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Molecular Rearrangements with Ethoxycarbonyl Group Migrations. 2. Rearrangement of 1,2-Glycols, Halohydrins, and Azidohydrins[1,2]

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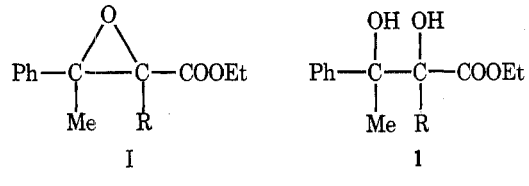
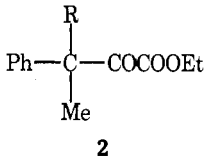
The ethoxycarbonyl group has been shown to undergo a facile 1,2 migration during the pinacol rearrangement of glyceric esters in fluorosulfonic acid. Pyruvic esters and 2-hydroxy-3-butenoic esters were also formed, and the prolonged treatment of some pyruvic esters in fluorosulfonic acid led to their isomerization into β-keto esters. The product of ethoxycarbonyl group migration was also found in the treatment of an azidohydrin with nitrosonium tetrafluoroborate, and that of halohydrins with silver salts. The rearrangement of *tert*-butyl 2-hydroxy-3-chloro-3-phenylbutyrate (**24**) without fragmentation upon treatment with silver carbonate argued against a mechanism involving a carboxylium ion, and in favor of a process in which the alkoxycarbonyl moiety acts as an internal nucleophile.

The migration of a carboethoxyl group in preference to hydrogen, alkyl, or aryl groups in the well-known pinacol rearrangement has not been previously noted,[3] but we were encouraged to look for it by its discovery in the acid-catalyzed isomerization of epoxides.[1,4] Glyceric esters **1**, obtained by mild hydrolysis of glycidic esters (I) or by hydroxylation of



I

1



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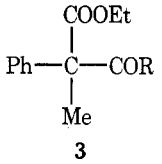

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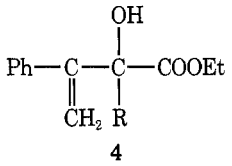

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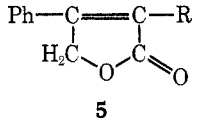

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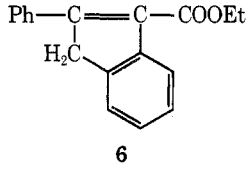


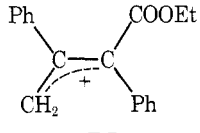
6

h, R = H
m, R = Me
e, R = Et
f, R = Ph

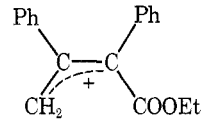
cinnamic esters, were treated with sulfuric acid, alone or in acetic acid, trifluoroacetic acid, or boron trifluoride, with poor results. For example, treatment of **1m** with sulfuric acid in acetic acid yielded the allylic alcohol **4m** with only minor amounts of 3-phenyl-2-butanone and of the desired rearrangement product **3m**. Fluorosulfonic acid used as solvent was found to be a most convenient catalyst for the desired pinacol rearrangement, and the standard procedure in this work consisted in dissolving **1** in pure fluorosulfonic acid, both having been precooled to 0 °C, pouring the reaction mixture over ice after 3 min at this temperature, and extracting with carbon tetrachloride. The crude extract was free from starting material.

The experimental results, presented in Table I, were very reproducible. They were generally similar to those obtained in the reaction of the related glycidic esters with boron trifluoride,[1,4] and the same sequence of apparent migratory aptitudes was deduced. The allylic alcohols **3** were not detected, but independent treatment of **4m, 4e,** and **4f** under the reaction conditions confirmed their reactivity and their partial conversion into the lactones **5m** and **5e** and the indene **6**, respectively.

The synthesis of indenes from phenyl substituted allylic cations has been previously described.[5] The intramolecular Friedel–Crafts reaction requires the allylic–benzylic cation to have the geometry shown in *E*-**7**. Whether or not the other



E-7



Z-7

isomer was formed was not established directly. The observed cyclization to **6** from each diastereoisomer of **1f** in the presence of boron trifluoride agreed with a facile interconversion of both cations,[5] but the absence of the lactone **5f** indicated a slow rate of cyclization from *Z*-**7**. Note that the indene **6** had not been observed in the boron trifluoride catalyzed rear-

Table I. Pinacol Rearrangement of Glyceric Esters with FSO_3H at 0 °C for 3 min (Yields from NMR Analyses)

	% products			
Precursor	2	3	5	Others
1h	*a*	6.5	*a*	*a*
1m (threo + erythro)	*b*	84	16	
threo-**1m**	*b*	84	16	
erythro-**1m**	*b*	84	16	
1m-d_3 (threo + erythro)	*b*	90	10	
1e (threo + erythro)	9	75	9	
1f (threo + erythro)	60	13		**6** (12), **8** (6), **9** (9)

[a] Too complex for analysis. [b] Trace.

rangement of **1f**, which yielded a single product, resulting from phenyl group migration, further indicating that **4f** was not formed under the conditions of that reaction.[1]

The dehydration of both isomers of **1m** into an almost single rearranged product **3m** (Table I) contrasted with the results of the boron trifluoride treatment of **1m**, from which the three rearranged products **2m, 3m,** and **4m** were obtained.[1] However, the isomerization of **1m** into the allylic alcohol was the preferred process in weaker acids, such as trifluoroacetic or dilute fluorosulfonic acids, and the treatment of **1m** with pure fluorosulfonic acid under conditions identical with those used with **1m** gave a somewhat different product distribution, 52% of **3m,** 48% of **5m,** and a trace of **2m.**

The migration of the phenyl group from the 3 to the 2 position would also have given **3m** from **1m,** but this process was ruled out by the study of **1m**-*3-methyl*-d_3, which yielded **3m**-d_3 with no deuterium at the acetyl position, a result which agrees with the behavior of **1m**.[1]

The acid treatment of **1f** yielded two unexpected products, ethyl 2,2-diphenylacetoacetate (**8**) and acetophenone (**9**), along with **2f, 3f,** and **6** (Table I). This reaction contrasted with that of **1f** with boron trifluoride, which yielded only **2f,**[2] and where the allylic alcohol **4f** could not have been an intermediate, since its treatment with boron trifluoride yielded the indene **6** as the sole product. Shorter reaction times did not have a marked effect on the yield of **9**, but reduced the formation of **8**, and these studies also demonstrated the very fast rate of this pinacol rearrangement, which was complete in less than 15 s at −5 °C and where only 6% of starting material was left after 15 s at −50 °C.

The formation of acetophenone described above must have taken place in the reaction of the starting material, since the reaction products did not yield it when submitted to the treatment with fluorosulfonic acid. The idea that an air oxidation reaction had taken place, formally the reverse of a pinacol synthesis, was dismissed by checking that bubbling air through a solution of **1f** did not lead to any detectable fragmentation. The most reasonable mechanism for the fragmentation of glyceric esters into carbonyl products involves a protonation at the ester carbonyl, followed by a retro-aldol cleavage reaction. This type of acid-catalyzed β fission had not

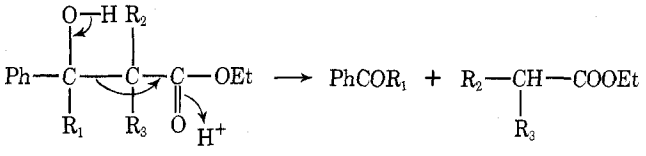


Table II. Isomerization of 2f Catalyzed by FSO_3H at 0 °C

Time, min	2f	3f	8
5	79	15	6
10	71	21	8
20	50	33	17
40	28	50	22
80	16	57	27
120	8	64	28
150	5	65	30
180	2	71	27
210	0	71	29

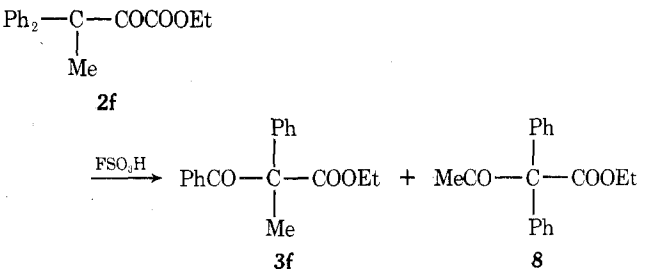
Table III. Isomerization of 2m Catalyzed by FSO_3H at 0 °C

Time, min	2m	3m	11
3	95	3	2
90	48	32	20
180	19	46	35
300	5	55	40
450	0	56	44

been previously reported with esters, although it was known for carboxylic acids[6] and ketones.[7] We also found that 2,3-diphenyl-3-hydroxybutyric acid yielded acetophenone and methyl phenylacetate upon attempted esterification with methanol catalyzed by sulfuric acid. However, a control experiment disclosed that fragmentation had taken place prior to exterification, since the ester formed by reaction with diazomethane did not undergo the fragmentation reaction when it was treated in the same acidic conditions.

We previously reported on the acid-catalyzed formation of benzophenone from ethyl 3,3-diphenylpyruvate, which we tentatively ascribed to a retro-pinacol rearrangement to a glyceric ester, followed by the above β fission.[8] Later work on the rearrangement of chlorohydrins, which also led to fission,[9] attracted our attention to the facile autoxidation of ethyl 3-phenylpyruvates, a reaction which best explains the formation of **9** in this case.

In the effort to establish whether acetophenone had been formed by reaction of the starting material or of the reaction products, **2f** was treated in the usual reaction conditions. To our surprise, it was converted into two other products, and acetophenone was not formed (Table II). These two products were purified by preparative TLC and identified as **3f** and **8,** the β-keto esters isomeric with **2f,** which were also observed in the direct reaction of **1f.**



We do not know the exact mechanism of the α-keto to β-keto ester rearrangement, for which there are at least two alternatives, differing by whether or not the ethoxycarbonyl group migrates,[8] and we still hope to see this problem elucidated in the near future, by studying the rearrangement of properly labeled precursors.

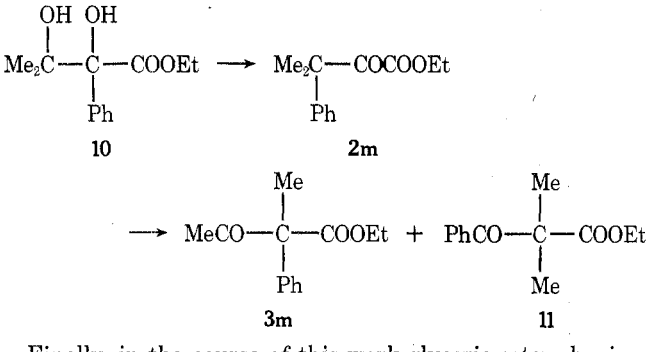
The generality of the fluorosulfonic acid catalyzed rearrangement of α-keto to β-keto esters has not been fully established, but we found that **2m** [the main product formed in

Table IV. Solvolysis of 17

Solvent	Temp, °C	Time, h	Ag salt	Ih	2h	3h	4h	1h	17	Other
None	132	22	None		50		50			9 (Tr)
None[a]	132	63	None		100					
None	132	63	None		25		44			9 (31)
50% EtOH	r.t.									23 (100)
MeOH	r.t.	4	Nitrate							22 (100)
C_6H_6	r.t.	21	Carbonate	60	5	14	18		4	
Acetone	r.t.	21	Carbonate	70	10	14	5			
Me_2SO	r.t.	21	Carbonate		17		3		80	
HMPTA	r.t.	21	Carbonate	*c*	*c*	0	*b*	*c*	*b*	*c*
CCl_4	r.t.	41	Carbonate	68	2	19	11			
THF	r.t.	41	Carbonate	35	2	10	3		50	
CH_3CN	r.t.	41	Carbonate	80	2	16	2			
Hexanes	r.t.	65	Carbonate	50	2	28	20			
Ether	r.t.	65	Carbonate	25	5	9	20		40	
Me_2SO	r.t.	96	Carbonate	*c*	*c*	0	*c*	*c*	*c*	
DMF	r.t.	96	Carbonate	*c*	*c*	*b*	*c*	*c*	*c*	
88% HCOOH	r.t.	16	None					100		
AcOH	r.t.	16	None						100	
AcOH	118	16	None				50			AcO-**4h** (50)
Ether	−10	1.5	Triflate				100			
Ether	0	2	Tosylate						100	
C_6H_6	r.t.	20	Tosylate	*c*	*c*	0	29	0	*c*	
C_6H_6	r.t.	46	Mesylate				80		14	**14** (6)

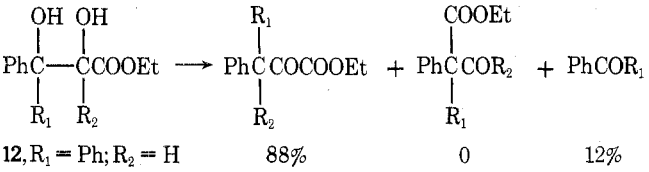
[a] In the absence of air. [b] Detected by NMR. [c] Mixture too complex for NMR analysis.

the acid treatment of ethyl 2-phenyl-3,3-dimethylglycerate (**10**)] did rearrange to yield the isomeric β-keto esters **3m** and **11** (Table III).



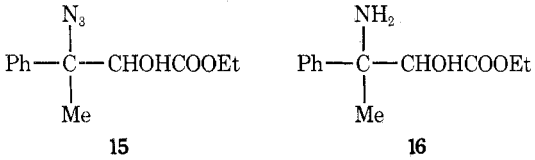
10 **2m** **3m** **11**

Finally, in the course of this work glyceric esters having different substitution patterns at the 3 position were also treated with fluorosulfonic acid, and the results are shown here:



12, R_1 = Ph; R_2 = H	88%	0	12%
13, R_1 = H; R_2 = Me	0	100%	0
14, R_1 = H; R_3 = Ph	95%	0	5%

Ethoxycarbonyl Group Migration from an Azidohydrin Precursor. Following the report of easy generation of carbonium ions by the nitrosonium tetrafluoroborate decomposition of azides,[10] the procedure was utilized with ethyl 2-hydroxy-3-azido-3-phenylbutyrate (**15**), which was readily obtained by treating Ih with hydrazoic acid.



15 **16**

There was no reaction when **15** was treated with an excess of the salt at room temperature in acetonitrile, benzene, or dimethoxyethane for up to 60 h. The starting material disappeared completely upon refluxing for 6 h in benzene, and the product of ethoxycarbonyl migration was detected in 18% yield, along with a trace of **2h** and 10% of the allylic alcohol **4h.** Acid-catalyzed decarbonylation and condensation reactions were probably responsible for the low yield of identified products, a situation similar to that observed with Ih[1] and **1h.**

The identification of **3h** in this reaction mixture was sufficient proof that the ethoxycarbonyl group could migrate when the azohydrin was used in the generation of the initial cation, and no further work was devoted to this reaction.

The synthesis of the amino alcohol **16** proved to be much more difficult than anticipated.[11] The treatment of the epoxide Ih with ammonia or sodamide did not yield **16.** Ring opening took place when Ih was treated with benzylamine, but the nitrogen was then doubly benzylic, and the hydrogenolysis cleaved the bond between the nitrogen and the adjacent tertiary carbon, rather than the desired one.

Acid-catalyzed reactions, such as the condensation with a nitrile to form the required carbon–nitrogen bond, instead resulted in the dehydration into **3h.** The reduction of **15** with sodium borohydride gave a low yield of **16,** which was purified with difficulty. Upon diazotization of this product with isoamyl nitrite, a very complex mixture was generated, where **3h** was absent as judged by NMR. Further work in this area will have to await the development of a convenient synthesis for **16.**

Ethoxycarbonyl Group Migrations from Halohydrins. Because of the ease with which the product of rearrangement with ethoxycarbonyl group migration could be detected by the NMR analysis of the aldehyde proton, much work was devoted to the chlorohydrin **17,** derived from Ih by treatment with hydrogen chloride in ether, and which was a 1:1 mixture of diastereoisomers.

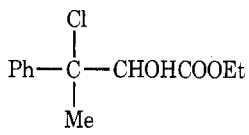
The solvolysis of **17** in 88% formic acid at room temperature for 16 h resulted in hydrolysis to the glyceric ester **1h.** No reaction was observed under the same conditions in acetic acid, but following reflux in this latter solvent for 16 h, the allylic alcohol **4h** and its acetate were formed in equal amounts.

Table V. Dehydrochlorination of 20 and 21 in the Presence of Silver Carbonate

Compd	Solvent	Time, h	Temp, °C	$COOC_2H_5$ migr	Epoxide	Starting material	Others
20	C_6H_6	15.5	65	8	61	31	
	Ether	16	r.t.	*a*	*a*	*a*	
	DMF	15	r.t.	0	*a*	*a*	
	DMF	40	75		100		
	CH_3CN	15.5	r.t.			100	
	CH_3CN	24	82		100		
	Acetone	15	r.t.	*a*	*a*	*a*	
21	DMF	66	68				**4m** (100)
	C_6H_6	16	r.t.	0	*a*	0	**4m**,[a] **5m**[a]

[a] Identified by NMR, but spectrum too complex for analysis.

The reaction of **17** was then carried out in a variety of solvents. Nucleophilic displacement of the chloride, but no rearrangement, was the rule in hydroxylic solvents. In aprotic



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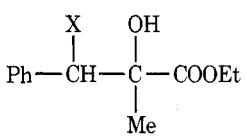
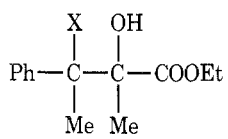


18, X = Cl
20, X = Br
22, X = OMe
23, X = OEt



19, X = Cl
21, X = Br

solvents, the dehydrochlorination took place in all possible manners, yielding the allylic alcohol and the epoxide as well as the products of molecular rearrangement, the α-keto ester **2h**, and the aldehyde **3h**. Qualitative variations in the product distribution were observed as a function of the solvent chosen, and they are recorded in Table IV. The nature of the silver salt used also had an effect on the product distribution, and no **3h** was detected with silver tosylate, mesylate, or triflate.

After this series of experiments was completed, silver carbonate was utilized with other halohydrins, in order to ensure that no strong Bronsted acidity would be developed during the course of the reaction, thereby ensuring that the migration of the ethoxycarbonyl group would not actually involve a protonated ester moiety. No reaction was observed at room temperature with the chlorohydrins **18** and **19**, but the corresponding bromohydrins **20** and **21** did undergo dehydrobromination in these conditions, yielding the epoxide and the product of ethoxycarbonyl group migration in each case, as well as the allylic alcohol in the case of **21** (Table V).[12]

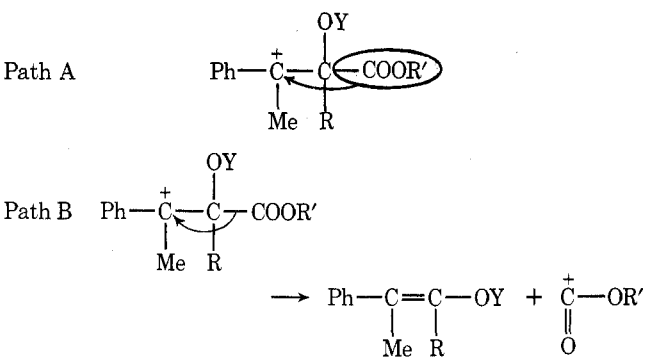
These observations confirmed the preference for the migration of the ethoxycarbonyl group over the methyl which was previously encountered in the rearrangement of glyceric and glycidic esters under certain conditions.

Much more work remains to be done to correlate the effect of the temperature and the stereochemistry of starting materials with the product composition. However, the present results are in line with those described for the rearrangement of the corresponding glycidic esters. The allylic alcohol **4** was the major product at low temperature. In the absence of electrophilic assistance, the product of methyl migration **2h** was formed next, and the formation of the product of ethoxycarbonyl migration **3h**, which has the highest activation energy, required electrophilic assistance.

Conclusion

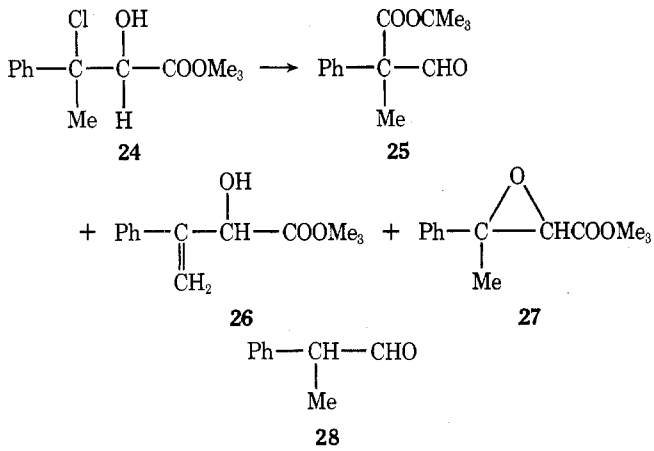
The simplest explanation for the pinacol and pinacol-like rearrangements described in this work starts with an ionization at the 3 position. We have no information yet on the lifetime of the 3-carbonium ion generated, compared to the rate of the subsequent migration of one group from the 2 to the 3 position, but it is anticipated to depend on the reaction conditions. The concertedness reported in other pinacol rearrangements,[13] and the recently disclosed concerted rearrangement of the epoxide Ih to **3h**,[14] suggest that a group migration from the 2 to the 3 position could well take place synchronously with the departure of the leaving group, resulting in inversion of configuration at the 3 position.

Formally, a distinction may be established between a process in which the carbonyl carbon remains with eight electrons throughout (path A) and that in which the bonding electrons are first attracted to the adjacent electron-deficient site (written here as a full cation for convenience), yielding an enol–carboxylium ion pair, which further undergoes the acylation reaction required by the structure of the final product (path B).



The fact that all the attempted syntheses of carboxylium ions have resulted in their decomposition with loss of carbon dioxide[15] gave a strong presumption against path B. Additional support for this view was derived from the study of *tert*-butyl 2-hydroxy-3-chloro-3-phenylbutyrate (**24**), which was treated with silver carbonate in benzene. If path B had been operative, decomposition to carbon dioxide and isobutene would have been expected. Instead, the rearrangement with ester group migration was observed, indicating that little or no positive charge was generated at the ester carbonyl, and that the carbon–carbon bonding electrons act as an internal nucleophile in the rearrangement.

Each diastereoisomer of **24** was treated under the same conditions. Although they yielded the same products, **25**, **26**, and **27**, considerable stereoselectivity was displayed and one isomer gave predominantly the aldehyde resulting from ester group migration (ca. 50% of the products) with only 25% of epoxide, while the other gave only 33% of this aldehyde and



24 25 26 27 28

56% of the diastereomeric epoxide (**27**). The formation of acetophenone in these dehydrochlorination reactions is interpreted as resulting from the autoxidation of *tert*-butyl 2-keto-3-phenylbutyrate,[9] giving a measure of the extent of hydrogen migration from the 2 to the 3 position. In contrast, the treatment of **27** with boron trifluoride in benzene resulted in complete cleavage to 2-phenylpropionaldehyde (**28**), coupled with the alkylation of the solvent, a decomposition reaction reminiscent of the thermal process.[16]

Although further work is obviously needed, the ability of the alkoxycarbonyl group to undergo 1,2 migrations in a variety of pinacol-like rearrangements is now firmly established. The ready availability of glycidic and glyceric esters, as well as chlorohydrins, suggests that the introduction of a carboxylic ester function adjacent to a carbonyl group via a pinacol-like rearrangement may occasionally compete with current methods based on nucleophilic reactions of enolate ions. From the practical viewpoint, a competition between two different substituents is usually the rule for the migration from the carbinol to the adjacent cationic position in these rearrangements. We previously demonstrated that a judicious choice of the reaction parameters often provided an effective control over the formation of the primary products.[1] Some selectivity over the subsequent isomerization of these products is also available, and may even lead to products not directly accessible from the starting material, such as **8** from **1f**. Further work will be directed at gaining a more effective control over the selection of the group which migrates in these competitive rearrangement reactions.

Experimental Section

Rearrangement of Ethyl 3-Methyl-3-phenylglycerate (1h). Fluorosulfonic acid (1 ml) precooled to 0 °C was added dropwise with stirring to 472 mg of the diastereoisomer of **1h** melting at 93–94 °C.[17] The reaction mixture was stirred for 3 min and poured onto an ice–water–carbon tetrachloride mixture. After separating the organic layer and extracting the aqueous phase twice with 50 ml of CCl_4, the combined organic layers were washed with two 50-ml portions of 5% $NaHCO_3$, dried, and concentrated. The NMR (CCl_4) was very complex, but showed the aldehyde signal of **3h** at 9.90 ppm. Preparative TLC on silica gel, developed successively with EtOAc–petroleum ether (1:9) and EtOAc–CCl_4 (1:9), led to many overlapping bands. The only product isolated in pure form was ethyl 2-formyl-2-phenylpropionate (**3h**, 20 mg), identical with an authentic sample. The same results were observed when either the lower melting or a mixture of both diastereoisomers of **1h** was treated as above.

Ethyl 2,3-Dimethyl-3-phenylglycerate (1m). The hydration of 2.0 g of Im with 30% by weight of perchloric acid in 50% aqueous THF for 16 h at room temperature led, after workup, to 1.5 g of **1m**, as a viscous oil which was purified by chromatography over silica gel. A mixture of both diastereoisomers was obtained: NMR ($CDCl_3$) 7.0–7.6 (br, 5 H), 4.07 (q, J = 7 Hz, 2 H), 3.55 (br, 2 H), 1.65 (s, 3 H), 1.40 (s, 3 H), and 1.13 ppm (tr, J = 7 Hz, 3 H) for one isomer, and 7.0–7.6 (m, 5 H), 4.03 (q, J = 7 Hz, 2 H), 3.55 (br, 2 H), 1.60 (s, 3 H), 1.43 (s, 3 H), and 1.08 ppm (tr, J = 7 Hz, 3 H) for the other. The signal at 3.55 ppm disappeared when D_2O was added. The fraction collected before **1m** was **4m**, obtained in 10% yield, and identified by comparison of the NMR with the known material. The same procedure was used to hydrate 400 mg of **Im-3-Me-d_3**, yielding 400 mg (92%) of ethyl 2-methyl-3-trideuteriomethyl-3-phenylglycidate (**1m-d_3**), which was 72% deuterated from the NMR analysis.

Rearrangement of 1m. A 576-mg sample of **1m** was treated with 1.15 ml of FSO_3H at 0 °C for 3 min, poured into an ice–water–CCl_4 mixture, and worked up as usual. The crude reaction products were fractionated by preparative TLC using EtOAc in petroleum ether (once with 6% and twice with 4% v/v). Three bands were visible under uv light. Ethyl 3,3-dimethyl-3-phenylpyruvate (**2m**), an oil (3.7 mg, 0.7%), was isolated from the fastest moving band. Its NMR (CCl_4) and mass spectra were superimposable onto those of the FSO_3H-catalyzed rearrangement of ethyl 3,3-dimethyl-2-phenylglycerate (**10**). Ethyl 2-methyl-2-phenylacetoacetate (**3m**, 418 mg, 78%), an oil, was obtained from the second band. Its NMR (CCl_4) and mass spectra were superimposable onto those of the major product of the BF_3-catalyzed rearrangement of ethyl 2,3-dimethyl-3-phenylglycidate (Im). The third band yielded 59.5 mg (14%) of 2-methyl-3-phenyl-4-hydroxy-2-butenoic acid lactone (**5m**): mp 120–122 °C (lit. mp 121–122 °C[18]); λ_{max} (cyclohexane) 211 and 260 nm; NMR ($CDCl_3$) 7.45 (s, 5 H), 5.04 (q, J = 2 Hz, 2 H), and 2.12 ppm (tr, J = 2 Hz, 3 H). The NMR analysis of the mixture before separation showed 84% of **3m** and 16% of **5m**, the signal at 1.18 ppm for **2m** being barely noticeable.

The same treatment was supplied to 300 mg of **1m-d_3**, which yielded 2 mg of **2m-d_3**, 209 mg of **3m-d_3** in which the singlet at 1.67 ppm integrated for only 0.67 H, and 15 mg of **5m-d_2**, having a full methyl at 2.12 ppm.

Rearrangement of *threo*- and *erythro*-1m. The above reaction was repeated using 133 mg of either *threo*- or *erythro*-**1m** in 0.26 ml of FSO_3H. After workup, 107 and 90 mg of an oil were obtained, respectively, each analyzing by NMR for 84% **3m**, 16% **5m**, and a trace of **2m**.

Rearrangement of Ethyl 2,3-Dimethyl-3-phenylglycidate (Im). Treatment of 200 mg of Im with 0.43 ml of fluorosulfonic acid for 3 min at 0 °C and workup yielded 140 mg of an orange semisolid product which contained 52% **3m** and 48% **5m** plus a trace of **2m** (NMR analysis).

Reaction of 1m in Dilute Fluorosulfonic Acid. Qualitative tests were performed using 200 mg of **1m** in (a) 0.4 ml of acid and 0.05 ml of water, (b) 0.3 ml of acid and 0.05 ml of water, and (c) 0.3 ml of acid and 0.1 ml of water. The major products were **3m** (along with some **4m** and **5m**), **4m** (along with some **3m**), and **4m**, respectively. In the last two experiments some starting material remained.

Ethyl 2-Ethyl-3-methyl-3-phenylglycerate (1e). A solution of 482 mg (2.06 mmol) of *E*-Ie in 2 ml of tetrahydrofuran was added to 25 ml of perchloric acid in 50% aqueous tetrahydrofuran (30% by weight). The reaction mixture was heated in an oil bath at 45 °C for 1 h, diluted with 150 ml of water, and extracted with two 50-ml portions of ether. The combined ether extracts were washed with two 50-ml portions of 5% aqueous sodium bicarbonate, dried, and concentrated.

Purification of the product mixture by preparative TLC, using 7.5% ethyl acetate in petroleum ether, yielded 385 mg (74%) of **1e**, a thick oil, as a 1:1 mixture of threo and erythro isomers: NMR (CCl_4) 7.0–7.6 (m, 10 H), 4.02 (q, J = 7 Hz, 2 H) and 4.13 (q, J = 7 Hz, 2 H), 3.33 (br s, exchanged with D_2O, 4 H), 1.5–2.1 (m, 4 H), 1.58 (s, 3 H) and 1.5 (s, 3 H), 1.18 (tr, J = 7 Hz, 3 H), and 0.5–0.85 ppm (m, 6 H).

Ethyl 2-ethyl-3-phenyl-2-hydroxy-3-butenoate (**4e**, 43 mg, 9%) was also obtained from the first band and was identified by 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, exchanged with D_2O), 1.90 (q, J = 7 Hz, 2 H), 1.12 (tr, J = 7 Hz, 3 H), and 0.90 ppm (tr, J = 7 Hz, 3 H).

Rearrangement of Ethyl 2-Ethyl-3-methyl-3-phenylglycerate (1e). This compound (385 mg, 1.53 mmol) was treated with 0.73 ml of FSO_3H at 0 °C for 3 min and worked up as described above. NMR analysis of the mixture showed 75% **3e**, 9% **2e**, and 16% **5e**. These components were separated by preparative TLC developing the plates four times with 5% ethyl acetate in petroleum ether. Three bands were seen under uv light. The bands were scraped off and extracted with 10% ethyl acetate in chloroform.

The lactone **5e** was obtained in 14% yield (40 mg) from the slowest moving band as prisms, mp 79 °C when recrystallized from CCl_4–petroleum ether: NMR (CCl_4) 7.50 (s, 5 H), 5.02 (2 H, tr, J = 1 Hz), 2.22–2.75 (d, q, J = 1 and 7 Hz, 2 H), and 1.21 ppm (tr, J = 7 Hz, 3 H); mass spectrum m/e 188 (M^+), 187, 159, 143, 129, 128, 115 (base peak), 91, 77, and 29.

The second band yielded 203 mg (58%) of **3e** identified by comparison of the NMR and mass spectra with those of the known compound.[1]

The fastest moving band yielded 29 mg of an oil which was purified further by preparative TLC (the plate was developed once in 3% ethyl acetate in petroleum ether, twice in 2% ethyl acetate in petroleum ether, once in 2% chloroform in carbon tetrachloride, and once in carbon tetrachloride) to give 11 mg of products which were not identified and 18 mg (5%) of **2e**, identified by NMR and mass spectral comparisons.

Ethyl 2,3-Diphenyl-3-methylglycerate (1f). Perchloric acid (120 ml, 30% by weight in 50% aqueous tetrahydrofuran) was added to a solution of 3.5 g (0.0124 mol) of ethyl 2,3-diphenyl-3-methylglycidate (If) in 2.5 ml of tetrahydrofuran. The reaction mixture was stirred at 60–65 °C (oil bath) for 20 min, poured onto ice, diluted with 300 ml of water, and extracted with three 100-ml portions of ether. Washing and drying of the ether extracts and removal of the solvent yielded an oily residue. Crystallization from ether–petroleum ether yielded 1.73 g (48%) of a 1:1 mixture of *threo*- and *erythro*-**1f**, white needles: mp 101–105 °C; NMR (CCl_4) 7.0–7.9 (m, 20 H), 4.27 (q, J = 7 Hz, 2 H), 4.09 (q, J = 7 Hz, 2 H), 3.7 (s, exchanged with D_2O, 4 H), 1.67 (s, 3 H) and 1.42 (s, 3 H), 1.26 (tr, J = 7 Hz, 3 H) and 1.12 ppm (tr, J = 7 Hz, 3 H).

Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.97; H, 6.72. Found: C, 71.91; H, 6.54.

Rearrangement of 1f. A. Treatment of 500 mg of **1f** with 0.8 ml of FSO_3H at 0 °C for 3 min and workup as above yielded a mixture containing (NMR analysis) 60% **2f**, 13% **3f**, 12% **6**, 6% **8**, and 9% **9**. This mixture, an oil, was treated by preparative TLC, developed four times in 1:3 benzene–carbon tetrachloride. Three almost overlapping bands seen under a uv light were scraped off and extracted with 10% EtOAc in $CHCl_3$. The first band yielded 49 mg of an oil which was a mixture of **2f** (5%) and **6** (6%), identified by GLC–mass and NMR spectra. Pure **2f** (215 mg) was obtained from the second band to yield a total of 51%. The third band yielded a mixture of **3f** (38 mg, 8%), **8** (19 mg, 4%), and **9** (10 mg, 5%), after further TLC with 0.5 and 0.3% EtOAc in petroleum ether. The identification of **6** was based on the NMR (CCl_4) at 4.21 (q, J = 7 Hz, 2 H), 3.77 (s, 2 H), 1.15 (tr, J = 7 Hz, 3 H), in addition to the aromatic protons between 7.00 and 7.50 ppm. The GLC–mass spectrum had signals at m/e 264 (M^+), 191 (base peak), and 189. The NMR (CCl_4) of **3f** was at 6.95–7.8 (m, 10 H), 4.05 (q, J = 7 Hz, 2 H), 1.78 (s, 3 H), and 0.98 ppm (tr, J = 7 Hz, 3 H), and its mass spectrum at m/e 282 (M^+), 239 (base peak), 194, 166, 77, and 43. The NMR (CCl_4) of **8** was at 7.00–7.80 (10 H), 4.18 (q, J = 7 Hz, 2 H), 2.05 (s, 3 H), and 1.17 ppm (tr, J = 7 Hz, 3 H), and its mass spectrum showed peaks at m/e 282 (M^+), 239 (base peak), 194, 166, 77, and 43.

The treatment of **1f** (50 mg) with concentrated FSO_3H (0.08 ml) at −50 °C for 15 s, followed by the usual workup, yielded an oil which contained 90% **2f**, 4% **9**, and 6% unreacted **1f** (NMR analysis). Various experiments were run at −5 °C with reaction times ranging from 4 to 45 s; 2% of starting material was left after 8 s, and none after 15 s. In this last case the product distribution was 91% **2f**, 4% **3f**, and 5% **9**.

Rearrangement of 1f with Dilute FSO_3H. A 75-mg sample of **1f** was treated for 3 min at 0 °C with 0.15 ml of acid and 0.05 ml of water. The reaction mixture was poured onto an ice–water–CCl_4 mixture and extracted with CCl_4. After drying and concentrating 65 mg of oil was obtained, containing 97% of **2m** and 3% of **9** (NMR analysis).

Ethyl 3,3-Dimethyl-2-phenylglycerate (10). A mixture of 2.5 g (22.36 mmol) of ethyl 3,3-dimethyl-2-phenylglycidate and 150 ml of 30% aqueous perchloric acid was allowed to stand at room temperature for 2 weeks, and extracted with two 150-ml portions of ether. The combined ether extracts were washed with 5% aqueous bicarbonate, dried, and concentrated. The oily residue was purified by column chromatography to yield 0.963 g of **10** (35%), a viscous oil which crystallized on standing: NMR (Me_2SO-d_6) 7.2–7.9 (m, 5 H), 5.50 (s, 1 H), 4.42 (s, 1 H), 4.24 (q, J = 7 Hz, 2 H), 1.22 (tr, J = 7 Hz, 3 H), 1.17 (s, 3 H), and 1.10 ppm (s, 3 H). The signals at 5.50 and 4.42 ppm disappeared upon addition of D_2O.

Rearrangement of 10. A 440-mg sample was treated with 0.88 ml of FSO_3H for 3 min at 0 °C and worked up as above to yield 353 mg (87%) of ethyl 3,3-dimethyl-3-phenylpyruvate (**2m**): NMR (CCl_4) 7.18 (s, 5 H), 4.0 (q, J = 7 Hz, 2 H), 1.58 (s, 6 H), and 1.07 ppm (tr, J = 7 Hz, 3 H); mass spectrum m/e 220 (M^+), 119 (base peak), 91, and 77. It gave a 2,4-DNP derivative in 63% yield after recrystallization: mp 153.5–154.5 °C; NMR ($CDCl_3$) 13.9 (br s, 1 H), 9.15 (d, J = 2 Hz, 1 H), 8.52 and 8.35 (d of d, J = 2, 9 Hz, 1 H), 8.16 (d, J = 9 Hz, 1 H), 7.28 (s, 5 H), 4.12 (q, J = 7 Hz, 2 H), 1.72 (s, 6 H), and 0.95 ppm (tr, J = 7 Hz).

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.

Ethyl 3,3-Diphenylglycerate (12). A solution of 2.000 g of ethyl 3,3-diphenylglycidate in 75 ml of 30% perchloric acid in 60% aqueous tetrahydrofuran was heated with stirring in an oil bath at 65 °C for 25 min, diluted with 300 ml of water, and extracted with two 100-ml portions of ether. The combined ether extracts were washed with 50-ml portions of 5% aqueous bicarbonate and water, dried, and concentrated to yield an oil which crystallized on standing. Recrystallization from aqueous ethanol yielded 900 mg (38%) of **12** as white crystals: mp 131–132 °C; NMR ($CDCl_3$) 7.05–7.78 (m, 10 H), 5.08 (s, 1 H), 3.98 (q, J = 7 Hz, 2 H), 3.35–3.40 (br, 2 H, disappeared in D_2O), and 0.92 ppm (tr, J = 7 Hz, 3 H).

Rearrangement of 12. A 200-mg sample of **12** was treated with 0.34 ml of FSO_3H at 0 °C for 3 min. After the usual workup the crude product was purified by preparative TLC, developing the plates twice with 5% ethyl acetate in petroleum ether. Two bands were seen under uv light and yielded 14 mg (12%) of ethyl 3,3-diphenylpyruvate: NMR ($CDCl_3$) 7.27 (s, 10 H), 5.91 (s, 1 H), 4.11 (q, J = 7 Hz, 2 H), and 1.11 ppm (tr, J = 7 Hz, 3 H) (an additional small singlet at 10.32 and a triplet at 0.7 ppm revealed the presence of the enol tautomer); mass spectrum m/e 268 (M^+), 195, 167 (base peak), and 77. These spectra were superimposable onto those of the major product of the boron trifluoride rearrangement of ethyl 2,3-diphenylglycidate.[1]

Ethyl 2-Methyl-3-phenylglycerate (13). A solution of 4 g of ethyl (*E*)-2-methylcinnamate and 4.65 g of *m*-chloroperoxybenzoic acid in 100 ml of chloroform was refluxed for 25 h and washed with 10% aqueous sodium sulfite and with 5% aqueous bicarbonate. The organic layer was dried and concentrated to yield 4.1 g (95%) of ethyl (*E*)-2-methyl-3-phenylglycidate, an oil: NMR (CCl_4) 7.3 (s, 5 H), 4.3 (s, 1 H), 4.2 (q, J = 7 Hz, 2 H), 1.27 (tr, J = 7 Hz, 3 H), and 1.25 ppm (s, 3 H).

A mixture of 2 g of this product and 100 ml of 30% aqueous sulfuric acid was stirred for 24 h at room temperature, and extracted with two 100-ml portions of ether. The combined ether extracts were washed with 5% sodium bicarbonate, dried, and concentrated to yield a viscous oil. After purification by column chromatography, there was obtained 1.5 g (69%) of a mixture of *threo*- and *erythro*-**13**, an oil: NMR (Me_2SO-d_6) 7.1–7.62 (m, 5 H), 4.6–5.6 (broad, 2 H, disappeared upon the addition of deuterium oxide), 4.82 (s, 1 H), 4.78 (s, 1 H), 4.18 and 4.11 (each a q, J = 7 Hz, 2 H), 1.24 and 1.18 (each a tr, J = 7 Hz, 3 H), 1.18 and 1.05 ppm (each a s, 3 H).

Rearrangement of 13. A 500-mg sample of **13** was treated with fluorosulfonic acid at 0 °C for 10 min. After workup the product (435 mg) had the NMR spectrum (CCl_4) of ethyl 2-phenylacetoacetate as a mixture of the ketonic (76%) and enolic (24%) forms: NMR (CCl_4) 14.17 (br s, 1 H), 7.08–7.50 (m, 5 H), 4.13 (q, J = 7 Hz, 2 H), 1.80 (s, 3 H), and 1.13 ppm (tr, J = 7 Hz, 3 H) for the enol; 7.08–7.50 (m, 5 H), 4.61 (s, 1 H), 4.15 (q, J = 7 Hz, 2 H), 2.07 (s, 3 H), and 1.22 ppm (tr, J = 7 Hz, 3 H) for the keto tautomer. Preparative TLC yielded 280 mg of this product and 101 mg of material with broad NMR signals, which appeared to be polymeric in nature.

Ethyl 2,3-Diphenylglycerate (14). A solution of 2 g of ethyl (*E*)-2,3-diphenylglycidate in 75 ml of 30% by weight perchloric acid in 65% aqueous tetrahydrofuran was heated in an oil bath with stirring at 65–70 °C for 15 min. The reaction mixture was poured onto 50 g of ice, diluted with 200 ml of water, and extracted with three 50-ml portions of ether. Washing the combined ether extracts with 5% aqueous bicarbonate followed by drying and evaporation of the solvent yielded 1.4 g of a semisolid residue. Crystallization from carbon tetrachloride yielded 330 mg (15.5%) of **14** as white needles, mp 135–137 °C. After recrystallization from benzene, the mp was 139–139.5 °C; NMR ($CDCl_3$) 7.17–7.77 (m, 10 H), 5.5 (br s, 1 H), 4.44 (q, J = 7 Hz, 2 H), 4.12 and 3.0 (each a broad s which disappeared in the presence of D_2O, 2 H), and 1.37 ppm (tr, J = 7 Hz, 3 H). Only one of the two possible diastereoisomers was obtained, judging from the NMR spectrum. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; Found: C, 71.35; H, 6.33.

Rearrangement of 14. A 192-mg sample of **14** was treated with FSO_3H (0.32 ml) at 0 °C for 3 min and worked up as described above. NMR showed the crude product to consist of 60% keto and 40% enol tautomers of ethyl 3,3-diphenylpyruvate. However, purification by preparative TLC on silica gel (5% ethyl acetate in petroleum ether) yielded 7.5 mg (6%) of benzophenone in addition to 153 mg (85%) of ethyl 3,3-diphenylpyruvate: NMR ($CDCl_3$) 7.27 (s, 10 H), 5.91 (s, 1 H), 4.11 (q, J = 7 Hz, 2 H), and 1.1 ppm (tr, J = 7 Hz, 3 H) for the keto tautomer; 8.5 (s, enol H), 7.27 (s, 10 H), 3.98 (q, J = 7 Hz, 2 H), and 0.72 ppm (tr, J = 7 Hz, 3 H) for the enol form. The keto:enol ratio was 90:10. This NMR was superimposable onto that of the major product of the boron trifluoride rearrangement of ethyl 2,3-diphenylglycidate. The mass spectrum had peaks at m/e 268 (M^+), 195, 167 (base peak), and 77.

Ethyl 2-Hydroxy-3-phenyl-3-azidobutyrate (15). A mixture of 35 g of sodium azide, 50 ml of water, and 100 ml of ether was treated with 30 ml of concentrated sulfuric acid, maintaining the temperature below 10 °C. The ether layer was dried over $CaCl_2$ and distilled. In

65 ml of this HN_3 solution, 6 g of Ih and 60 mg of *p*-toluenesulfonic acid were allowed to stand at room temperature for 3 days. After concentration under vacuum, 50 ml of ether was added, and the solution was washed with 25 ml of water, 25 ml of saturated aqueous $NaHCO_3$, and 25 ml of aqueous NaCl and dried.

The crude product, **15**, was used in further reactions. A sample distilled bulb-to-bulb at 75 °C (0.07 Torr). This material was contaminated with a trace of **4h** (seen by NMR). Ir showed the characteristic signal at 2150 cm^{-1}. NMR (CCl_4) 7.10–7.45 (m, 5 H), 4.26 and 4.20 (each a s, 1 H), 4.02 (q, J = 7 Hz, 2 H), 3.65 (1 H, disappeared in the presence of D_2O), 1.80 and 1.75 (each a s, 3 H), 1.08 and 0.90 ppm (each a tr, 3 H). The ratio of diastereomers was 1:3.9.

Reaction of 15 with Nitrosonium Tetrafluoroborate. A solution of 665 mg of **15** and 1.25 g of $NO^+BF_4^-$ in 20 ml of benzene was refluxed for 6 h, concentrated under vacuum, treated with water, and extracted with ether.[10] After drying and concentration, NMR analysis showed 18% **3h**, 10% **4h**, and a trace of **2h**. No starting material remained.

No reaction was observed at room temperature for up to 60 h when **15** was treated with $NO^+BF_4^-$ in benzene, acetonitrile, or dimethoxyethane.

Ethyl 2-Hydroxy-3-chloro-3-phenylbutyrate (17). A 6.39-g sample of Ih cooled at −190 °C was treated with 75 ml of HCl-saturated ether, allowed to warm up to room temperature with stirring, and kept for 18 h. After concentration under vacuum, 50 ml of ether were added and the solution was washed with 25 ml of saturated aqueous NaCl, 25 ml of saturated $NaHCO_3$, and 25 ml of saturated NaCl, dried over $MgSO_4$, and concentrated to yield 6.50 g of **17**, mp 53–59 °C, a mixture of diastereomers (1:1). Anal. Calcd for $C_{12}H_{15}ClO_2$: C, 59.42; H, 6.22; Cl, 14.60. Found: C, 59.44; H, 6.22; Cl, 14.58.

NMR (CCl_4) 7.2–7.6 (m, 5 H), 4.50 and 4.34 (each a d, J = 8 Hz, 1 H), 4.12 and 3.96 (each a q, J = 7 Hz, 2 H), 3.15 and 2.99 (each a d, J = 8 Hz, 1 H), and 1.15 and 0.95 ppm (each a tr, J = 7 Hz, 3 H).

Reaction of Ethyl 2-Methyl-3-phenyl-2-hydroxy-3-butenoate (4m) with Fluorosulfonic Acid. An 82-mg sample of **4m** was treated with 0.178 ml of FSO_3H at 0 °C for 3 min and poured onto a mixture of ice, water, and 20 ml of CCl_4, and the aqueous layer was extracted with 20 ml of ether. After washing each of the organic extracts with 20 ml of 5% aqueous sodium bicarbonate, they were combined, dried, and concentrated to yield 60 mg of a semisolid product which was analyzed by NMR to contain 70% **3m**, 30% **5m**, and a trace of **2m**.

Reaction of Ethyl 3-Phenyl-2-hydroxy-3-butenoate (4e) with Fluorosulfonic Acid. At 0 °C for 3 min, 90 mg (0.384 mmol) of **4e** was treated with 0.18 ml of FSO_3H. The mixture was poured onto a mixture of ice, water, and 20 ml of CCl_4. The aqueous phase was extracted again with 10 ml of chloroform and the organic layers were combined, washed with two 15-ml portions of 5% aqueous $NaHCO_3$, dried, and concentrated to yield 50 mg of a semisolid residue, which contained 45.5% **3e**, 7.5% **2e**, and 47% **5e** (NMR).

Reaction of Ethyl 2,3-Diphenyl-2-hydroxy-3-butenoate (4f) with Boron Trifluoride. Boron trifluoride was bubbled through a solution of 40 mg of **4f** in 2 ml of carbon tetrachloride for 10 min at 28 °C. After quenching the reaction with aqueous sodium chloride, the mixture was extracted with 10 ml of carbon tetrachloride and with 10 ml of chloroform. The combined organic phases were washed with 5% aqueous bicarbonate, dried, and concentrated. The NMR spectrum of the product (90% yield) was superimposable onto that of 2-phenyl-3-carbethoxyindene (**6**).

Reaction of Halohydrins with Silver Salts. A mixture of 200 mg of the halohydrin and ca. 1.5 equiv of silver salt in 20 ml of solvent was stirred in the dark. The spent silver salt was filtered over Celite and the filtrate was concentrated and analyzed by NMR (Tables IV and V).

Ethyl 2-Hydroxy-2-methyl-3-chloro-3-phenylpropionate (18). A solution of 500 mg of ethyl (*E*)-2-methyl-3-phenylglycidate in 20 ml of hydrogen chloride saturated ether was allowed to stand at room temperature for 1 h, washed thrice with water, dried, and concentrated to yield 565 mg of **18**. The major isomer (ca. 90%) had NMR (CCl_4) at 7.10–7.60 (5 H), 5.00 (s, 1 H), 4.05 (q, J = 7 Hz, 2 H), 3.50 (br, 1 H), 1.51 (s, 3 H), and 1.16 ppm (tr, J = 7 Hz, 3 H). The minor isomer had its corresponding signals at 7.10–7.60, 5.20, 4.20, 3.50, 1.15, and 1.16 ppm, respectively.

Ethyl 2-Hydroxy-2-methyl-3-bromo-3-phenylpropionate (20). A solution of 200 mg of ethyl 2-methyl-3-phenylglycidate in 7 ml of hydrogen bromide saturated ether was allowed to stand at room temperature for 44 h. After dilution with 15 ml of ether, it was washed thrice with water, dried, and concentrated to yield 787 mg of an oil, a mixture of the two diastereoisomers of **20**: NMR (CCl_4) 7.00–7.50 (m, 5 H), 5.05 (s, 1 H), 3.94 (q, J = 7 Hz, 2 H), 3.58 (br, 1 H), 1.53 (s, 1 H), and 1.07 (tr, J = 7 Hz, 3 H) for the major isomer (80%), and 7.00–7.50 (m, 5 H), 5.30 (s, 1 H), 4.07 (q, J = 7 Hz, 2 H), 3.58 (br, 1 H), 1.72 (s, 3 H), and 1.24 ppm (tr, J = 7 Hz, 3 H) for the minor isomer (20%).

Ethyl 2-Hydroxy-2-methyl-3-chloro-3-phenylbutyrate (19). A solution of 250 mg of Im in 10 ml of HCl-saturated ether was allowed to stand for 26 h at room temperature, washed several times with water, dried, and concentrated to give a mixture of **4m** (16%) and **19** (84%) as a mixture of diasteisomers: NMR (CCl_4) 7.15–7.65 (m, 5 H), 4.02 and 4.12 (each a q, J = 7 Hz, 2 H), 3.56 (br, 1 H), 2.02 (s, 3 H), 1.38 (s, 3 H) and 1.16 ppm (q, J = 7 Hz, 3 H).

Ethyl 2-Hydroxy-2-methyl-3-bromo-3-phenylbutyrate (21). A solution of 250 mg of Im (mixture of *E* and *Z*) in 10 ml of HBr-saturated ether was refluxed for 2 h, washed with water, dried, and concentrated to yield a mixture of 21% **4m** and 79% **21** (a mixture of diastereoisomers). Similar results were obtained at room temperature for 1 h. The NMR of **21** (CCl_4) had signals at 7.1–7.8 (m, 5 H), 4.09 and 3.95 (each a q, J = 7 Hz, 2 H), 3.78 (br, 1 H), 2.29 and 2.30 (each a s, 3 H), 1.53 and 1.48 (each a s, 3 H), and 1.35 and 1.10 ppm (each a tr, J = 7 Hz, 3 H).

Acid Treatment of *tert*-Butyl 3-Methyl-3-phenylglycidate (27). A 200-mg sample of **27**[16] (mixture of diastereoisomers) in 20 ml of benzene was treated with BF_3 for 30 s at room temperature. The solution was washed with aqueous $NaHCO_3$ and saturated NaCl and dried over $MgSO_4$. The NMR (CCl_4) showed a mixture of **28** at 9.70 (d, J = 1.5 Hz, 1 H), 6.9–7.3 (5 H), 3.45 (q, d, J = 7 and 1.5 Hz, 1 H), and 1.35 ppm (d, J = 7 Hz, 3 H), and *tert*-butylbenzene at 6.9–7.3 (4 H) and 1.26 ppm (s, 12 H). This was proved by GLC against authentic samples. Using an internal standard of *p*-nitrotoluene, the two components were shown to have been formed in ca. 25% yield each. The remainder probably had polymerized, as in the reaction of the ethyl ester analogue Ih.[1]

***tert*-Butyl 3-Chloro-3-phenyl-2-hydroxybutyrate (24).** A 300-mg sample of **27** was treated at room temperature for 30 min with 10 ml of anhydrous ether saturated with HCl. After concentration under vacuum, addition of CCl_4, and concentration again, 345 mg of residue was obtained, which was a mixture of *threo*- and *erythro*-**24**. Pure samples of both diastereoisomers were obtained after fractional crystallization in several solvents. The isomer of mp 79–80 °C had NMR (CCl_4) at 7.67–7.10 (m, 5 H), 4.30 (d, J = 7 Hz, 1 H), 3.03 (d, J = 7 Hz, 1 H, exchanged in D_2O), 2.00 (s, 3 H), and 1.30 ppm (s, 9 H), and the isomer of mp 36–38 °C had NMR (CCl_4) at 7.33–7.17 (m, 5 H), 4.30 (d, J = 7 Hz, 1 H), 3.25 (d, J = 7 Hz, 1 H, exchanged in D_2O), 1.97 (s, 3 H), and 1.15 ppm (s, 9 H).

Reaction of 24 with Silver Carbonate. A mixture of 130 mg of **24**, 207 mg of silver carbonate, and 10 ml of benzene was refluxed for 23 h, cooled, and filtered through Celite. The filtrate was concentrated under vacuum and the residue analyzed by NMR in CCl_4. From the isomer of mp 79–80 °C, the mixture contained ca. 8% of **26**, 11% of **9**, 51% of **25**, 25% of *E*-**27** and 5% of *Z*-**27**. From the isomer of mp 36–38 °C the mixture contained 4% of **26**, 7% of **9**, 33% of **25**, 56% of *E*-**27**, and a trace of *Z*-**27**. The NMR spectra of the individual compounds in CCl_4 follow. **26:** 7.15–7.50 (m, 5 H), 5.40 (m, 1 H), 5.35 (m, 1 H), 4.80 (br, 1 H), 3.10 (br, OH), and 1.22 ppm (s, 9 H). **25;** 9.78 (s, 1 H), 7.15–7.55 (s, 5 H), 1.57 (s, 3 H), and 1.45 ppm (s, 9 H). *E*-**27:**[19] 7.20–7.55 (m, 5 H), 3.18 (s, 1 H), 1.72 (s, 3 H), and 1.50 ppm (s, 9 H). *Z*-**27:**[19] 7.20–7.50 (m, 5 H), 3.38 (s, 1 H), 1.68 (s, 3 H), and 1.05 ppm (s, 9 H). The phenylhydrazone of **25** had mp 151 °C; mass spectrum *m/e* 324, 267, 223 (base peak), 130, 92, and 77; NMR (Me_2CO-d_6) 7.65 (s, 1 H), 7.10–7.43 (m, 9 H), 2.75 (s, 1 H, exchanged with D_2O), 1.73 (s, 3 H), and 1.43 ppm (s, 9 H).

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Registry No.—*erythro*-**1e**, 59069-63-5; *threo*-**1e**, 59069-64-6; *erythro*-**1f**, 59069-65-7; *threo*-**1f**, 59069-66-8; **1h**, 38082-38-1; *erythro*-**1m**, 59069-67-9; *threo*-**1m**, 59069-68-0; *erythro*-**1m**-d_3, 59069-69-1; *threo*-**1m**-d_3, 59069-70-4; **2f**, 38491-43-9; **2m**, 54934-36-0; **2m** 2,4-DNP, 59069-71-5; **3f**, 38491-44-0; **4e**, 59069-72-6; **4f**, 59069-73-7; **4m**, 59069-74-8; **5e**, 59069-75-9; **5m**, 1575-48-0; **6**, 59069-76-0; **8**, 38491-45-1; **10**, 59069-77-1; **12**, 5461-98-3; *erythro*-**13**, 40707-70-8; *threo*-**13**, 59069-78-2; **14**, 59069-79-3; *erythro*-**15**, 59069-80-6; *threo*-**15**, 59069-81-7; *erythro*-**17**, 59069-82-8; *threo*-**17**, 59069-83-9; *erythro*-**18**, 59069-84-0; *threo*-**18**, 59069-85-1; *erythro*-**19**, 59069-86-2; *threo*-**19**, 59069-87-3; *erythro*-**20**, 59069-88-4; *threo*-**20**, 59069-89-5; *erythro*-**21**, 59069-90-8; *threo*-**21**, 59069-91-9; **22**, 59069-92-0; *erythro*-**24**, 59069-93-1; *threo*-**24**, 59069-94-2; **25**, 59069-95-3; **25** phenylhydrazone, 59069-96-4; **26**, 59069-97-5; *E*-**27**, 21309-21-7; *Z*-**27**,

21309-20-6; *erythro*-**28**, 93-53-8; *E*-Ie, 19464-94-9; If, 59069-98-6; Ih, 77-83-8; *E*-Im, 59069-99-7; *Z*-Im, 59070-00-7; Im-d_3, 59070-01-8; ethyl 3,3-dimethyl-2-phenylglycidate, 59070-02-9; ethyl 3,3-diphenylglycidate 5449-40-1; ethyl 3,3-diphenylpyruvate 6362-64-7; ethyl (*E*)-2-methylcinnamate, 7042-33-3; ethyl (*E*)-2 methyl-3-phenylglycidate, 7141-24-4; ethyl 2-phenylacetoacetate, 5413-05-8; ethyl 2-phenylacetoacetate enol, 59070-03-0; ethyl (*E*)-2,3-diphenylglycidate, 7042-27-5; ethyl 3,3-diphenylpyruvate enol, 59070-04-1.

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Valence Photoisomerization of 1-Ethoxycarbonyl-1*H*-azepine and Its Thermal Reversion. Quantitative Aspects Including Energy Surface Relationships

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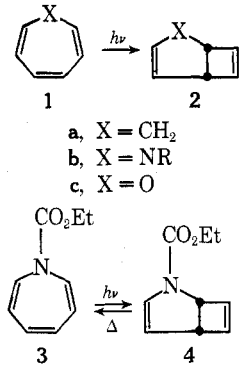
Photolysis of 1-ethoxycarbonyl-1*H*-azepine (**3**) at 325–385 nm gives quantitatively the valence isomer, 2-ethoxycarbonyl-2-azabicyclo[3.2.0]hepta-3,6-diene (**4**). The quantum yield in benzene is 0.013, virtually unchanged in other solvents including *n*-propyl bromide and with the addition of triplet quenchers. Sensitization with fluorenone, benzophenone, or valerophenone does not lead to valence isomerization. Azepine **3** acts as a quencher of the photoelimination of valerophenone ($k_q = 7.0 \times 10^9$ M^{-1} s^{-1}) and the phosphorescence of biacetyl ($k_q = 5.3 \times 10^8$ M^{-1} s^{-1}). Laser photolysis at 457.9 nm affects isomerization **3** → **4** with a quantum efficiency of 0.013. On the basis of absorption, sensitization, and quenching data for **3**, energies of low-lying excited states are estimated (E_{S_1} = 60 ± 1 kcal/mol and E_{T_1} = 55 ± 1 kcal/mol). Pyrolysis of **4** gives **3** in a clean, exothermic, first-order reaction at 113–143 °C in diglyme-d_{14} (E_a = 28.7 kcal/mol, $A = 10^{12.3}$ s^{-1}) or in hexadecane ($k = 4.60 \times 10^{-4}$ s^{-1}, 127.5 °C). A mechanism for **3** → **4** and related photochemical isomerizations is suggested, with emphasis on the proximity of ground and excited state potential surfaces at diradical or biradicaloid geometries. For cyclic triene systems, charge separation in diradical species appears to be important in facilitating photochemical ring closure and thermal back reaction.

The photochemistry of 1,3,5-cycloheptatriene (**1a**), its heterocyclic analogues, 1*H*-azepine (**1b**) and oxepin (**1c**), and their derivatives has received considerable attention.[1] A reaction of general importance is valence photoisomerization to bicyclic dienes **2**; in many cases the process is thermally reversible. We became interested in the photoisomerization of 1-ethoxycarbonyl-1*H*-azepine (**3**), since the reported[1d] behavior of this system showed promise for the storage and conversion of radiant energy (in principle, a portion of solar energy). In particular, photolysis of **3**, which absorbs light in the visible, gives **4** cleanly and photochromatically (with bleaching). Photoisomer **4** is kinetically stable but reverts to **3** in a thermal reaction which is uncatalyzed and apparently exothermic.[1d] We wish to provide quantitative details concerning this isomerization of a sort not generally available for the cyclic trienes. The data allow characterization of interconverting states and suggestions for pathways for photochemical and thermal reaction.



Results

The ultraviolet spectrum of **3**[2] displays a weak transition at 330 nm. This absorption, which is blue shifted in polar solvent and probably n,π^* in character,[3] tails into the visible with onset at about 480 nm and gives **3** its orange color. Luminescence was not observed for **3**, either in benzene at room temperature or in EPA glass at 77 K. Irradiation of **3** at 325–385 nm gave **4** without the appearance of side products (>97% yield by GLC and NMR). Quantum yields for isomerization as a function of solvent and the presence of additives are shown in Table I. Notably, the photolysis was not appreciably altered by (1) moderate concentrations of potential