF_4$: C, 52.05; H, 4.37; S, 9.26. Found: C, 51.95; H, 4.30; S, 9.31.

Preparation of Diphenylthetin (IIIb).—Amberlite resin IRA-400 was converted into its hydroxide form by stirring a suspension in saturated sodium hydroxide solution for 1 week. After the resin had been separated by filtration, it was washed thoroughly with distilled water. A solution of 1.50 g (4.34 mmol) of diphenyl(carbomethoxymethyl)sulfonium fluoroborate in 100 ml of distilled water was treated with 8.5 ml of the above prepared resin. After the solution had been stirred for 1 hr at 25°, filtration removed the resin. Lyophilization *in vacuo* left 885 mg (84%) of white powder, mp 106–107° dec. The infrared spectrum[20] showed a carbonyl peak at 1630 cm^{-1}. The nmr spectrum[16] had a multiplet at δ 7.60–8.05 (10 H) and a singlet at δ 5.02 (2 H). The latter absorption slowly disappeared, indicating facile H–D exchange, in D_2O.

Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95; S, 13.12. Found: C, 68.70; H, 4.96; S, 12.98.

Preparation of Dimethylthetin Anion (IVa). Method A.—A solution of dimsylsodium in dimethyl sulfoxide was prepared by the method of Corey from 400 mg (9.16 mmol, 55% mineral oil dispersion) of sodium hydride in 25 ml of dry (freshly distilled from calcium hydride) dimethyl sulfoxide. Then 989 mg (8.3 mmol) of dimethylthetin was added portionwise under nitrogen through a pressure-equalizing solid addition funnel. Upon completion of the addition, the suspension was stirred for 1 hr at 25° to produce a thick, off-white suspension of dimethylthetin anion (IVa).

Method B.—A solution of dimsylsodium in dimethyl sulfoxide under nitrogen was prepared by the method of Corey from 1.5 g

(15) Melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on an Aerograph Model 90P instrument.

(16) Determined as a solution in deuterium oxide.

(17) A modification of the procedure of Franzen and coworkers. See V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

(18) Determined as a solution in chloroform.

(19) Determined as a solution in deuteriochloroform.

(20) Determined as a KBr pellet.

(35.4 mmol, 56.6% mineral oil dispersion) of sodium hydride in 50 ml of dry dimethyl sulfoxide. A few crystals of triphenylmethane were added to produce a brillant red solution. In a second flask fitted with a magnetic stirrer and two serum caps and flushed under nitrogen was placed 1.184 g (9.90 mmol) of dimethylthetin in 15 ml of dry dimethyl sulfoxide. To this suspension the red dimsylsodium solution was added dropwise *via* syringe until the red color persisted for 30 min.

Preparation of Diphenylthetin Anion (IVb).—This anion could be prepared by either of the above procedures. Alternatively, it was produced by treatment of diphenylthetin with *n*-butyllithium. In a nitrogen atmosphere, 0.47 ml (1.5 *M*, 0.70 mmol) of *n*-butyllithium in hexane was added to 2.0 ml of hexamethylphosphoramide (HMPA). A few crystals of triphenylmethane were added as an indicator. At this point, 0.171 g (0.70 mmol of diphenylthetin was added. A thick, gray slurry was produced.

Reaction of Dimethylthetin Anion with Chalcone.—In a nitrogen atmosphere, 2.08 g (10.0 mmol) of chalcone was added all at once to a solution of the anion generated from 1.24 g (10.3 mmol) of dimethylthetin. A brown solution formed and was stirred for 15.5 hr at 25°. The mixture was poured onto 50 g of ice and acidified to pH 1 with dilute aqueous hydrochloric acid. Ether extraction of the mixture followed by washing of the ether layers with water produced a pale yellow solution. After drying, the solution was treated with diazomethane and the excess diazomethane was destroyed by addition of acetic acid. Washing with aqueous potassium carbonate removed excess acetic acid. After the solution had been dried and concentrated *in vacuo*, the ether layers produced 2.48 g of crude product which showed three major spots on thin layer chromatography[21] utilizing 15% ethyl acetate in cyclohexane as eluent. The fastest moving spot (R_f *ca.* 0.39) was chalcone. The second spot (R_f *ca.* 0.3) was isolated by preparative thin layer chromatography.[21] From 112 mg of crude oil, 38.3 mg (30%) of this component was isolated. The infrared spectrum[22] showed absorptions at 1730 (ester carbonyl), 1672 (ketone carbonyl), and 1600, 1587, and 1500 cm^{-1} (aromatic rings). The ultraviolet spectrum[23] exhibited λ_{max} 247 nm (ϵ 17,000). The nmr spectrum[22] showed a multiplet (2 H) at δ 8.00–8.25, a multiplet (3 H) at δ 7.1–7.7 superimposed upon which is a singlet (5 H) at δ 7.25, three sets of doublets of doublets (1 H each) at δ 3.75 (J = 4.5 and 6.5 Hz), 3.14 (J = 6.5 and 10 Hz), and 2.77 (J = 4.5 and 10 Hz), and a singlet (3 H) at δ 3.50. Its mass spectrum exhibited a molecular ion at *m/e* 280 and intense peaks at *m/e* 249, 222, 221, 175, 115, 105 (base peak), 91, and 77. These data allow assignment of structure VI to this cyclopropane derivative.

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.23; H, 5.66.

The third spot (R_f *ca.* 0.23) was also isolated by preparative thin layer chromatography. From 112 mg of crude oil, 36.6 mg (29%) of this component was isolated. The infrared spectrum[22] showed absorptions at 1725 (ester carbonyl), 1672 (ketone carbonyl), and 1600, 1584, and 1499 cm^{-1} (aromatic rings). The ultraviolet spectrum[23] showed λ_{max} 248 nm (ϵ 21,600). The nmr spectrum[22] exhibited a multiplet (2 H) at δ 7.80–8.05, a multiplet (3 H) at δ 7.19–7.60, a singlet (5 H) at δ 7.12, a singlet (3 H) at δ 3.75, and an ABC pattern for the cyclopropylhydrogens with H_A at δ 3.50, H_B at δ 3.26, and H_C at δ 3.20 (J_{AB} = 5.0 Hz, J_{AC} = 10.0 Hz, and J_{BC} = 7.0 Hz). The mass spectrum showed, in addition to a molecular ion at *m/e* 280, abundant peaks at *m/e* 221, 115, 105 (base peak), and 77. These data allow assignment of structure V to this compound.

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.91; H, 5.76.

Reaction of Diphenylthetin Anion with Chalcones.—In a nitrogen atmosphere a suspension of the sodium salt of diphenylthetin anion prepared from 173 mg (9.77 mmol) of diphenylthetin in DMSO was prepared. To this mixture was added 143 mg (0.69 mmol) of chalcone all at once. After the mixture had been stirred at 25° for 20 hr, it was worked up as described above. Preparative thin layer separation of the products yielded, in addition to diphenyl sulfide, 173 mg (89%) of a mixture of V and VI. Nmr analysis[22] indicated the ratio of V to VI to be *ca.* 1.5.

Reaction of Dimethylthetin Anion with Cyclohexanone.—To a suspension of 6.6 mmol of IVa at 25° under nitrogen was added 612 mg (6.2 mmol) of cyclohexanone in one portion. The temperature rose slightly. After having been stirred for 3 hr at room temperature, the clear solution that evolved was cooled to 20°, poured onto ice, and acidified to pH 1 with hydrochloric acid. After ether extraction and drying, the ethereal solution was treated with diazomethane. Vpc analysis[24] of the oil that resulted after solvent removal utilizing ethyl phenylacetate as internal standard indicated 610 mg (60%) of glycidic ester VII (R = H). Comparison of its infrared spectrum with that of an authentic sample confirmed the structural assignment. The nmr spectrum[19] of the acid prior to diazomethane treatment showed the carboxyl proton at δ 10.10, the epoxide methine hydrogen as a singlet at δ 3.16, and the ring protons as a multiplet centered at δ 1.53.

Reaction of Dimethylthetin Anion with 4-*t*-Butylcyclohexanone.—In a nitrogen atmosphere, 772 mg (5.0 mmol) of 4-*t*-butylcyclohexanone in 2 ml of dry DMSO was added dropwise to a suspension of dimethylthetin anion in DMSO generated from 626 mg (5.22 mmol) of dimethylthetin. Upon completion of the addition, the mixture was stirred for 20 hr at 25°, poured onto ice, acidified to pH 1, and extracted with ether. After esterification with diazomethane and destruction of excess diazomethane with acetic acid, the solution was washed with aqueous potassium carbonate, dried, and concentrated *in vacuo*. Distillation at 73–78° (0.03 mm) generated 664 mg (57%) of a mixture of glycidic esters VII and VIII (R = *t*-C_4H_9). Vpc analysis[24] showed essentially one peak. Nmr analysis[22] also indicated great preponderance of one isomer over the other. The nmr spectrum exhibited singlets at δ 3.70 (3 H), 3.17 (1 H), and 0.88 (9 H) as well as complex absorption between δ 1.1 and 2.1 (9 H). The infrared spectrum[22] showed a doublet at 1730 and 1755 cm^{-1} characteristic of glycidic esters. The mass spectrum showed a molecular ion at *m/e* 226 and abundant peaks at *m/e* 168, 81, 67, 57 (base peak), and 55.

Anal. Calcd for $C_{13}H_{22}O_3$: mol wt 226.15688. Found: mol wt, 266.15674 ± 0.00439.

Conversion of Methyl β,β-(γ-*t*-Butylpentamethylene)glycidate (VII and VIII, R = *t*-C_4H_9) into 4-*t*-Butyl-1-ethylcyclohexanol. Reduction of Ester.[25]—A solution of 664 mg (2.91 mmol) of VII and VIII (R = *t*-C_4H_9) in 2.0 ml of dry ether was added slowly at 0° to a slurry of 230 mg (6.07 mmol) of lithium aluminum hydride in 5 ml of ether. After the mixture had been stirred for 7 hr, wet ether followed by water was added. Ether extraction, drying, and concentration *in vacuo* generated 501 mg (86%) of an isomeric mixture of 1-(2-hydroxyethyl)-1-hydroxy-4-*t*-butylcyclohexane. A small portion of this material was recrystallized from carbon tetrachloride–hexane to give colorless needles, mp 102–102.5°. The infrared spectrum[18] showed broad hydroxyl absorption at 3400 cm^{-1} and a sharper peak at 3630 cm^{-1}. The nmr spectrum[19] possessed a triplet (2 H) at δ 3.89 (J = 6.0 Hz), a broad singlet (2 H) at δ 3.00, a triplet at δ 1.67 (J = 6.0 Hz) superimposed on a complex multiplet at δ 0.9–2.0 (total 11 H), and a singlet (9 H) at δ 0.87. The mass spectrum showed no molecular ion but showed weak M − 1^+ and M − 2^+ peaks as well as abundant peaks at *m/e* 107, 93, 91, 79, 69, 57 (base peak), 56, 55, 45, and 43.

Anal. Calcd for $C_{11}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.01; H, 12.08.

Conversion of Diol into Monotosylate.—The crude diol mixture (396 mg, 2.0 mmol) was dissolved in 4 ml of pyridine and cooled to 0° with stirring in a nitrogen atmosphere. Addition of 420 mg (2.2 mmol) of *p*-toluenesulfonyl chloride in 3 ml of pyridine proceeded dropwise. After the addition, stirring was continued for 1.5 hr at 0° and 1.5 hr at 25°. After the solution had been poured onto ice, an oil resulted. The mixture was extracted with ether and the ether was washed with dilute aqueous hydrochloric acid and then water. Subsequent drying over sodium sulfate and concentration *in vacuo* produced 663 mg of crude monotosylate product. The nmr spectrum[19] possessed an AB pattern with H_A at δ 7.78 and H_B at δ 7.35 (J_{AB} = 8 Hz) and a singlet at δ 2.42 for the tosylate moiety. The remaining protons appeared as a triplet (2 H, J = 7 Hz) at δ 4.23, a triplet (2 H, J = 7 Hz) at δ 1.77, a singlet (1 H) at δ 2.44, a multiplet (9 H)

(21) Silical gel (Merck) PF 254 was employed.

(22) Determined as a solution in carbon tetrachloride.

(23) Determined as a solution in ethanol.

(24) A 5 ft × 0.25 in. 20% SE-30 on Chromosorb P column was employed for this analysis.

(25) For similar reductions of glycidic esters, see H. M. Walborsky and C. Colombini, *J. Org. Chem.*, **27**, 2387 (1962); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 1042 (1952).

at δ 0.9–1.8, and a singlet (9 H) at δ 0.83. The product was not purified further.

Reduction of Monotosylate.—In a nitrogen atmosphere, a solution of 379 mg (1.1 mmol) of crude monotosylate in 3 ml of dry tetrahydrofuran was added dropwise to a stirred slurry of 900 mg (24 mmol) of lithium aluminum hydride in 10 ml of dry tetrahydrofuran. After the mixture had been stirred for 1 hr at room temperature and 3 hr at reflux, addition of ethyl acetate at 0° destroyed excess lithium aluminum hydride. The mixture was diluted with 100 ml of water and extracted with ether. Subsequent drying and concentration *in vacuo* produced 230 mg of crude oil. Vpc analysis[26] of the crude mixture showed two peaks in the ratio of 97:3. The shorter retention time peak (97% isomer) was identified as 1-ethyl-*trans*-4-*t*-butylcyclohexanol (IX) by comparison of retention time and infrared spectrum with that of an authentic sample. The longer retention time peak (3% isomer) was identified as 1-ethyl-*cis*-4-*t*-butylcyclohexanol (X) by comparison of vpc retention time with that of an authentic sample and physical properties and infrared spectral data with the published information.[13]

Reaction of Dimethylthetin Anion with Diisopropyl Ketone.—To a solution of 6.5 mmol of dimethylthetin anion was added 775 mg of diisopropyl ketone. The resulting suspension was stirred for 16 hr at room temperature; however, the suspension remained. It was poured onto ice and acidified to pH 1 with hydrochloric acid. Ether extraction followed by drying and diazomethane treatment produced an oil which exhibited three peaks on vpc.[27] The first peak (73%) was diisopropyl ketone. The second peak (12%) showed no carbonyl group in its infrared spectrum.[22] The nmr spectrum[22] exhibited a singlet (2 H) at δ 2.45, a multiplet (2 H) at δ 1.96, a doublet (6 H) at δ 0.90 (J = 6.5 Hz), and a doublet (6 H) at δ 0.85 (J = 6.5 Hz). From this data, the compound is tentatively identified as 1,2-epoxy-2-isopropyl-3-methylbutane (XI).

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.75; H, 12.56.

The third component (14%) showed ester carbonyl stretching absorption (1740 cm^{-1}) in its infrared spectrum.[22] The nmr spectrum[19] exhibited three singlets at δ 3.72, 3.18, and 2.20 in the ratio 3:2:3. These data identify this material as methyl methylthioacetate; comparison with an authentic sample confirmed the assignment.

(26) An 8 ft × 0.25 in. 20% diethylene glycol glutarate on Chromosorb P column was employed for this analysis.

(27) An 8 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column was employed for this analysis.

Registry No.—IIb, 23511-07-1; IIIb, 23511-06-0; V, 23511-08-2; VI, 23511-09-3; VII, 23511-10-6; VIII, 23511-11-7; XI, 23511-12-8; 1-(2-hydroxyethyl)-1-hydroxy-4-*t*-butylcyclohexane, 23511-13-9.

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The Stereochemistry of Electroreductions. III. Carbon–Oxygen Single Bonds[1]

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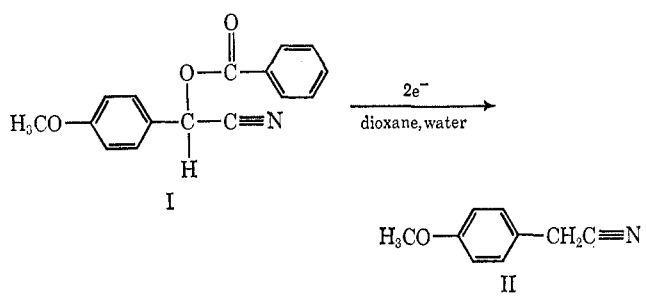
Optically active O-benzoylatrolactic acid and methyl O-benzoylatrolactate are reduced electrochemically to 2-phenylpropionic acid with almost complete loss of optical activity. This is in sharp contrast with the electroreduction of the related 2-chloro-2-phenylpropionic acid, which has been reported to undergo reduction with 77–92% inversion of configuration. The exact mechanisms of the two processes must differ.

Numerous workers have investigated aspects of carbon–halogen bond electroreductions. Lambert[2] has attempted a quantitative correlation between polarographic half-wave potentials and Taft polar and steric constants. Several papers have been concerned with the effect of structure on half-wave potentials[3] and mass electrolysis data.[4] Annino, *et al.*,[1] have examined the stereochemical nature of these reductions using cyclopropyl halide derivatives. They explained their results on the basis of the formation and subsequent breakdown of an intermediate electrode complex.

In contrast to carbon–halogen bond reductions, the electroreduction of carbon–oxygen single bonds has received little attention. Wawzonek and Fredericksen[5] examined several mandelonitriles and mandelonitrile esters polarographically and reduced I to II in good yield by mass electrolysis. Kabaskalian and



McGlotten reduced a series of hydroxy keto steroids polarographically and followed this study with several controlled potential mass electrolyses.[6]

We report in this paper on the stereochemistry of the electroreduction of atrolactic acid derivatives. The compounds were chosen for initial stereochemical study because (a) analogy with Wawzonek and Fred-

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