Addition of 2-Methyl-1,3-cyclopentanedione to Vinyl Ketone 17 (→18). Sulfide **15** (954 mg, 2 mmol) was converted to sulfoxide **16** and the latter rearranged as above to the mixture of **17** and **3**. This, in turn, was dissolved in 10 ml of toluene and 1 ml of pyridine and 250 mg (2.2 mmol) of 2-methyl-1,3-cyclopentanedione was added; the resulting solution was stirred at 100° for 48 h under argon. After removal of solvent in vacuo, the residue was triturated with cold methylene chloride and unreacted dione was recovered by filtration. Florisil chromatography of the filtrate, with gradient elution employing ether–hexane mixtures, eventually afforded 479 mg (52%) of **18**, which was further purified for analysis by "kugelrohr" distillation (210 °C (0.01 Torr)): ir (neat) 1750, 1730, 1720, 1262, 1183, 860, 784, and 700 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.25 (t, J = 7 Hz, 6 H), 1.83 (t, J = 6 Hz, 2 H), 2.37 (t, J = 6 Hz, 2 H), 2.77 (s, 4 H), 2.88 (s, 2 H), 3.33 (s, 2 H), 3.75 (s, 3 H), 4.18 (q, J = 7 Hz, 4 H), and 6.5–7.3 (complex m, 4 H).

Anal: ($C_{25}H_{32}O_8$) C, H.

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(11) For example, 1-chloro-3-phenylsulfinylcyclohexene and 4-chloro-2-phenylsulfinyl-3-heptene begin to rearrange *while* the precursor sulfides are being oxidized (*m*-chloroperbenzoic acid in CH_2Cl_2 at 0°), and they are approximately half converted to ketones (ir) within 30 min after careful, low-temperature workup. In contrast, 2-chloro-3-phenylsulfinylcyclohexene is readily prepared and handled without apparent change (unpublished observations by L. P. Sendlak).
(12) It is not unreasonable to assume that once an α-chloro sulfenate is produced its fragments *intramolecularly* without reverting to sulfoxide, although we have no evidence bearing on this point. Even *intermolecular* trapping of allylic sulfenates by external thiophiles can effectively prevent their return to sulfoxides (ref 5).
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(14) **4**, as we generate it (ref 22), contains ca. 5–10% of the unremovable *E* isomer, which is carried along in forming **5**, **6**, 11, **12**, etc. However, enones **8** and **17** have no geometric isomerism relatable to chloroalkene double-bond geometry. The latter stereochemistry is probably unimportant in produce configuration about the enone double bond, which is generally trans. Indeed, double-bond geometry has been "inverted" by two sequential sulfoxide–sulfenate rearrangements, during prostaglandin synthesis (cf. K. G. Untch, G. Stork, et al., *J. Am. Chem. Soc.*, **96**, 6774 (1974)).
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Molecular Rearrangements with Ethoxycarbonyl Group Migrations. 1. The Rearrangement of Epoxides

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Abstract: A superficial analysis of the reaction products for the boron trifluoride catalyzed isomerization of 2-substituted-3-phenyl-3-methylglycidates led to an acceptable sequence of migratory aptitudes, phenyl > ethyl and ethoxycarbonyl > methyl and hydrogen. However, its predictive value was nil, since the actual course of most rearrangement reactions was dependent on the temperature as well as on the solvent used. With **1h**, **1m**, and **1e**, the products formed with lowest activation energy were the allylic alcohols **4**, and next the α-keto esters **2**. The β-keto esters **3**, which were the most stable products, required the highest activation energy for their formation. This appears to be the first study of the effect of the temperature on the course of a pinacol-like rearrangement, and leads to the hope that in many cases it will be possible to achieve a selective control of the products formed in a competitive set of rearrangements by the proper selection of the solvent and reaction temperature.

Introduction

Several years ago, we observed the unexpected acid-catalyzed rearrangement of glycidic esters with ethoxycarbonyl group migration, which yielded β-keto esters rather than pyruvic esters which were then anticipated.[1] The novelty of this rearrangement encouraged us to pursue a study in this area, and we now wish to describe the results of this work.

Our initial observations of the ethoxycarbonyl group migration in epoxide rearrangements were made with a series of glycidic esters which did not all have the same substituents at the 3 position, the initial site of carbonium ion formation, and the sequence of migratory aptitudes established then was therefore questionable. The esters **1** were subsequently examined because the substitution at the 3 position theoretically favored the initial formation of a stabilized tertiary, benzylic,

Table I. Product Distribution in the Treatment of **1h** with BF_3

Solvent	Conditions, g/ml	Temp, °C	Time, min	Polymer, %	% volatile products[a] 2h	3h	4h
CCl_4	0.2/5	−50 to −30	15[b]	35	8	0	92
C_6H_6	10/150	−20	5	77	11	33	56
C_6H_6	0.2/5	0	5	76	6	2	92
CCl_4	0.2/5	20	5	33	11	44	45
CCl_4	0.5/10	20	5	63	20	37	43
CCl_4	0.5/300	20	5	84	15	64	21
C_6H_6	0.2/5	20	5	65	11	57	32
CCl_4	0.2/5	60	5	60	11	89	tr
CCl_4	10/150	60	5	67	11	87	2
CCl_4	0.5/300	60	5	79	16	84	0
CCl_4	0.5/10	60	3	56	19	77	4
C_6H_6	0.2/5	60	5	70	4	87	9

[a] The small amount of acetophenone usually present was neglected. [b] 48% of **1h** remained unreacted.

carbonium ion, and the relative ease of migration of the two groups attached to the same atom at the 2 position, R and $COOC_2H_5$, would be directly obtained from the analysis of the major reaction products.

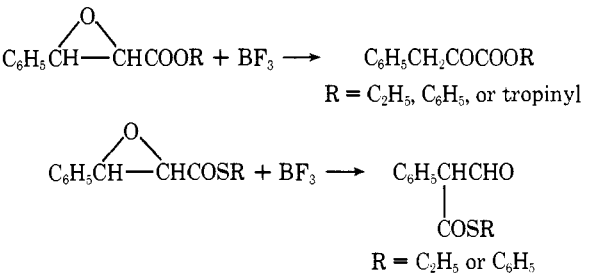
Boron trifluoride in carbon tetrachloride, which gave clean reactions at room temperature, was used throughout. Benzene was also used as solvent in the early experiments, but Friedel-Crafts reaction of the initially formed cations with benzene was occasionally encountered, and thus lowered the yield of rearrangement products. Another type of solvent participation was observed in the reaction of **1h** with BF_3 in acetic acid, which yielded the acetate of the allylic alcohol **4h** in pure form.

The general sequence of migratory aptitudes developed earlier was confirmed. The ethyl group, which had not been studied before, was found to migrate approximately as well as the ethoxycarbonyl, and the sequence derived from these experiments was therefore $C_6H_6 > C_2H_5$ and $COOC_2H_5 > CH_3$ and H. As we shall see, however, such a sequence is a poor representation of the reactions actually encountered, which depend not only on the nature of the acid, but also on the solvent and the reaction temperature.

Results

The qualitative relationship between the nature of the ester moiety and its migratory aptitude was not thoroughly examined. Wemple[2] has studied 3-phenylglycidic thioesters, and convincingly reported on the superior migratory aptitude of the phenylthiocarbonyl and ethylthiocarbonyl groups over hydrogen in these compounds, a very interesting finding in relation to the problem of the biosynthesis of tropic acid. We found, however, that the phenyl and tropinyl esters behaved like the ethyl esters, and that no ester migration took place in these 3-phenylglycidates, which only yielded the pyruvic esters resulting from hydrogen migration from the 2 to 3 position. We also determined that ethyl 2-formylphenylacetate, the product which would have been formed by ethoxycarbonyl migration, was stable under the reaction conditions and therefore could not have been an intermediate in the observed transformation. (Actually, it is the conversion of α-keto to β-keto esters which is known to take place,[3] rather than the reverse.) The behavior of the 3-phenylglycidate is thus different from that of 3-methyl-3-phenylglycidates, which we will now describe in greater detail.

The treatment of **1f** with boron trifluoride yielded a single product **2f,** resulting from phenyl migration. In contrast, the treatment of **1h** yielded a mixture of products which was difficult to analyze by NMR because of the overlapping signals. The signals for the aldehyde **3h** were quite conspicuous because



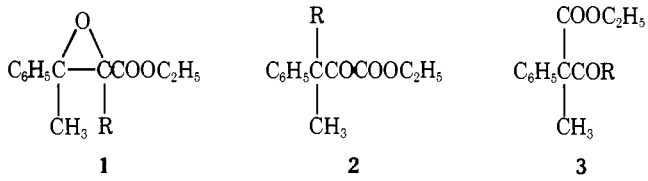
of the lack of coupling, but this was not the major product at room temperature or below, and GLC analysis revealed that the product distribution varied with the temperature. As seen in Table I, the effect of the temperature alone on the course of the epoxide rearrangement was dramatic, providing control toward the synthesis of either the allylic alcohol **4h** at low temperature, or the product of rearrangement with ethoxycarbonyl migration **3h** at higher temperatures. The pyruvic ester **2h** was found to be stable to boron trifluoride and not to isomerize under these conditions. However, some autoxidation to acetophenone was always observed.

We already reported on the rearrangement of **4h** to **2h,** catalyzed by hydrogen chloride,[4] but we also studied the reaction in the presence of boron trifluoride in carbon tetrachloride. The treatment of **4h** for 5 min at room temperature gave a mixture of 12% of **2h,** 10% of **3h,** and 78% of unreacted starting material, corresponding to 55% of **2h** and 45% of **3h** in the converted fraction. Similarly, there was 36% conversion to 36% of **2h** and 64% of **3h** after 5 min at 60°. In both cases, therefore, the α-keto ester was formed to a much greater extent than in the direct reactions with **1h,** showing that **4h** was not an obligatory precursor to **3h** in these conditions.

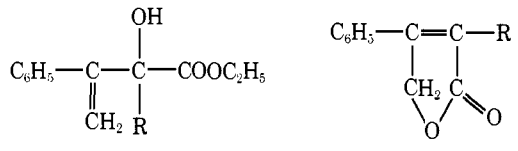
The favored formation of **4h** under mild conditions was further evidenced in reactions utilizing boron trifluoride etherate, a weaker Lewis acid. With this reagent in ether at room temperature, **1h** was converted in a slow reaction to a mixture of 16% of **2h,** 2% of **3h,** and 82% of **4h,** almost twice as much of this last product as in the reaction in carbon tetrachloride. In acetic acid, finally, the allylic alcohol was the only product, in the form of its acetate.

Although we have described the analysis of the volatile reaction products, the reaction of **1h** with boron trifluoride always yielded variable amounts of polymeric materials, ranging in yield between 33 and 84% (Table I). The reaction of boron trifluoride with **1h** was quite exothermic, and usually produced an oil insoluble in carbon tetrachloride or benzene (but soluble in ether). This heterogeneity probably explains the observed variations in the extent of polymerization.

The boron trifluoride treatment of **1m** yielded three prod-



1 2 3



4 5

h, R = H
m, R = CH_3
e, R = C_2H_5
f, R = C_6H_5

ucts, **2m** (2%) formed by methyl migration from the 2 to the 3 position, **3m** (83%) formed by migration of either the ethoxycarbonyl to the 3 position or that of the phenyl to the 2 position, and the allylic alcohol **4m** (15%). The ambiguity concerning the mechanism of the rearrangement of **1m** to the main product **3m** was removed by labeling the starting material with deuterium, as well as with carbon-14. Both compounds were obtained by a Darzens condensation reaction of ethyl 2-bromopropionate with a labeled acetophenone. In the first case the methyl hydrogens were exchanged for deuterium in deuterium oxide in the presence of sodium carbonate. In the second case, the required acetophenone was made by Friedel-Crafts condensation of benzene with acetic-*1*-^{14}C acid. The rearrangement of these labeled glycidic esters gave labeled **3m**. NMR and mass spectroscopic analysis of the product showed that deuterium resided exclusively at the acetyl site. Base-catalyzed deacetylation of the radioactive rearrangement product proved unequivocally that the label was exclusively in the phenylpropionic acid moiety (Scheme I), and that the rearrangement of **1m** had therefore proceeded with ethoxycarbonyl rather than methyl group migration.[5]

A temperature effect was observed, and the allylic alcohol was about twice as abundant at −20° as it was at 25 or 70°. At the highest temperature a new minor product was observed, the unsaturated lactone **5m**. A solvent effect was also observed, and the pyruvic ester **2m** was not detected when the rearrangement was performed near 25° in chloroform rather than in carbon tetrachloride (Table II).

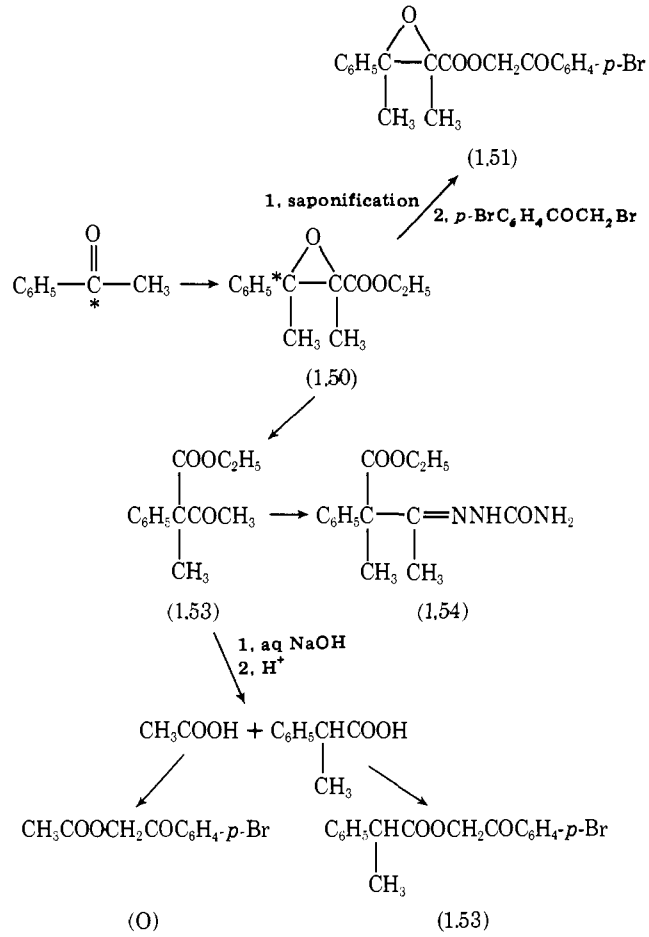
The allylic alcohol **4m**, which was a major product at low temperature, was found to rearrange into the other reaction products under the reaction conditions, as shown in Table III.

The difference observed in the product distribution at the higher temperatures when the glycidic ester **1m** and the allylic alcohol **4m** were treated with boron trifluoride clearly showed that independent pathways were available for the formation of **4m** on the one hand and the ketonic products on the other, and that **4m** was not a necessary precursor of **2m** and **3m**.

The behavior of **1e** in the presence of boron trifluoride was similar to that of **1m**, but the effect of the temperature on the migratory aptitudes was even more striking. Thus, the product of ethyl group migration was isolated in 62% yield after reaction at −15°, whereas it was the product of ethoxycarbonyl group migration which was formed in 69% yield at 60° (Table IV). Here again, the allylic alcohol did rearrange under the reaction conditions, but gave a product distribution quite different from that observed in the direct rearrangement reaction of the glycidic ester (Table IV).

The ketonic products formed above were found to be stable in the conditions of the rearrangement reactions, and the difference in product composition observed at different temperatures did not result from the subsequent acid-catalyzed

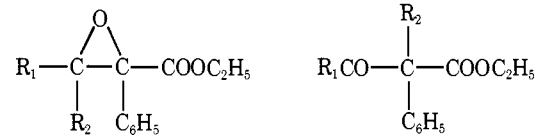
Scheme I. Degradation of the Rearrangement Product from **1m**-*3*-^{14}C, with Specific Activities in μCi/mmol



isomerization of a product of kinetic control, a situation which contrasts greatly with the pinacol rearrangements, which gave different product compositions at different temperatures, but which were proved to involve the interconversion of carbonyl compounds.[6]

A solvent effect was also observed in the reaction of **1e** with boron trifluoride, as shown in Table V, where one noteworthy feature is the lower extent of the ethoxycarbonyl group migration taking place in carbon tetrachloride, as compared to the other solvents.

The rearrangement of glycidic esters having the phenyl group at the 2 position showed that the formation of a benzylic cation was preferred over that of a primary or secondary alkyl cation, but not over that of a tertiary alkyl cation. Thus, the β-keto esters **7p** and **3m** were obtained from **6p** and **6s**, re-



6 7

p, $R_1 = R_2 = H$
s, $R_1 = H$, $R_2 = CH_3$
t, $R_1 = R_2 = CH_3$

spectively, but it was the pyruvic ester **2m** which was formed from **6t**. No allylic alcohols were observed in these transformations.

The result of the acid-catalyzed isomerization of **6t** with exclusive phenyl group migration was somewhat different from that previously described with the corresponding glycidic acid,[7] where we had found a competition between the formation of

Table II. Product Distribution (%) in the BF_3-Catalyzed Rearrangement of **1m**[a]

Solvent	Temp, °C	2m	3m	4m	5m
CCl_4	−20	4	58	38	0
CCl_4	28	2	83	15	0
CCl_4	70	2	78	16.5	3.5
$CHCl_3$	25	0	92	8	0
$CHCl_3$	−50[b]	5	76	18	0
$CHCl_3$	−50[c]	7	67	26	0

[a] *E* and *Z*; reaction time 10 min. [b] Trans isomer. [c] Cis isomer.

Table III. Product Distribution in the BF_3-Catalyzed Rearrangement of **4m** in CCl_4 for 10 Min

Temp, °C	2m	3m	4m	5m
−20	Trace	19	81	0
28	Trace	38	51	11
60	Trace	41	42	16

the tertiary alkyl cation and that of the benzylic cation, and from Wemple's latest results, which indicate an epoxide ring opening at the 3 position and competitive migration of the phenyl and thioester groups to that position in the corresponding phenylthio ester.[8] It appears likely now that the outcome of the rearrangement reaction might be affected by the experimental conditions, but this remains to be investigated.

A detailed study of the behavior of each diastereoisomer remains to be performed for several of the compounds herein reported. We note, however, that a single product was obtained from diastereoisomeric mixtures of **1f** and **6s**, and that only a very small difference in product composition was noticed when the diastereoisomers of **1m** were rearranged at −50°. Whether this difference was due to unequal intrinsic reactivities or slightly different experimental conditions remains to be determined. However, we also observed the pure diastereoisomeric glyceric esters corresponding to **1h** and **1m** to give identical products when treated with fluorosulfonic acid.[9] This lack of stereospecificity, the formation of the allylic alcohols **4** and their conversion into **2** and **3**, and the Friedel-Crafts condensation reactions in aromatic solvents were all in support of a mechanism in which an electron deficient character is developing at the 3 position. The timing of the subsequent steps relative to the breaking of this carbon-oxygen bond may be expected to depend both on the structure of the starting material and the experimental conditions, such as temperature and solvent. During the final preparation of this manuscript, we were informed that optically active **1h** had been found to rearrange to **3h** with inversion of configuration at the migration terminus, proving that the migration of the ethoxycarbonyl group could be concerted with the opening of the oxirane.[10]

Examples of stereospecific rearrangements of diastereoisomeric epoxides have been recorded,[11a] as well as the conversion of other optically active epoxides into optically active products.[12] The formation of a single product from the diastereoisomeric precursors mentioned above, for which there are precedents in the literature,[11b] may be interpreted in terms of the formation of the same long-lived cation from either precursor, but is equally compatible with concerted processes yielding the same product from two different precursors. This point can only be clarified by further studies utilizing optically active substrates.

Conclusion

Regardless of the picture chosen for representing the motion of the migrating group, the driving force in simple Wagner-Meerwein rearrangements is always assumed to be the conversion of a less stable cation into a more stable cation, but it is often impossible to predict the actual group which is to migrate and the extent of its migration.[13] Aromatic groups have been recognized as being particularly good migrating groups, and bridged intermediates are usually proposed. These intermediates, which may explain how the migration takes place, do not explain why it does. Furthermore, the frequent extrapolation that a group must be capable of stabilizing a positive charge in order to migrate readily has no theoretical or experimental basis, as shown by the long list of electronegative substituents which have recently been found to migrate to adjacent cationic centers.[14]

In the dienone-phenol rearrangement, the ethoxycarbonyl group was found to migrate in preference to either an alkyl or an aryl group,[15] and one readily conceptualizes the sequence of reactions shown in Scheme II, where the penultimate step

Table IV. Product Distribution in the BF_3-Catalyzed Rearrangement of **1e** and **4e** in CCl_4[a]

Compd	Temp, °C	2e	3e	4e	5e
1e	−15	62	18	20	0
1e	28	46	40	14	0
1e	60	19	69	11	0
4e	−15	4	14	78	4
4e	28	11	24	57	8
4e	60	14	40	30	16

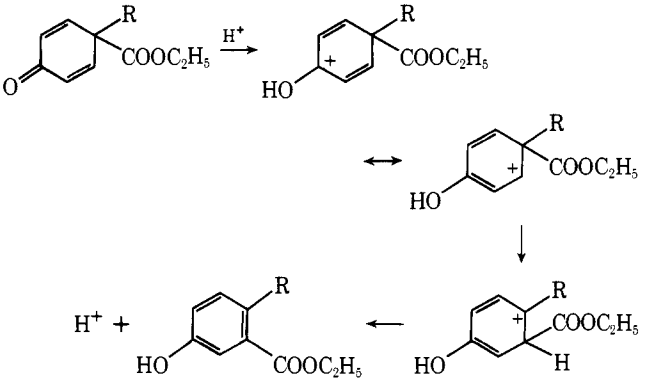
[a] Reaction time 10 min.

Table V. Solvent Effect in the BF_3-Catalyzed Rearrangement of **1e** at Room Temperature[a]

Solvent	2e	3e	4e
CCl_4	46	40	14
C_6H_6	24	61	15
Pet. ether[b]	14	65	21
$CHBr_3$	32	56	12
$CHCl_3$	18	70	12
CH_2I_2	26	57	17
CH_2Cl_2	11	73	12

[a] Reaction time 10 min. [b] Bp 37–49 °C.

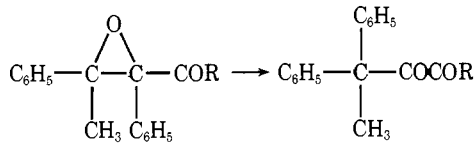
Scheme II



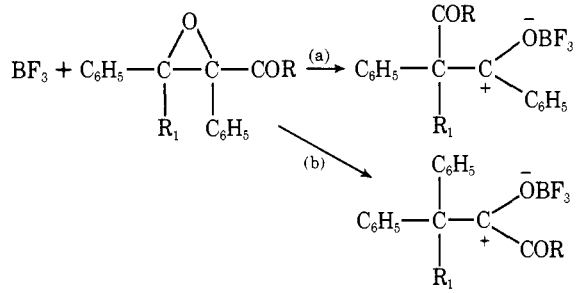
involves the conversion of a secondary cation into a tertiary cation, both being further stabilized by resonance.

It is logical to expect the group R, which is best capable of stabilizing a positive charge on the carbon to which it is attached, to have the lowest migratory aptitude and the notorious destabilizing effect of a carbonyl group adjacent to a cationic site would force substituents containing this group, such as an ethoxycarbonyl group, to have a high migratory aptitude, as observed experimentally. However, the work of House and

co-workers on the rearrangement of epoxy ketones[16] determined that the carbonyl substituent migrated less readily than a phenyl group, and our work showed a similar situation in glycidic and glyceric esters.[17]

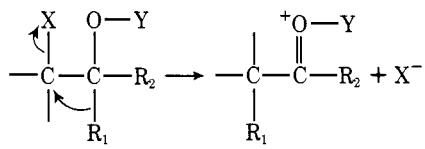


If the stability of the final cation were the determining mechanistic element in these rearrangements, the migration of the carbonyl substituent giving a benzylic cation (path a) should have been much preferred over that of the phenyl (path b), as observed in the dienone–phenol rearrangement.[15] The



conclusion that another factor must be of major consequence is inescapable, and the rearrangement of one initial cation into another, discrete, stable cation must be of minor importance at best.

The key energetic step in epoxide-to-carbonyl and related rearrangements must be the conversion of one oxygen atom from singly to doubly bonded to carbon, rather than in the conversion of one cation into another, more stable, cation. These rearrangements may be viewed as being apparented to the (base-catalyzed) conversions of alkoxides to carbonyl products, such as in the benzylic acid, acetoin, and halo ketone rearrangements, and in the synthesis of carbonyl products from halohydrins, glycol monotosylates, etc., in which the migrating group acts as an internal nucleophile, utilizing its bonding electrons. We have shown that no positive charge developed



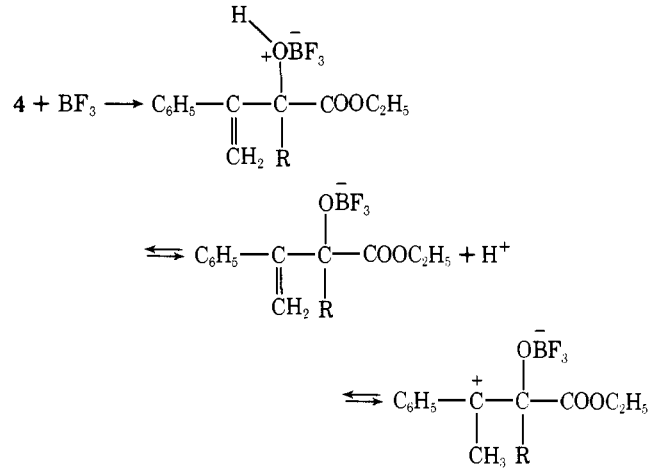
X = leaving group or positive charge
Y = H, BF_3^-, BF_2, negative charge, etc.

on the carbonyl during the alkoxycarbonyl group migration in a chlorohydrin rearrangement,[9] a result which suggests that the same could be true for the migration of carbonyl groups (ketones and esters) in epoxide and pinacol rearrangements.

In view of our experience with α-keto esters which could be further isomerized into β-keto esters,[3] it may be surmised that the α-keto esters obtained above following phenyl migration away from the 2 position are products of kinetic rather than thermodynamic control. The rearrangement reactions performed at higher temperatures should, therefore, lead to some of the other isomers, and this area is now being investigated.

Some aspects of this work deserve special comments. For example, the conversion of the allylic alcohols **4** into their isomers **2** and **3** presumably involves the benzylic cation postulated in the direct rearrangement of **1**. However, it is unlikely that the allylic cation isomerizes directly into the benzylic cation. Rather, we suspect that an intermolecular or intramolecular proton transfer operates as shown in Scheme III. The mechanism of this rearrangement is probably quite different from that reported for the copper-catalyzed isomerization of primary and secondary allylic alcohols in the gas phase at high temperatures,[18] which was believed to involve hydrogen abstraction generating an unsaturated aldehyde or ketone operating as intermediate in a chain reaction. Such products could not be formed from **4m** or **4e**.

Scheme III



We have now shown that, with a given catalyst, the migratory aptitudes in pinacol-like rearrangements are both solvent and temperature dependent. To our knowledge, this last variable has not been studied in any previous work in this area, and is not even mentioned as being of any importance in Collins' classical review on these rearrangements,[19] where the potential importance of the nature of the solvent was not mentioned either. One exception is in the work of Vitullo and Grossman on the dienone–phenol rearrangement of a molecule which, unfortunately, had two identical substituents and thus could only give a single product.[20]

Before our first paper describing the ethoxycarbonyl group migration, 2-hydroxy-3-butenoic or pyruvic esters were the only types of products which had been reported when glycidic esters were treated with acids or salts,[21] with the exception of one example,[22] which had been discredited by House, Blaker, and Madden. The results uncovered here with **1h, 1m,** and **1e** showed that the β-carbonyl esters were the most stable products, the pyruvic esters were next, and the allylic alcohols were the least stable. However, the activation energies for the conversion of the initial carbonium ions into these products are ranked in the opposite order, the lowest activation energy being required for going to the least stable product. If these results can be generalized, the course of many rearrangement reactions in which competition is possible will be controlled by a simple, judicious, choice of the solvent and temperature.

When this work was started, we believed that the ethoxycarbonyl group migration which we had observed represented the general mode of rearrangement for the glycidic esters in which they occurred, and that the previous workers in this area who had not reported them must have been in error. We now recognize that these rearrangements are very sensitive to the experimental conditions, and that the concept of migratory aptitude being a genetic property of a group in one or more molecules is a myth. Ideally, it is the determination of the energy of activation for each of the possible rearrangement pathways which is important, and we look forward to seeing ab initio calculations predict and extend results such as described in this work by incorporating solute–solvent interactions in the determination of energy surfaces.[23]

Finally, we note that House had started his investigations on the rearrangement of glycidic esters with a question on the validity of the earlier work by Tiffeneau and Levy.[22] This work was discredited on the basis of results obtained with a different

catalyst at a much lower temperature, but, in light of our present results, it may prove to be correct after all, and certainly deserves a new investigation.

Experimental Section

Boron Trifluoride-Catalyzed Rearrangements of Glycidic Esters: General Procedure. A solution of the glycidic ester in the proper solvent was brought to the desired temperature and treated with a slow stream of BF_3 gas. A dark oil usually separated, but disappeared during the workup, which consisted of washing with a saturated aqueous solution of NaCl (after addition of more solvent if required), followed by 5% aqueous $NaHCO_3$ and by water, drying the organic phase over $MgSO_4$, and removing the solvent under vacuum in a rotary evaporator. The NMR spectra were recorded at 60 MHz utilizing an internal Me_4Si standard, the mass spectra were obtained with a Perkin-Elmer 270 GLC–mass spectrometer, and the microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois. A 6801-6804 Nuclear-Chicago liquid scintillation counter was used for the radioactivity measurements. The samples were dissolved in 10 ml of Bray's mixture[25] and 1 ml of water, and counted at room temperature. Benzoic-*1*-^{14}C acid was used for calibration, and the results are the average of six determinations.

Treatment of 1h with BF_3; Temperature and Solvent Effects. Typical reactions involved solutions of ca. 200 mg of **1h**[26] (containing a trace of acetophenone) in 5 ml of solvent, which were brought to the desired temperature, and treated with BF_3. Alternatively, a solution of **1h** in a few drops of the appropriate solvent was added to the solvent, which had been previously saturated with BF_3 at the desired temperature. These two methods led to the same product distribution when analyzed by GLC. Usually, 80–90% of the theoretical weight was recovered, but a large portion of the reaction mixture was a poorly defined, high boiling material with broad NMR absorptions in the aromatic, methylene, and methyl regions, which did not show any peaks when analyzed at 220° by GLC on the 6-ft 15% EGSS-X column used for the analysis of the products **2, 3,** and 4 at 100–140 °C. The results of the GLC analyses are presented in Table I. In a typical reaction on a preparative scale, 9.9 g of **1h** (containing 8% of **4h**) was treated with BF_3 in CCl_4 at 60° for 5 min. After workup, the residue was distilled at 1.25 Torr. A forerun of 0.5 g (5%) contained acetophenone, **2h,** and **3h,** a second fraction boiling at 95–100 °C contained 2.9 g (29%) of a mixture of **2h** (9%) and **3h** (81%), and a residue of 4.5 g of polymeric material (45%) could not be distilled. From the column, 0.4 g of trapped material (4%) was recovered. The NMR spectra in CCl_4 were 9.80 (s, 1 H), 7.24 (br s, 5 H), 4.10 (q, J = 7 Hz, 2 H), 1.60 (s, 3 H), and 1.23 ppm (t, J = 7 Hz, 3 H) for **3h,** and 7.20 (s, 5 H), 4.38 (q, J = 7 Hz, 1 H), 4.03 (q, J = 7 Hz, 2 H), 1.37 (d, J = 7 Hz, 2 H), and 1.07 ppm (t, J = 7 Hz, 3 H) for **2h.** The spectral and GLC properties of both compounds were identical with those of authentic samples.[4]

Several experiments where ethyl 3-phenylglycidate (250-mg samples) was treated with BF_3 for 45–60 s at room temperature yielded a crude reaction mixture containing some starting material, ethyl phenylpyruvate, and what is believed to be ethyl 2-hydroxy-3-fluoro-3-phenylpropionate, which was isolated by preparative TLC as an oil: NMR (CCl_4) 7.28 (br s, 5 H), 5.65 (dd, J = 2 and 45 Hz, 1 H), 4.27 (dd, J = 2 and 25 Hz, 1 H), 4.19 (q, J = 7 Hz, 2 H), 3.53 (br s, 1 H), and 1.21 ppm (t, J = 7 Hz, 3 H). This product was unstable and its preparation could not always be repeated.

Treatment of 1h with BF_3 in Acetic Acid. A solution of 500 mg of **1h** in 50 ml of AcOH was treated with BF_3 at room temperature for 7 min, allowed to stand for 30 min, and worked up. The NMR of the crude product was that of the acetate of **4h:** NMR (CCl_4) 7.10–7.55 (5 H), 5.85 (s, 1 H), 5.53 (s, 1 H), 5.44 (s, 1 H), 4.06 (q, J = 7 Hz, 2 H), 2.00 (s, 3 H), and 1.03 ppm (t, J = 7 Hz, 3 H).

Treatment of Ethyl 2-Formyl-2-phenylpropionate with BF_3. A solution of 0.5 g of ethyl 2-formyl-2-phenylpropionate in 50 ml of benzene was treated with BF_3 for 30 min at room temperature, and worked up. Preparative TLC on silica gel with ethyl acetate–petroleum ether (1:9) yielded 0.453 g of starting material (NMR).

Rearrangement of Phenyl 3-Phenylglycidate. A solution of 0.300 g of phenyl 3-phenylglycidate[27] in 25 ml of CCl_4 was treated with BF_3 for 20 min and worked up. The reaction product was phenyl 3-phenylpyruvate as a mixture of the ketonic (recognized by the NMR singlet at 4.20 ppm) and the enolic forms (recognized by the singlets at 6.40 and 6.72 ppm in $CDCl_3$), the aromatic protons being at 6.9–8.3 ppm. It yielded a 2,4-DNP derivative: NMR ($CDCl_3$) 11.62 (br s, 1 H), 9.25 (d, J = 2 Hz, 1 H), 8.50 (d, d, J = 2 and 9 Hz, 1 H), 8.10 (d, J = 9 Hz, 1 H), 6.9–7.5 (10 H), and 4.18 ppm (s, 2 H).

Rearrangement of Tropinyl (*E*)-3-Phenylglycidate. The starting material was prepared by treating sodium 3-phenylglycidate with $SOCl_2$, followed by tropine. After workup, there was obtained 38% of an oil: NMR ($CDCl_3$) 7.46 (s, 5 H), 5.25 (m, 1 H), 4.17 (d, J = 1.5 Hz, 1 H), 3.52 (d, J = 1.5 Hz, 1 H), 3.3 (br s, 2 H), 2.38 (s, 3 H), and 1.55–2.70 ppm (m, 8 H). A solution of 110 mg in 10 ml of $CHCl_3$ was treated with BF_3 for 10 min, and yielded after workup 80 mg of a thick oil. The NMR ($CDCl_3$) showed the absence of aldehyde or enol protons down to 13 ppm.

Treatment of Ethyl 2-Formylphenylacetate with BF_3. A solution of 300 mg of ethyl 2-formylphenylacetate[28] in 15 ml of CCl_4 was treated with BF_3 for 10 min. After workup, the NMR showed that the starting material had been recovered.

Rearrangement of Ethyl 2,3-Dimethyl-3-phenylglycidate (1m). The starting material[29] was a 60:40 mixture of the *E*:*Z* isomers, bp 100–115 °C (0.8 Torr): NMR (CCl_4) 7.26 (m, 5 H), 3.70 (q, J = 7 Hz, 2 H), 1.62 (s, 6 H), and 0.73 ppm (t, J = 7 Hz, 3 H) for the *Z* isomer, 7.26 (m, 5 H), 4.27 (q, J = 7 Hz, 2 H), 1.58 (s, 3 H), 1.33 (t, J = 7 Hz, 3 H), and 1.33 ppm (s, 3 H) for the *E* isomer. A solution of 1.88 g of **1m** in 95 ml of CCl_4 was treated with BF_3 for 10 min. After workup, the crude reaction mixture contained 2% of **2m,** 83% of **3m,** and 15% of **4m** (NMR), and was treated by preparative TLC on silica gel and developed twice in ethyl acetate–petroleum ether (6:94 v/v). Three bands were observed. The fastest moving yielded 19 mg of **2m:** NMR (CCl_4) 7.18 (s, 5 H), 4.00 (q, J = 7 Hz, 2 H), 1.58 (s, 6 H), and 1.07 ppm (t, J = 7 Hz, 3 H); mass spectrum *m/e* 220 (M^+), 119 (base peak), 91, and 77 amu. The structure was further confirmed by GLC, NMR, and mass spectral comparisons, which showed this material to be different from the isomeric ethyl 2,2-dimethylbenzoylacetate and ethyl 2-methyl-2-phenylacetoacetate. The absence of a benzoyl group was obvious from the NMR and the mass spectrum, which had a negligible peak at *m/e* 105 amu. This product was identical (GLC and spectral comparisons) with that obtained in the rearrangement of **6t,** which yielded a 2,4-DNP derivative, mp 152–153 °C. Anal. Calcd for $C_{19}H_{20}N_4O_6$: C, 56.99; H, 5.04; N, 13.99. Found: C, 57.26; H, 5.01; N, 14.22.

The second band yielded 1.55 g of **3m:** NMR (CCl_4) 7.24 (s, 5 H), 4.20 (q, J = 7 Hz, 2 H), 2.02 (s, 3 H), 1.67 (s, 3 H), and 1.25 ppm (t, J = 7 Hz, 3 H); mass spectrum 220 (M^+), 178 (base peak), 147, 132, 103, 77, and 43 amu; semicarbazone mp 130–131 °C. Anal. Calcd for $C_{14}H_{19}N_3O_3$: C, 60.62; H, 6.92; N, 15.15. Found: C, 60.56; H, 7.00; N, 15.24.

The third band yielded 226 mg of **4m:** NMR (Me_2SO-d_6) 7.32 (s, 5 H), 5.7 (br s, 1 H, disappeared upon addition of D_2O), 5.50 (d, J = 1 Hz, 1 H), 5.25 (d, J = 1 Hz, 1 H), 4.02 (q, J = 7 Hz, 2 H), 1.46 (s, 3 H), and 1.00 ppm (t, J = 7 Hz, 3 H); mass spectrum 220 (M^+), 202, 174, 147 (base peak), 119, 103, 91, 77, and 43 amu. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.90; H, 7.27. Found: C, 70.81, H, 7.53. **5m** was also obtained, mp 120–122 °C (lit mp 121–122 °C[30]), NMR ($CDCl_3$) 7.45 (s, 5 H), 5.04 (q, J = 2 Hz, 2 H), and 2.12 ppm (t, J = 2 Hz, 3 H), uv λ_{max} (cyclohexane) 211 and 260 nm (lit. 212 and 260 nm[30]).

Rearrangement of Ethyl 2-Methyl-3-trideuteriomethyl-3-phenylglycidate. The starting material (23:77 *E*:*Z*) was prepared as above using acetophenone-d_3, and was about 75% deuterated from NMR. A solution of 150 mg in 7.5 ml of CCl_4 was treated with BF_3 for 10 min, worked up, and chromatographed as above, yielding 2.1 mg of **2m**-d_3 (with the singlet at 1.58 ppm integrating only for ca. 4 H), 117 mg of **3m**-d_3 (with the signal at 1.78 board and integrating for 0.7 H, and with the acetyl fragment remaining at *m/e* 43 in the mass spectrum), and 9.6 mg of **4m**-d_2 (in which the NMR signals at 5.5 and 5.7 ppm were broad and integrated only for 0.23 H each).

Ethyl 2,3-Dimethyl-3-phenylglycidate-3-^{14}C (1m*). Acetic-*1*-^{14}C acid (250 μCi/mmol, New England Nuclear) was diluted with acetic acid and condensed with benzene in the presence of $AlCl_3$. The redistilled acetophenone-*carbonyl*-^{14}C (1.56 μCi/mmol) had bp 57–58 °C (1.3 Torr), and was pure from NMR and GLC. Following the same procedure as above, condensation of 9.2 g of this material with 14.2 g of ethyl 2-bromopropionate yielded a product which was distilled three times to yield **1m*** ((65% *E*, 35% *Z*), 1.53 μCi/mmol, bp 74 °C (0.05 Torr). The saponification[31] of 0.440 g yielded 0.388 g of sodium salt, mp 297–300 °C dec. A 0.214 g portion was converted into a mixture of *p*-bromophenacyl esters, which was recrystallized to constant specific activity (1.56 μCi/mmol) and melting point (108–110 °C); NMR ($CDCl_3$) 7.2–8.0 (m, 9 H), 5.47 and 4.92 (each

a s, total 2 H), 1.77, 1.30, 1.82, and 1.72 ppm (each a s, total 6 H). Anal. Calcd for $C_{19}H_{17}O_4Br$: C, 58.62; H, 4.41; Br, 20.53. Found: C, 58.62; H, 4.32; Br, 20.38.

Rearrangement of 1m*. A solution of 2 g of **1m*** in 100 ml of CCl_4 was treated with BF_3 for 10 min, worked up, and chromatographed as above, to yield 1% of **2m*,** 11.5% of **4m*,** and 82.5% of **3m*** (1.53 μCi/mmol), which gave a semicarbazone, mp 130.5–131.5 °C after two recrystallizations from benzene–ether, specific activity 1.56 μCi/mmol. Anal. Calcd for $C_{14}H_9N_3O_3$: C, 60.62; H, 6.92; N, 15.15. Found: C, 60.56; H, 7.00; N, 15.24.

Degradation of 3m*. A mixture of 1 g of **3m*** and 20 ml of 5% aqueous NaOH was stirred for 20 h at room temperature and extracted with 50 ml of $CHCl_3$. The aqueous layer was adjusted to pH 3 and extracted with three 30-ml portions of $CHCl_3$, which were combined, washed with water, dried, and concentrated to yield 613 mg of 2-phenylpropionic-*2*-^{14}C acid as an oil; NMR ($CDCl_3$) 11.9 (br s, 1 H), 7.26 (s, 5 H), 3.72 (q, J = 7 Hz, 2 H), and 1.48 ppm (d, J = 7 Hz, 3 H); its *p*-bromophenacyl ester was recrystallized to constant specific activity (1.535 μCi/mmol), and melted at 63–64 °C. All the aqueous layers and washings were combined, saturated with NaCl, and extracted with four 30-ml portions of ether, which were dried and concentrated by distillation. The residue was neutralized with 5% aqueous NaOH and taken to dryness. NMR of the residue showed a mixture of sodium acetate (85%) and 2-phenylpropionate (15%). Three recrystallizations of the *p*-bromophenacyl ester yielded the pure acetate derivative, mp 85.5–86 °C (lit. mp 85 °C[32]), which showed no activity.

Temperature and Solvent Effects on the Rearrangement of 1m. The experiments were performed on 50-mg samples dissolved in 2.5 ml of CCl_4 or $CHCl_3$, and treated with BF_3 for 10 min at −50, −20, 28, or 70 °C. After workup, the crude material (ca. 48 mg in each case) was analyzed by NMR. The results are found in Table I. The pure *E* and *Z* isomers were obtained from the corresponding cinnamic acids, which were esterified and epoxidized with *m*-chloroperoxybenzoic acid. The *E* isomer had NMR (CCl_4) at 7.05–7.40 (m, 5 H), 4.22 (q, J = 7 Hz, 2 H), 1.58 (s, 3 H), 1.33 (t, J = 7 Hz, 3 H), and 1.13 ppm (s, 3 H). The *Z* isomer had NMR (CCl_4) at 7.05–7.20 (br, 5 H), 3.70 (q, J = 7 Hz, 2 H), 1.62 (s, 6 H), and 0.73 ppm (t, J = 7 Hz, 3 H).

Rearrangement of Ethyl 2-Ethyl-3-methyl-3-phenylglycidate (1e). The starting material was prepared in 28% yield by a Darzens condensation of ethyl 2-bromobutyrate and acetophenone. Only the *E* isomer was obtained: NMR (CCl_4) 7.38 (s, 5 H), 4.28 (q, J = 7 Hz, 2 H), 1.6–2.1 (compl, 2 H), 1.56 (s, 3 H), 1.33 (t, J = 7 Hz, 3 H), and 0.75–1.15 ppm (compl, 3 H). A solution of 200 mg of this product in 10 ml of CCl_4 was treated with BF_3 for 10 min. After workup, the crude product was analyzed by NMR to contain 46% of **2e,** 40% of **3e,** and 14% of **4e.** The components were separated by preparative TLC on silica gel, utilizing two developments with 5% EtOAc in petroleum ether. The fastest moving band yielded 79 mg (40%) of **2e**: mass spectrum 234 (M^+), 133 (base peak), 91, 77, 55, and 29 amu; NMR (CCl_4) 7.28 (s, 5 H), 3.98 (q, J = 7 Hz, 2 H), 2.02 (m, 2 H), 1.58 (s, 3 H), 1.02 (t, J = 7 Hz, 3 H), and 0.76 ppm (t, J = 7 Hz, 3 H); its 2,4-DNP derivative melted at 111–112.5 °C. Anal. Calcd for $C_{20}H_{22}N_4O_6$: C, 57.95; H, 5.36; N, 13.52. Found: C, 57.94; H, 5.29; N, 13.63.

The second band yielded 70 mg (35%) of **3e**: NMR (CCl_4) 7.28 (s, 5 H), 4.24 (q, J = 7 Hz, 2 H), 2.34 (m, 2 H), 1.65 (s, 3 H), 1.28 (t, J = 7 Hz, 3 H), and 0.97 ppm (t, J = 7 Hz, 3 H); mass spectrum *m/e* 234 (M^+), 178, 161, 132, 105, 104, 103, 91, 77, 57, 43, and 29 amu; 2,4-DNP derivative, mp 93.5–94.5 °C. Anal. Calcd for $C_{20}H_{22}N_4O_6$: C, 57.95; H, 5.36; N, 13.52. Found: C, 57.71; H, 5.22; N, 13.71.

The third band yielded 24 mg (12%) of **4e**: NMR (CCl_4) 7.20 (s, 5 H), 5.45 (d, J = 1 Hz, 1 H), 5.14 (d, J = 1 Hz, 1 H), 4.12 (q, J = 7 Hz, 2 H), 3.28 (s, 1 H, disappeared in the presence of D_2O), 1.90 (q, J = 7 Hz, 2 H), 1.12 (t, J = 7 Hz, 3 H), and 0.90 ppm (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.60; H, 7.89.

Temperature and Solvent Effects in the Rearrangement of 1e and 4e. The experiments were performed on 50-mg samples, dissolved in 2.5 ml of solvent, and treated with BF_3 for 10 min at the appropriate temperature. After workup, ca. 48 mg of oil was obtained, which was analyzed by NMR, giving the results presented in Tables III and IV. The structural assignment of **5e** was based on its NMR (CCl_4) at 7.50 (s, 5 H), 5.02 (t, J = 1 Hz, 2 H), 2.22–2.75 (d, q, J = 1 and 7 Hz, 2 H) and 1.21 ppm (t, J = 7 Hz, 3 H) and mass spectrum at *m/e* 188 (M^+), 187, 159, 143, 128, 115 (base peak), 91, 77, and 29 amu, and on the TLC and spectral comparison with the sample, mp 79 °C, obtained by FSO_3H treatment of ethyl 2-ethyl-3-methyl-3-phenylglycerate.[9] Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.60; H, 6.38. Found: C, 76.53; H, 6.31.

Rearrangement of Ethyl 2,3-Diphenyl-3-methylglycidate (1f). The starting material[33] was prepared by condensation of the Ivanoff derivative of phenylacetic acid with acetophenone, yielding 2,3-diphenyl-3-hydroxybutyric acid as a mixture of two diastereoisomers, which yielded a single one by recrystallization, mp 205–206 °C (lit. mp 182–183, 192 °C[34]): NMR $(CD_3)_2SO$ 7.00–7.65 (m, 10 H), 4.10 (s, 1 H), and 1.22 ppm (s, 3 H). The hydroxyl and carboxyl protons were not seen, but gave an HDO signal upon exchange with D_2O. The mixture of diastereoisomers (20 g) was treated with diazomethane, and dehydrated by refluxing for 2 h in 200 ml of benzene, using a Dean–Stark condenser. After workup and recrystallization from benzene–hexanes, 10 g of ethyl 2,3-diphenyl-3-butenoate was obtained, mp 81–82 °C: NMR (CCl_4) 6.94–7.28 (br s, 10 H), 5.43 (s, 1 H), 5.12 (d, J = 1 Hz, 1 H), 4.83 (d, J = 1 Hz, 1 H), and 3.50 ppm (s, 3 H). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 81.18; H, 6.36.

A 4.5-g sample of this compound was refluxed for 16 h in 200 ml of 20% aqueous KOH, poured onto ice, acidified to pH 3, and extracted with two 150-ml portions of $CHCl_3$. The combined extracts were washed with water, dried, and concentrated. Recrystallization of the residue from CCl_4 yielded 4 g of 2,3-diphenyl-2-butenoic acid, mp 146–157 °C, as a mixture of diastereoisomers (52:48 ratio) (lit. mp 160 °C[34]). After H_2SO_4-catalyzed esterification in ethanol and workup, the corresponding diastereoisomeric esters were obtained in the same ratio. Their epoxidation was performed by refluxing 4.5 g with 5.2 g of 85% *m*-chloroperoxybenzoic acid for 46 h in a mixture of $CHCl_3$–CH_2Cl_2 (1:2 v/v). After cooling, washing with 10% aqueous Na_2SO_3 and 5% aqueous $NaHCO_3$, and drying and concentrating, **1f** was obtained as an oil in 98% yield: NMR (CCl_4) 7.30 (m, 10 H), 4.22 (q, J = 7 Hz, 2 H), 1.73 (s, 3 H), and 1.33 ppm (t, J = 7 Hz, 2 H) for the *E* isomer (45%), and 7.30 (m, 10 H), 3.73 (q, J = 7 Hz, 2 H), 1.32 (s, 3 H), and 0.77 ppm (t, J = 7 Hz, 3 H) for the *Z* isomer (55%). The mixture was treated with a few drops of heptane at −10°. Further cooling of the heptane layer yielded some crystalline material, which had mp 50–55 °C after three recrystallizations, and contained ca. 90% of the *Z* isomer. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38. Found: C, 76.47; H, 6.53. The other isomer could not be obtained in crystalline form.

A solution of 180 mg of **1f** in 9 ml of CCl_4 was treated with BF_3 for 10 min. After workup, the residue was purified by preparative TLC on silica gel and developed in 5% EtOAc in petroleum ether, yielding 135 mg (85%) of **2f**: NMR (CCl_4) 7.23 (s, 10 H), 3.96 (q, J = 7 Hz, 2 H), 1.93 (s, 3 H), and 1.03 ppm (t, J = 7 Hz, 3 H). The molecular ion was not seen in the mass spectrum, which had a base peak at 181, 166, 103, and 77 amu. A 2,4-DNP derivative was obtained, mp 148–149 °C. Anal. Calcd for $C_{24}H_{22}N_4O_6$: C, 62.32; H, 4.80; N, 12.12. Found: C, 62.33; H, 4.84; N, 12.25.

Boron Trifluoride Catalyzed Friedel–Crafts Reaction of a Glycidic Ester with the Solvent. A solution of 4.80 g of ethyl 2-methyl-3-phenylglycidate in 50 ml of toluene was treated with BF_3 at room temperature for 10 min. After workup, the NMR of the crude reaction mixture showed that it was mostly a mixture of diastereoisomeric ethyl 2-hydroxy-2-methyl-3-phenyl-3-toluylpropionate. Crystallization from ethanol yielded 2.12 g of one pure isomer, mp 91.5 °C: NMR (CCl_4) 6.90–7.67 (m, 9 H), 4.15 (s, 1 H), 4.06 (q, J = 7 Hz, 2 H), 3.34 (s, 1 H, exchanged with D_2O), 2.24 (s, 3 H), 1.35 (s, 3 H), and 1.14 ppm (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.51; H, 7.38. Found: C, 76.38; H, 7.54.

Rearrangement of Ethyl 2-Phenylglycidate (6p). The starting material was prepared by epoxidation of the corresponding acrylic ester,[35] and had NMR (CCl_4) at 1.20 (t, J = 7 Hz, 3 H), 2.75 (d, J = 6 Hz, 1 H), 3.28 (d, J = 6 Hz, 1 H), 4.17 (q, J = 7 Hz, 2 H), and 7.1–7.5 ppm (m, 5 H). The treatment of 500 mg in 50 ml of benzene with BF_3 for 10 min, followed by workup, yielded a mixture of the *E* and *Z* enols, which yielded 200 mg of a 2,4-DNP derivative, mp 109–110 °C, identical with the one obtained from the product of formylation of ethyl phenylacetate.[36]

Rearrangement of Ethyl 2-Phenyl-3-methylglycidate (6s). A solution of 200 mg of **6s** as a mixture of the *E* and *Z* isomers (1:2.5) in 15 ml of benzene was treated with BF_3 for 30 min. After workup, the NMR (CCl_4) of the crude product was that of essentially pure ethyl 2-phenylacetoacetate (enolic form): 1.26 (t, J = 7 Hz, 3 H), 1.97 (s, 3

H), 4.40 (q, J = 7 Hz, 2 H), and 7.24 ppm (br s, 5 H). A 2,4-DNP derivative was obtained (230 mg), mp 95–96 °C, mol wt 386 (MS), identical with that obtained from the rearrangement of ethyl 2-methyl-3-phenylglycidate.

Rearrangement of Ethyl 2-Phenyl-3,3-dimethylglycidate (6t). The starting material was prepared by base-catalyzed condensation of acetone with phenylacetonitrile,[37] hydrolysis, esterification, and epoxidation with *m*-chloroperoxybenzoic acid. It showed NMR (CCl_4) at 0.97 (s, 6 H), 1.20 (t, J = 7 Hz, 3 H), 4.10 (q, J = 7 Hz, 2 H), and 7.10–7.55 ppm (m, 5 H). A solution of 100 ml of **6t** in 30 ml of benzene was treated with BF_3 for 30 min and worked up to yield 95 mg of pure **2m**, identical with the sample obtained in the rearrangement of **1m**.

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Molecular Rearrangements with Thiol Ester Group Migration. *S*-Phenyl (*E*)- and (*Z*)-2,3-Diphenylthiolglycidates

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Abstract: The boron trifluoride etherate induced rearrangement of *S*-phenyl (*E*)- and (*Z*)-2,3-diphenylthiolglycidate was studied. Principally, α-phenyl migration (85%) occurs in the case of the *E* isomer (**1**). Thiol ester (35%), α-phenyl (25%), and β-phenyl (14%) migrations occur in the rearrangement of the *Z* isomer (**2**). Thiol ester migration was established by the ^{14}C labeling study described in Scheme II. Thus diastereomeric differences exist in the rearrangement of certain α,β-epoxy carbonyl systems. Mechanistic implications of this result are discussed.

Although numerous reports are available on the boron trifluoride induced rearrangement of α,β-epoxy carbonyl systems,[1-4] relatively little is known about the mechanism of these reactions. The process is of interest, since it involves migration of a carbonyl function wherein an electron-deficient carbonyl carbon moves to a positive migration terminus. The transformation of thiolglycidates to β-oxo thiol esters (Z = SR) is of particular interest, since it represents the first nonbiochemical example of migration of a thiol ester group.[3] The enzyme-catalyzed conversion of succinyl coenzyme A (CoA) to methylmalonyl CoA involving the shift of the coenzyme A thiol ester is well known.[5] In different cases, concerted as well as nonconcerted ring opening migration processes have been considered for the epoxy carbonyl rearrangement reac-