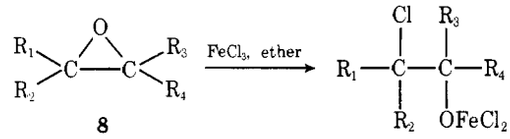
ization to diphenylacetaldehyde, even though an independent treatment of the expected chlorohydrin showed it to be stable under the reaction conditions. In this case, it is likely that the phenyl migration took place concertedly with the epoxide ring opening, or (less probably) from an organoiron derivative of the chlorohydrin itself.[9]

In all this work, we made no attempts to characterize the intermediate organoiron compounds produced in the reactions, which we formulate as **8** by analogy with the reaction of other metal halides with epoxides.[2]



8

Ether seemed to be the solvent of choice since **1** did not react with $FeCl_3$ in chlorobenzene, toluene, dimethyl sulfoxide, or when no solvent was used. In carbon tetrachloride, there was only 50% conversion after 25 min, while in acetonitrile the conversion was very slow, yielding 30% of **2** after 16 h. In methanol, the solvent participated in the reaction, and *Z*-**1** gave *threo*-3-methoxy-3-phenyllactate stereospecifically in 30% yield after 20 h. Under the same conditions, there was no reaction with the *E* isomer. Benzene gave mixed results: $FeCl_3$ is appreciably soluble in this solvent, and the conversion of *Z*-**1** to **2** took place readily with good stereoselectivity (66% threo). However, **4** did not yield any chlorohydrins in these conditions, and instead isomerized quantitatively into 2-methylcyclohexanone, a reaction reminiscent of that described with $MgBr_2$ in ether.[5]

The high solubility of $FeCl_3$ in ether containing hydrogen chloride has been used for the selective extraction of this salt from aqueous solutions,[10] and the crystalline mono- and dietherates of $HFeCl_4$ were prepared from such ether solutions.[11] Similarly, the preparation of a mono-[11,12] and a dietherate[11] of $FeCl_3$ itself has been claimed, but the physical properties of these compounds were barely described. However, the monoetherate obtained by concentration of a solution of $FeCl_3$ in ether was reported to be soluble in benzene.[12] We therefore attempted to use such a solution for preparing **2** from **1**. Here the conversion took place smoothly at room temperature, but without stereoselectivity.

The reaction of **4** with ferric chloride etherate in benzene yielded a mixture of the isomeric 1-methylcyclopentanecarboxaldehyde (33%) and 2-methylcyclohexanone (66%), while it gave a mixture of the chlorohydrin (50%), the aldehyde (26%), and the ketone (24%) with ferric chloride etherate in carbon tetrachloride.

We also observed that benzene provided no improvement over ether in the reaction of **7** with ferric chloride etherate. Complete rearrangement to diphenylacetaldehyde also took place.

Finally, the superior solvent power of isopropyl ether over ethyl ether for $FeCl_3$[12] suggested the use of that solvent as a possible improvement in the procedure. However, when treated with $FeCl_3$ in isopropyl ether, *Z*-**1** could be recovered quantitatively.

In conclusion, although $FeCl_3$ or its etherate(s) may be occasionaly used in other solvents, no combination proved superior to $FeCl_3$ in ether, which is a very convenient, if not general, reagent for synthesizing chlorohydrins from epoxides.[14]

Experimental Section

Representative Reaction of an Epoxide with Ferric Chloride in Ether. Anhydrous $FeCl_3$ (150 mg, 0.73 mmol) was dissolved in 50 ml of anhydrous ether. The reaction was exothermic, and produced an orange solution, to which 150 mg (0.73 mmol) of **1** was added. After 2 min of stirring, the green-black solution was diluted with 25 ml of ether and washed with two 50-ml portions of water. The aqueous extracts were combined and extracted with 50 ml of ether. The combined ether extracts were dried over $MgSO_4$ and concentrated under vacuum, and yielded 145 mg (0.60 mmol, 82% yield) of a slightly yellow liquid which crystallized slowly. The solid melted at 45–70 °C: mass spectrum *m/e* 242 (M^+), 206, 190, 11/, 116, 115, 105, and 91; NMR ($CDCl_3$) 1.15 (t, J = 7 Hz, 3 H), 1.60 (s, 3 H), 4.05 (q, J = 7 Hz, 2 H), and 5.07 ppm (s, 1 H) for the erythro (22.5%), and 1.18 (s, 3), 1.32 (t, J = 7 Hz, 3 H), 4.30 (q, J = 7 Hz, 2 H), and 5.12 ppm (s, 1 H) for the threo isomer (77.5%). The aromatic signals were centered at 7.32 ppm (m, 5 H), and the hydroxyls at 3.30 ppm (disappearing in the presence of D_2O) for both diastereoisomers.[18]

Registry No.—*E*-**1**, 7141-24-4; *z*-**1**, 7042-28-6; *threo*-**2**, 59069-85-1; *erythro*-**2**, 59069-84-0; $FeCl_3$, 7705-08-0.

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(6) The synthesis of both chlorohydrins was described by H. Bodot, J. Jullien, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 1097 (1958). The trans isomer obtained by reaction of **4** with HCl in ether was believed to contain 45% of the cis isomer. This came from rate studies in the reaction of this product with base, assumed to convert the trans isomer quantitatively into **4**. Our GLC analysis showed the product of the HCl treatment to be pure trans, but its complete conversion into **4** in the presence of base was more sluggish than anticipated, thereby accounting for the discrepancy. The synthesis of the cis isomer was accomplished by these authors by reducing 2-chloro-2-methylcyclohexanone with $LiAlH_4$. We did not repeat this reaction and cannot confirm whether 19% of the trans isomer was indeed formed along with the cis chlorohydrin which melted at 19 °C. The reduction with $NaBH_4$ in ethanol yielded the cis isomer which contained ca. 7% of trans (GLC analysis), but the dehydrochlorination of this cis isomer (mostly to 2-methylcyclohexanone) took place at an appreciable rate under the published conditions, thus also invalidating this type of analysis. Our recrystallized cis chlorohydrin melted at 27 °C.
(7) We encountered some difficulties in the characterization of one of the chlorohydrins. Although pure by all spectroscopic criteria, it melted sharply at 90 °C, when 72 and 107 °C are the values reported for the two diastereoisomeric 1-benzoyl-2-chloro-2-phenylethanols.[8a] We later found that 90 °C was the melting point for a different crystalline modification of the compound which usually melts at 107 °C.
(8) (a) H. O. House, *J. Org. Chem.*, **21**, 1306 (1956); (b) *J. Am. Chem. Soc.*, **76**, 1235 (1954), and references cite, therein.
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(14) It is interesting to mention three other recent reports where $FeCl_3$ was also used for cleaving ethers. In one[15] $FeCl_3$ in acetic anhydride was shown to convert ethers into a mixture of acetates, while in the other $FeCl_3$ in dimethylformamide cleaved and oxidized the trimethylsilyl ethers of bicyclic cyclopropanols into β-chloro ketones.[16] Finally, the poorly defined $FeCl_3$–*n*-BuLi system was shown to deoxygenate epoxides into olefins.[17]
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(18) Our limited experience suggests that it is not necessary to have complete solution of the $FeCl_3$ in ether prior to its reaction with an epoxide. The reagent dissolves rapidly as the reaction proceeds, and the total volume of solvent necessary for larger scale reactions may therefore be kept small.

Synthesis of 5-(*tert*-Alkyl)resorcinols

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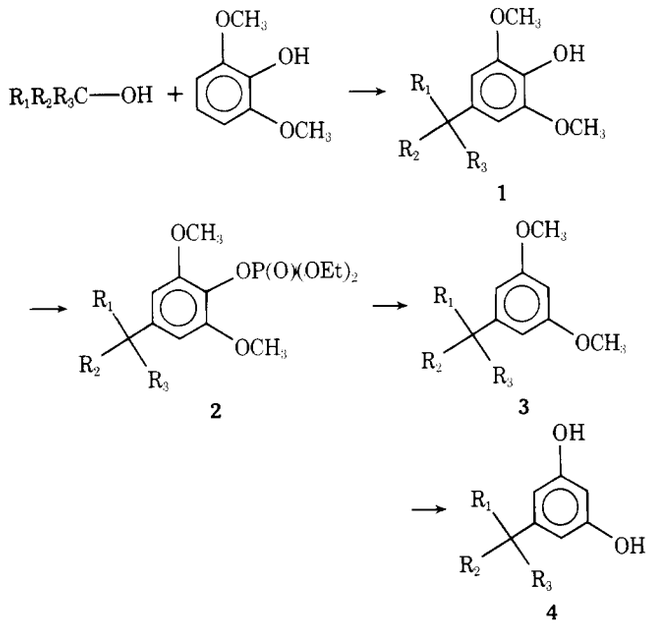
In connection with other work underway in these laboratories, a short and efficient method for the preparation of large

quantities of 5-(1,1-dimethylheptyl)resorcinol was required. Previous syntheses of this material, from 3,5-dimethoxybenzyl cyanide[1] and 3,5-dimethoxybenzonitrile,[2] have been devised but are somewhat lengthy and require relatively expensive starting materials. In recent years, numerous syntheses of 5-alkylresorcinols have appeared[3-12] but almost without exception these are applicable to the preparation of normal alkyl resorcinols only. A preparation of 5-*tert*-butylresorcinol has also appeared.[13]

Our synthesis is based upon the finding that alkylation of 2,6-dimethoxyphenol with tertiary carbonium ion precursors occurs predominantly, if not exclusively, para to the hydroxyl group. Thus, treatment of the dimethoxyphenol with 1,1-dimethyl-*n*-hexylcarbinol in methanesulfonic acid at 50 °C afforded a 98% crude yield of 5-(1,1-dimethylheptyl)-2,6-dimethoxyphenol which, without further purification,[14] was converted to a crystalline phosphate ester with diethyl phosphonate, carbon tetrachloride, and triethylamine in 75% yield. Treatment with Li/NH_3,[15] followed by demethylation of the product with boron tribromide, provided the crystalline resorcinol in 50–60% yield. The sequence has been successfully



carried out on a scale of several hundred grams with comparable yields, and has been applied to the preparation of some new resorcinols (see Table I, **4a–f**).

As can be seen from Table I, yields are generally excellent except for the last (demethylation) step. Boron tribromide was found to be the reagent of choice, other reagents (e.g., pyridine hydrochloride, methylmagnesium iodide) giving substantially poorer results. The alkylation step (i.e., preparation of **1**) could only be accomplished in high yield with sulfuric acid, but methanesulfonic acid gave cleaner reactions and easier purifications. Attempts to alkylate 2,6-dimethoxyphenol with oxygenated carbinols, e.g., $EtO(CH_2)_2C(CH_3)_2OH$, gave only decomposition products.

Experimental Section

Melting points are uncorrected. Chromatographic purifications were performed on columns of Woelm silica gel, activity 1. The tertiary carbinols were prepared and purified by standard methods. A representative procedure follows.

4-(1′,1′-Dimethylheptyl)-2,6-dimethoxyphenol (1a). A mixture of 15.4 g (0.10 mol) of 1,1-dimethyl-1-heptanol, 15.49 (0.10 mol) of 2,6-dimethoxyphenol, and 20 ml of technical methanesulfonic acid was stirred at 50 °C for 3 h and then at room temperature overnight. The mixture was poured onto ice and extracted with methylene chloride. The extracts were washed with H_2O and saturated $NaHCO_3$, dried ($MgSO_4$), and evaporated to afford 27.4 g (98%) of an oil used directly in the next step.

Table I

Compd	R_1	R_2	R_3	% yields[a] 1	2	3	4
a	CH_3	CH_3	n-C_6H_{13}	98	70	95	85
b	CH_3	CH_3	C_6H_5	98	98	86	67[b]
c	CH_3	CH_3		92	74	87	60[b]
d	CH_3	C_6H_5	n-C_6H_{13}	99	75	92	45[b]
e	CH_3	CH_3		98	76	92	17[b]
f				85	100	85	70

[a] Crude yields; purified yields generally 10–15% lower. [b] After chromatography.

4-(1′,1′-Dimethylheptyl)-2,6-dimethoxyphenyl Diethylphosphate (2a). A solution of 35.9 g (0.128 mol) of crude **1a** in 20 ml of CCl_4 was stirred and cooled in an ice bath. Diethyl phosphonate (19.4 ml, 0.15 mol) was added, followed by dropwise addition of 20.8 ml (15.2 g, 0.15 mol) of triethylamine. The mixture was stirred at 0 °C for 1 h and then at room temperature overnight. The mixture was then diluted with 20 ml of methylene chloride, washed (H_2O, 4 N NaOH, H_2O, 1 N HCl, H_2O, saturated NaCl), filtered to remove a trace of solid, and dried ($MgSO_4$). Removal of the solvent provided a residue which upon crystallization from 100 ml of *n*-hexane afforded 37.0 g (70%) of needles: mp 61–64 °C; NMR ($CDCl_3$) δ 6.55 (s, 2 H), 4.30 (2 q, 4 H), 3.85 (s, 6 H), 1.4 (t, 6 H), 1.25 (s, 6 H), 1.8–0.5 (m, 13 H).

1-(1′,1′-Dimethylheptyl)-3,5-dimethoxybenzene (3a). A solution of 36.5 g (0.09 mol) of **2a** in 75 ml of Et_2O and 15 ml of THF was added dropwise to 200 ml of NH_3 as a total of 1.25 g (0.18 g-atom) of Li metal was added at a rate to maintain a blue color. After 1 h, excess Li was destroyed with NH_4Cl, the mixture was diluted with 100 ml of Et_2O, and the NH_3 was allowed to evaporate. The mixture was treated with H_2O and the layers separated. The Et_2O layer was washed (4 N, NaOH, H_2O, saturated NaCl), dried ($MgSO_4$), and evaporated to afford 22.1 g (95.4%) of **3a** as an oil which was purified chromatographically: NMR ($CDCl_3$) δ 6.45 (d, 2 H), 6.25 (t, 1 H), 3.75 (s, 6 H), 1.25 (s, 6 H), 1.8–0.5 (m, 13 H).

5-(1′,1′-Dimethylheptyl)resorcinol (4a). A solution of 26.4 g (0.10 mol) of **3a** in 100 ml of methylene chloride was added dropwise to a stirred, cold (ice bath) solution of 62.5 g (0.25 mol) of boron tribromide in 200 ml of methylene chloride over 1 h. The reaction mixture was then stirred at 0 °C for 2 h and allowed to warm to room temperature overnight. The mixture was then recooled to 0 °C and cautiously treated dropwise with H_2O (200 ml). The organic layer was separated and extracted thoroughly with 2 N NaOH. The NaOH extracts were acidified with 1 N HCl and the mixture extracted with Et_2O. The combined Et_2O extracts were washed with saturated NaCl, dried, and evaporated to provide 20.2 g (85%) of **4a:** mp 97–99 °C; NMR ($CDCl_3$) δ 6.35 (d, 2 H), 6.15 (t, 1 H), 5.2 (bs, 2 H, exchanges with D_2O), 1.20 (s, 6 H), 1.8–0.5 (m, 13 H).

Other resorcinols prepared: **4b,** mp 108–110 °C (C_6H_6–Skelly B); **4c,** mp 145–147 °C (EtOAc–hexane); **4d,** oil (purified by chromatography); **4e,** mp 125–127 °C (C_6H_6–Skelly B); **4f,** mp 284–285 °C (toluene–EtOAc).

Registry No.—**1a,** 60526-69-4; **1b,** 60526-70-7; **1c,** 60526-71-8; **1d,** 60526-72-9; **1e,** 60526-73-0; **1f,** 60526-74-1; **2a,** 60526-75-2; **2b,** 60526-76-3; **2c,** 60526-77-4; **2d,** 60526-78-5; **2e,** 60526-79-6; **2f,** 60526-80-9; **3a,** 60526-81-0; **3b,** 60526-82-1; **3c,** 60526-83-2; **3d,** 60526-84-3; **3e,** 60526-85-4; **3f,** 60526-86-5; **4a,** 56469-10-4; **4b,** 60526-87-6; **4c,** 60526-88-7; **4d,** 60526-89-8; **4e,** 60526-90-1; **4f,** 60526-91-2; 1,1-dimethyl-1-heptanol, 628-44-4; α,α-dimethylbenzenemethanol, 617-94-7; α,α-dimethylcyclohexanemethanol, 16664-07-6; α-hexyl-α-methylbenzenemethanol, 7252-61-1; α,α-dimethyltricyclo[3.3.1.1^{3,7}]decane-1-methanol, 775-64-4; tricyclo[3.3.1.1^{3,7}]decan-1-ol, 768-95-6; 2,6-dimethoxyphenol, 91-10-1.

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Generation of the Trans Enolate of Chloroacetaldehyde via a β-Oxido Carbenoid

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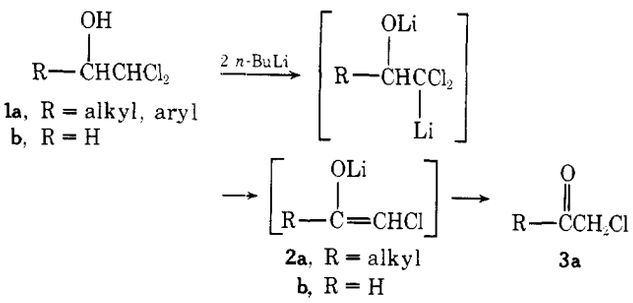
On treatment with 2 equiv of *n*-butyllithium, 1-substituted 2,2-dichloroethanols **1a** and related species undergo rearrangement via β-oxido carbenoids to afford ketones **3a** in high



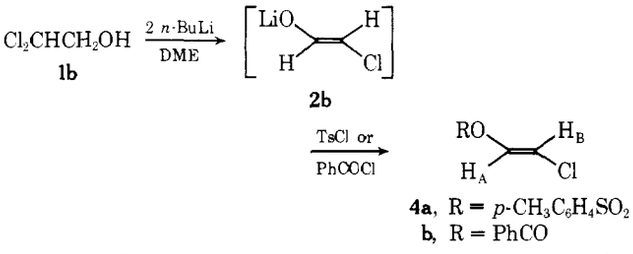
1a, R = alkyl, aryl
b, R = H

2a, R = alkyl
b, R = H

3a

yields.[1] Although the chemistry of β-oxido carbenoids has been intensively investigated by us[2] and others,[3] the stereochemistry of the double bond of the enolate anion **2** has not been elucidated. Investigation of the reaction of the parent compound, 2,2-dichloroethanol (**1b**), would give us not only information about the stereochemical outcome of this rearrangement, but also a way for the preparation of chloroacetaldehyde enolate (**2b**), a previously unknown enolate species.

We have found that 2 equiv of *n*-butyllithium effects rearrangement of 2,2-dichloroethanol (**1b**)[4] at −78 °C to give the lithium enolate of chloroacetaldehyde (**2b**). This enolate is subsequently allowed to react with *p*-toluenesulfonyl chloride and is isolated as the O-tosylated derivative **4a** in 86%



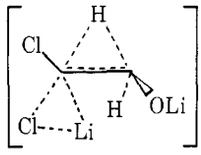
1b

2b

4a, R = *p*-$CH_3C_6H_4SO_2$
b, R = PhCO

yield. In addition, this rearrangement reaction gives exclusively the *E* isomer of the enol tosylate **4a** (vide infra). Although alcohols **1a** react rapidly (−50 °C, 30 min) with *n*-butyllithium,[2b] less than half of 2,2-dichloroethanol (**1b**) was consumed under the same conditions. At a higher temperature (−20 °C, 2 h) the yield of the enol tosylate **4a** was reduced to 58%, yet under the optimum conditions (−78 °C, 5 h), it reached the highest value of 86%. It is interesting that the enolate **2b** gives the O-tosylated derivative in high yield, and as a single isolable product, since the reaction of an enolate anion with arenesulfonyl chloride has long been known to afford mainly chlorinated products instead of sulfonylated products.[5]

In order to establish the stereochemistry of the enolate **2b**, the enolate **2b** was transformed to the corresponding enol benzoate **4b**, since a reliable stereochemical assignment by NMR spectroscopy is possible with enol ester derivatives.[6] The enolate **2b** generated in DME was treated with benzoyl chloride to give the expected enol benzoate **4b** in 56% yield. On NMR analysis the benzoate **4b** exhibited the same value of the coupling constant as the tosylate **4a**, i.e., J_{AB} = 11 Hz. A coupling constant between two vicinal protons attached to a disubstituted double bond is known to be closely related to the electronegativity of the substituents, and its magnitude is greatly reduced by both acyloxy and chloro groups.[6] Therefore, the value (J_{AB} = 11 Hz) of the enol benzoate **4b** should point out an *E* geometry of the double bond, and at the same time, the same geometry of the double bond of the lithium enolate **2b**.[7] With respect to the stereochemistry of the enolate **2b**, reactions at temperatures ranging from −100 to −20 °C uniformly gave the same result. An electronic repulsion in the transition state **6** is most likely the reason of the stereospecificity of this rearrangement.



6

Experimental Section

General. Melting points, which were determined in glass capillaries, and boiling points are uncorrected. Infrared spectra were obtained on a Hitachi EPI G3 spectrometer. NMR spectra were determined on a Varian Associates Model T-60 spectrometer and the chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra were determined on a Hitachi RMU-7M spectrometer at Mass Spectral Laboratory, Tokyo Institute of Technology. Microanalyses were performed at Microanalytical Laboratory, Tokyo Institute of Technology.

(*E*)-2-Chloroethenyl 4-Toluenesulfonate (4a). 2,2-Dichloroethanol (114 mg, 1.00 mmol) in 5 ml of DME was treated with 1.55 M *n*-butyllithium in hexane (1.42 ml, 2.20 mmol) at −78 °C for 5 h. The resulting white suspension was treated with 197 mg of *p*-toluenesulfonyl chloride (1.00 mmol) dissolved in 2 ml of DME at −78 °C for 30 min and for 1 h at room temperature. The white reaction mixture was poured into 10 ml of water, and extracted with ether (10 ml × 3). The ethereal extract was dried ($MgSO_4$) and concentrated in vacuo to leave a yellow oil, which was homogeneous on TLC (R_f 0.45, benzene) and NMR analysis. Purification by preparative TLC gave the title tosylate **4a** (202 mg, 86%): bp 95–100 °C (bath temperature, 0.014 mm); ir (neat) 1600 (m), 1380 (s), 1195 (s), 1180 (s), 1070 (s), 890 cm^{-1} (m); NMR (CCl_4) δ 2.45 (s, 3 H, CH_3–), 6.00 (d, J = 11 Hz, 1 H, ClCH=C), 6.75 (d, J = 11 Hz, 1 H, OCH=C), 7.30 (unresolved d, J = 8 Hz, 2 H, aromatic protons ortho to methyl group), 7.70 (unresolved d, J = 8 Hz, 2 H, aromatic protons meta to methyl group); mass spectrum (70 eV) *m/e* (rel intensity) 232 and 234 ($M^{\cdot+}$), 155 (23), 91 (100), 65 (59), 63 (23), 51 (20), 49 (24), 39 (30).

Anal. Calcd for $C_9H_9O_3ClS$: C, 46.46; H, 3.90; S, 13.78. Found: C, 46.35; H, 3.95; S, 13.69.

1-Benzoyloxy-2-chloro-(*E*)-ethene (4b). The DME (8 ml) solution of the lithium enolate **2b** which was prepared in the same manner as described above using 177 mg of 2,2-dichloroethanol (1.55 mmol) and 1.42 M *n*-butyllithium (2.18 ml, 3.10 mmol) was treated