in varying amounts. The analytical sample was obtained by preparative glpc on a 10-ft 20% SE-30 on Chromosorb column at 165°: nmr ($CDCl_3$) δ 1.90 (s, 6, CH_3), 5.92 (s, 1, =CH), 7.3 (s, 5, PhS).

Anal. Calcd for $C_{10}H_{12}S$: C, 73.11; H, 7.36. Found: C, 72.99; H, 7.31.

Phenylthiomethylenecyclohexane (18d).—Distillation of the residue afforded 2.62 g (65%) of **18d**: bp 133° (1.1 mm); nmr ($CDCl_3$) δ 1.58 (br s, 6, CH_2), 2.3 (m, 4, allylic CH_2), 5.90 (s, 1, C=CH), 7.30 (s, 5, Ph).

Anal. Calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89. Found: C, 76.22; H, 7.74.

1-Phenylthio-2,3,3-trimethyl-1-butene (18e).—Fractional distillation of the crude product from reaction of pinacolone with **2** resulted in the recovery of 1.7 g (45%) of **17** and isolation of 2.1 g (55%) of **18e**, bp 110° (1.2 mm), as a mixture of cis and trans isomers. The mixture was *ca.* 3:2 by nmr analysis of the crude product. No assignment is being made at present as to which isomer is the major component and which is the minor component. Major component: nmr ($CDCl_3$) δ 1.28 (s, 9, *tert*-Bu), 1.85 (s, 3, CH_3), 5.90 (m, 1, C=CH), 7.28 (m, 5, SPh). Minor component: nmr ($CDCl_3$) δ 1.13 (s, 9, *tert*-Bu), 1.82 (s, 3, CH_3), 6.03 (s, 1, C=CH), 7.28 (m, 5, SPh).

A sample of the mixture was purified by preparative glpc on Carbowax at 190°.

Anal. Calcd for $C_{13}H_{18}S$: C, 75.66; H, 8.79. Found: C, 75.51; H, 8.64.

3-Phenylthiomethylene-1-cyclohexene (18f).—Distillation of the crude product afforded 3.0 g (75%) of **18f** as a mixture of cis and trans isomers: bp 131° (0.55 mm); nmr ($CDCl_3$) δ 1.75 (m, 2, CH_2), 2–2.7 (m, 4, allylic CH_2), 5.8–6.8 (m, 3, C=CH), 7.3 (m, 5, SPh).

The analytical sample of the mixture was obtained by preparative glpc on Carbowax at 190°.

Anal. Calcd for $C_{13}H_{14}S$: C, 77.17; H, 6.97. Found: C, 76.95; H, 6.87.

2-Phenylthiomethyleneadamantane (18g).—The nmr of the crude product indicated an 80% yield of **18g**. Recrystallization from absolute ethanol gave the analytical sample: mp 65°; nmr ($CDCl_3$) δ 1.90 (s, 12, CH_2 and bridgehead CH), 2.58 (br s, 1, allylic CH), 3.16 (br s, 1, allylic CH), 5.80 (s, 1, C=CH), 7.20 (s, 5, SPh).

Anal. Calcd for $C_{17}H_{20}S$: C, 79.63; H, 7.86. Found: C, 79.58; H, 7.69.

Registry No.—**1**, 33521-83-4; **2**, 30536-77-7; **6f**, 18689-34-4; **6g**, 33536-50-4; **7**, 33521-85-6; **8**, 33521-86-7; **14**, 33536-51-5; **18c**, 13640-71-6; **18d**, 33521-88-9; *cis*-**18e**, 33536-52-6; *trans*-**18e**, 33536-53-7; *cis*-**18f**, 33536-54-8; *trans*-**18f**, 33536-55-9; **18g**, 33521-89-0; diethyl 2-phenyl-2-dimethylaminovinylphosphonate, 33521-90-3; methoxymethylethyldimethylsilane, 33521-91-4.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work.

The Lithium Salt Catalyzed Rearrangement of Epoxides. II. Glycidic Esters[1,2]

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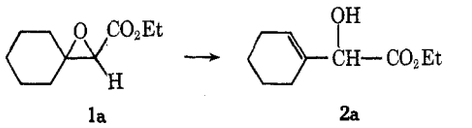
The rearrangement of glycidic esters catalyzed by lithium salts and other Lewis acids has been explored. Lithium halide catalyst leads to a mixture of products derived from both α and β cleavage of the oxirane. Lithium perchlorate causes β cleavage of 3,3-disubstituted glycidic esters, with subsequent elimination yielding the 2-hydroxy-3-alkenoic acid ester product. Catalytic hydrogenation gives the glycolic ester, which on oxidation affords the corresponding glyoxylic ester. Attempted isomerization of a 2-hydroxy-3-alkenoate by ethanolic sodium ethoxide gave instead double bond reduction. The presumed intermediate glyoxylic ester is similarly reduced under these conditions.

The availability of glycidic esters from the Darzens condensation is an attractive feature for synthesis, and consequently we were interested in examining the behavior of these materials under the conditions of lithium salt catalyzed epoxide rearrangement.[2,3] Simple alkyl-substituted epoxides rearrange to carbonyl compounds with these catalysts, *via* either hydrogen or alkyl migration. Glycidic esters can undergo epoxide scission at either the α or β carbon, and a sizable number of further products from these ring-opened intermediates can be envisioned.

Earlier studies using protic or Lewis acid catalysts have in fact led to a variety of rearrangement products. Boron trifluoride is an effective catalyst for phenyl-substituted glycidates, where, depending on the starting material structure, either α-keto ester[4] products or products of carboethoxy migration[5] may result. Hydrogen chloride at elevated temperature has been used to convert ethyl 3,3-diphenylglycidate to ethyl diphenylglyoxylate,[6] whereas sulfuric acid is reported[7] to cause rearrangement of compound **1a** to **2a** as shown in



1a **2a** (1)

eq 1. A similar result using hydrochloric acid catalyst has been noted by Camps and coworkers.[8] In contrast, ethyl dimethylglyoxylate was obtained in low yield in acid treatment of 3-methyl-2,3-epoxybutanoate.[9]

Also relevant to the present study is the report that Grignard reagents in reaction with glycidic esters yield exclusively α addition, α-hydroxy product,[10] presumably by initial rearrangement to the glyoxylate ester followed by addition. This mechanism is supported by the fact that Darzens[11] has actually isolated the α-

(1) Supported in part by the National Science Foundation, GP-6043.

(2) Part I: B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **93**, 1693 (1971).

(3) B. Rickborn and R. M. Gerkin, *ibid.*, **90**, 4193 (1968).

(4) H. O. House, J. W. Blaker, and D. A. Madden, *ibid.*, **80**, 6386 (1958).

(5) S. P. Singh and J. Kagan, *ibid.*, **91**, 6198 (1969).

(6) F. F. Blicke and J. A. Faust, *ibid.*, **76**, 3156 (1954).

(7) W. S. Johnson, J. S. Belew, L. J. Chinn, and R. H. Hunt, *ibid.*, **75**, 4995 (1953).

(8) F. Camps, J. Castells, and J. Pascual, *J. Org. Chem.*, **31**, 3510 (1966).

(9) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).

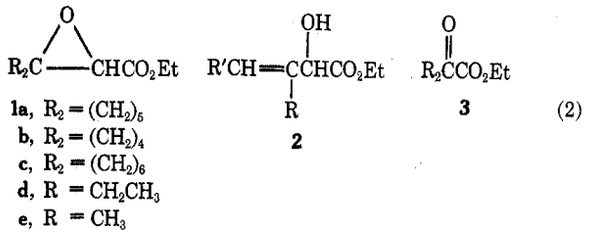
(10) E. P. Kohler, N. K. Richtmeyer, and W. F. Hester, *J. Amer. Chem. Soc.*, **53**, 205 (1931).

(11) G. Darzens, *C. R. Acad. Sci.*, **152**, 443 (1911).

keto ester (in low yield) from the addition of organozinc reagent to ethyl 3,3-dimethylglycidate.

Results and Discussion

The rearrangement of some β-dialkylglycidic esters catalyzed by lithium and magnesium halides is shown in eq 2 and the results are presented in Table I.



1a, $R_2 = (CH_2)_5$
b, $R_2 = (CH_2)_4$
c, $R_2 = (CH_2)_6$
d, $R = CH_2CH_3$
e, $R = CH_3$

(2)

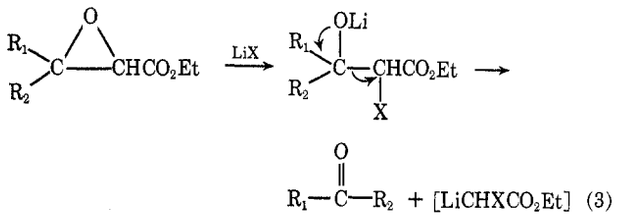
TABLE I
METAL HALIDE CATALYZED REARRANGEMENT OF GLYCIDIC ESTERS[a]

Ester	Salt	Product distribution, % 2	3	Yield,[b] %	Time,[c] hr
1a	LiBr·HMPA	94	6	26	70
	LiI	60	40	14	7
1b	LiBr·HMPA	10	90	65	3
	LiI	4	96[d]	17	0.6
1c	LiBr·HMPA	51	49	36	216
	LiI	12	88	36	1.5
1d	MgI_2	87	13	52	44
1e	LiBr·HMPA	0	100	8	22
	LiI	0	100	37	1
	LiI·HMPA	6	94	51	3.3
	LiI[e]	0	100	33	40
	$MgBr_2 \cdot Et_2O$[f]	39	61		0.5
	$MgBr_2$[f]	33	67	66	0.5
	$MgCl_2$·HMPA[g]	35	65[d]	46	44
	MgI_2	8	92	82	1.5

[a] Unless otherwise noted, the reactions were carried out in benzene solvent with [salt] = 0.21 and $[ester]_{init} \doteq 0.35$. [b] Yields were determined by vpc using an inert internal standard. [c] Approximate time required for disappearance of the starting glycidic ester. [d] A small amount of unidentified product, of approximately the same retention time as **2**, was formed in this run. [e] CH_2Cl_2 solvent. [f] 0.1 *M*. [g] 0.35 *M*.

The products **2** and **3** both arise from cleavage of the oxirane ring at the β carbon, followed by elimination or hydrogen migration. Both products could arise by a carbonium ion process, or might involve an intermediate halohydrin salt. Evidence favoring the latter mechanism in the LiBr reaction of alkyl-substituted epoxides has been presented earlier.[2] Attempts to further delineate this question using glycidic esters with a secondary (as opposed to tertiary) β carbon have not given tractable products, although facile reaction mitigates against a carbonium ion process.

Lithium bromide, solubilized with 1 mol of hexamethylphosphoramide (HMPA), gives at best moderate yields of rearranged material, and in several instances (Table I) this material is a mixture of both **2** and **3**. Other metal halides were explored in an effort to increase the yield or improve the selectivity of the rearrangement process. The use of very hygroscopic LiI (which does not require HMPA for solubility) in general leads to a shorter reaction time and an increase in the glyoxylate product, **3**, relative to **2**. The overall yield, however, does not seem to vary in a uniform manner. The yield is directly related to the relative amounts of α- and β-cleavage processes that occur; it appears that α cleavage of the oxirane leads to reverse Darzens condensation, as shown in eq 3.[12] Thus in the reaction of **1a** with LiBr·HMPA and LiI, 12 and 34%



(3)

of cyclohexanone, respectively, was recovered from the reaction mixture. Similarly in the reaction of **1c**, cycloheptanone accounted for at least 22 (LiBr·HMPA) and 44% (LiI) of the starting glycidic ester. Fragmentation products were not pursued with the other systems examined. However, it seems reasonable to conclude from the yield data in Table I that the lithium halide reaction does not exhibit significant regioselectivity, *i.e.*, preference for reaction by α or β cleavage. It should be noted that the amounts of rearrangement and fragmentation may not be directly correlatable to the extents of β- and α-halide attack, since the halohydrin lithium salt may reclose to epoxide. This kind of rapid prior equilibrium has been established in the reaction of simple aliphatic epoxides.[2] In contrast, there is evidence that a magnesium salt of a halohydrin may not revert to epoxide as readily as it is rearranged.[13] We have examined one system, **1e**, with both lithium and magnesium halides (see Table I) and find that the latter in general lead to enhanced rearrangement yields (more β cleavage) but diminished selectivity in the rearrangement product mixture.

Control experiments with **2a** and a mixture of **2b** and **3b** established that the rearrangement products are stable under the reaction conditions; *i.e.*, they are neither interconverted nor transformed to other materials.

The lithium perchlorate catalyzed rearrangement of simple epoxides occurs by a carbonium ion mechanism.[2] A similar process with a glycidic ester should lead to exclusive β cleavage. In fact, the $LiClO_4$ reaction proved to be quite regioselective and hence synthetically useful. Results are given in Table II. The overall

TABLE II
REARRANGEMENT OF GLYCIDIC ESTERS BY $LiClO_4$ AND H_2SO_4

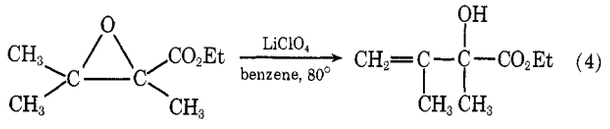
Ester	Catalyst	Product distribution, % 2	3	Yield, %	Time, hr
1a	$LiClO_4$	99.5	0.5	95	2.8
1b	$LiClO_4$	92	8	82	0.25
1c	$LiClO_4$	99	1	98	0.04
1e	$LiClO_4$	66	34	58	0.25
1a	H_2SO_4	100	0	70	2
1b	H_2SO_4	96	4	43	0.05
1c	H_2SO_4	100	0	54	0.05
1e	H_2SO_4	60	40	35	0.5

yields range from good to excellent, and, for the three spiro compounds examined, there is observed highly

(12) Related "dealdolization" is known to occur in some instances under Darzens condensation conditions; see F. W. Bachelor and R. K. Bansal, *J. Org. Chem.*, **34**, 3600 (1969).
(13) H. O. House, *J. Amer. Chem. Soc.*, **77**, 5083 (1955).

selective formation of the allylic alcohol product **2**. Only in the case where elimination would involve abstraction of a primary proton (to give **2e**) is a significant quantity of α-keto ester formed. In general, the $LiClO_4$ catalyzed reaction is faster than a comparable metal halide catalyzed rearrangement. The relative rates of the various spiro systems with $LiClO_4$ (Table II) is as anticipated for a carbonium ion process,[14] *i.e.*, with the six-membered ring reacting slower than either the five- or seven-membered glycidate.

Also in keeping with the carbonium ion mechanism, systems lacking the tertiary β center, *e.g.*, ethyl 2,3-epoxybutyrate, fail to react at all with $LiClO_4$. Similarly, no evidence for α cleavage is observed; no ketone fragmentation product could be detected in the reactions of **1a** and **1c**. One system containing both α and β tertiary centers was examined (**4**), and again exclusive β cleavage was observed, leading to **5** in essentially quantitative yield.[15] Control experiments again established that the rearrangement products (Table II) were not interconverted.



(4)

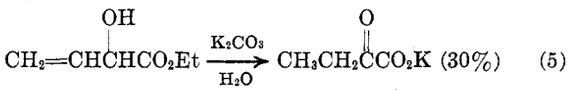
4 **5**

For purposes of comparison with the $LiClO_4$ catalyzed reaction, the rearrangement of the same glycidic esters by sulfuric acid in ether was examined. The data are also shown in Table II. The ratio of products **2** and **3** is quite similar for both catalysts, with sulfuric acid showing somewhat higher selectivity for **2**. However, the overall yields of rearrangement products were uniformly higher using $LiClO_4$.

The preference for formation of allylic alcohol product **2** in the $LiClO_4$ and protic acid catalyzed rearrangements is likely a result of the unfavorable electronic situation of the transition state leading to **3**. The same factor that prevents α cleavage of the glycidic ester, *i.e.*, generation of a positive charge adjacent to the ethoxycarbonyl group, must also come into play in the transition state for rearrangement of the β-cleaved intermediate. It is worth noting that allylic alcohol products were never observed in the lithium salt rearrangements of alkyl-substituted epoxides.[2]

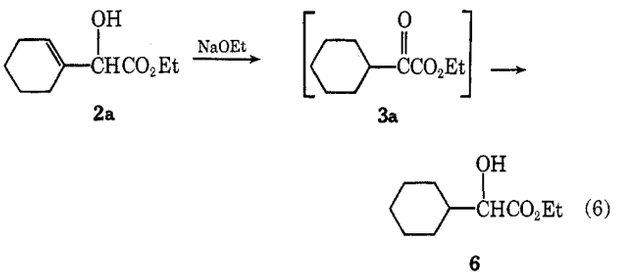
A high-yield synthesis of glyoxylic esters (**3**) using glycidic ester starting materials is accomplished by subjecting the $LiClO_4$ rearrangement product mixture to catalytic hydrogenation (to give ethyl glycolates) followed by chromic acid oxidation to **3**. For the synthesis of β-disubstituted glyoxylic esters, this procedure compares quite favorably with other methods in the literature.[16]

Rambaud[17] has reported that mild base treatment can effect the rearrangement shown in eq 5.



(5)

In an effort to convert **2a** directly to the glyoxylic ester **3a**, it was treated with sodium ethoxide in refluxing ethanol. A rather slow reaction occurred giving exclusively the glycolic ester **6** (eq 6). This unusual



(6)

ethoxide-induced reduction of a double bond presumably occurs *via* rearrangement to the glyoxylic ester **3a** followed by hydride donation from the alkoxide to yield **6**. The intermediacy of **3a** is given credence by a separate experiment in which it was shown that **3a** is in fact reduced to **6** under identical conditions, in a reaction that occurs considerably faster than the **2a** to **6** interconversion.[18]

Experimental Section

Glycidic Esters.—Ethyl chloroacetate, ethyl 2-bromopropionate, acetone, 3-pentanone, cyclopentanone, cyclohexanone, and cycloheptanone were used as obtained from commercial sources. The Johnson procedure[20] for the Darzens condensation gave the following materials in moderate to good yields: ethyl 1-oxaspiro[2.5]octane-2-carboxylate (**1a**), bp 90° (1.5 Torr);[20] ethyl 1-oxaspiro[2.4]heptane-2-carboxylate (**1b**), bp 72° (1 Torr);[21] ethyl 3-ethyl-2,3-epoxypentanoate (**1d**), bp 109–110° (25 Torr);[22] ethyl 3-methyl-2,3-epoxybutanoate (**1e**), bp 82–84° (25 Torr);[7] ethyl 2,3-dimethyl-2,3-epoxybutanoate (**4**), bp 83–87° (25 Torr).[23]

Ethyl 1-oxaspiro[2.6]nonane-2-carboxylate (**1c**) had bp 90° (1 Torr); nmr δ 1.25 (t, 3, J = 7 Hz), 1.3–1.9 (m, 13), 3.10 (s, 1), 4.10 ppm (q, 2, J = 7 Hz); ir (thin film) 860, 920, 1036, 1198, 1293, 1730, 1750,[24] 2845, 2915, and 2975 cm^{-1}.

(14) (a) H. C. Brown and M. Borokowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952); (b) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(15) Compound **4** proved to be inert to LiBr·HMPA, presumably because of steric hindrance to attack by bromide.

(16) Procedures for the formation of glyoxylic acids, esters, and closely related materials are found in (a) R. Rambaud, *Bull. Soc. Chim. Fr.*, 1317 (1941); (b) F. Kögl and A. J. Ultee, Jr., *Recl. Trav. Chim. Pays-Bas*, **69**, 1576 (1960); (c) J. D. Chanley, *J. Amer. Chem. Soc.*, **70**, 244 (1948); (d) F. F. Blicke and M. U. Tsao, *ibid.*, **66**, 1645 (1944); (e) J. Kollontisch, *J. Chem. Soc. A*, 456 (1966); (f) J. Lubochinsky and P. Maitte, *C. R. Acad. Sci., Ser. C.*, **263**, 732 (1966); (g) E. Baer and M. Kates, *J. Amer. Chem. Soc.*, **67**, 1482 (1945); (h) J. W. Cornforth, *Org. Syn.*, **31**, 59 (1951); (i) E. Zbiral and E. Werner, *Tetrahedron Lett.*, 2001 (1966); (j) F. Adickes and G. Andressen, *Justus Liebigs Ann. Chem.*, **555**, 41 (1943); (k) R. Fischer and T. Wieland, *Chem. Ber.*, **93**, 1387 (1963); (l) J. D. Fissekis, C. G. Skinner, and W. Shive, *J. Amer. Chem. Soc.*, **81**, 2715 (1959); (m) E. Müller and B. Zeeh, *Tetrahedron Lett.*, 3951 (1965); (n) J. B. Wright, *J. Amer. Chem. Soc.*, **77**, 4883 (1955); (o) W. W. Wisaksono and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **80**, 846 (1961); (p) N. Rabjohn and C. A. Harbert, *J. Org. Chem.*, **35**, 3240 (1970); (q) M. Igarashi and H. Midorikawa, *Bull. Chem. Soc. Jap.*, **34**, 1543 (1961). (r) NOTE ADDED IN PROOF.—A useful general preparative method for α-keto esters has recently appeared: E. L. Eliel and A. A. Hartmann, *J. Org. Chem.*, **37**, 505 (1972).

(17) R. Rambaud, *Bull. Soc. Chim. Fr.*, **1**, 1342 (1934); R. Rambaud and M. L. Dondon, *C. R. Acad. Sci., Paris*, **223**, 381 (1946).

(18) Ethoxymagnesium halides have been reported to similarly reduce glyoxylic esters.[19]

(19) I. I. Lapkin and N. A. Karavanov, *Zh. Obshch. Khim.*, **30**, 2677 (1960).

(20) R. H. Hunt, L. J. Chinn, and W. S. Johnson, *Org. Syn.*, **34**, 54 (1954).

(21) M. S. Newman, *J. Amer. Chem. Soc.*, **57**, 732 (1935).

(22) B. Phillips, P. S. Starcher, and D. L. MacPeek, British Patent 863, 446 (1961); *Chem. Abstr.*, **55**, 25982*d* (1961).

(23) A. Oku, M. Okano, T. Shono, and R. Oda, *Kogyo Kagaku Zasshi*, **68**, 821 (1965).

(24) A double carbonyl absorption is characteristic of glycidic esters.[25] Conversely, the glyoxylic esters **3a** and **3d** exhibited a single carbonyl absorption, as reported for pyruvic acid and its esters.[26]

(25) G. Chiurdoglu, M. Mathieu, R. Baudet, A. Delsemme, M. Planchon, and P. Tullen, *Bull. Soc. Chim. Belg.*, **65**, 664 (1956).

(26) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., London, 1958, p 141.

Anal.[27] Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.33; H, 8.89.

Rearrangements.—Small-scale runs were made in refluxing benzene under a nitrogen atmosphere using the appropriate lithium salt and glycidic ester (and HMPA where noted); the extent of rearrangement and product yields were determined by vpc examination of water-washed samples. The inert internal standards employed for vpc analysis were *p*-dibromobenzene, *p*-chlorobromobenzene, and bromobenzene. Vpc response factors were determined for mixtures of **1e**, **2e**, and **3e**; no corrections were needed for these isomeric materials, and identical response factors were therefore assumed for other isomeric sets.

Preparative scale rearrangements were carried out as in the following example. Glycidic ester **1a**, 10.8 g (0.06 mol), and 1.6 g of $LiClO_4$[28] in 25 ml of benzene gave after 1 hr at reflux 8.8 g (81%) of a mixture, bp 116–118° (10 Torr), which was 0.5% (by vpc) of ethyl 2-keto-2-cyclohexylacetate (**3a**) and 99.5% of ethyl 2-hydroxy-2-(1-cyclohexenyl)acetate (**2a**): nmr δ 1.41 (t, 3 H), J = 8 Hz), 1.50–2.50 (broad m, 8 H), 4.10 (s, OH), 4.72 (q, 2 H, J = 8 Hz), 4.93 (s, 1 H), 6.47 ppm (broad s, 1 H); ir 1735, 3100–3650 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_3$ (**2a**): C, 65.19; H, 8.75. Found: C, 65.05; H, 8.65.

On a larger scale, 100 g of **1a** and 10 g of $LiClO_4$ in 450 ml of benzene gave after 72 hr 96.0 g (96%) of **2a**.

Similarly 14.4 g (0.10 mol) of **1e** gave 8.0 g (56%) of a mixture, bp 68–69° (10 Torr), consisting of 72% of **2e**[9] (ethyl 2-hydroxy-3-methyl-3-butenoate) and 28% of **3e**[9] (ethyl 2-keto-3-methylbutanoate). A viscous pot residue (3.7 g) was recovered after distillation but was not further examined.

Compound **1d**, 8.3 g (0.05 mol), gave a distillate, bp 80–81° (5 Torr), which contained 1% (vpc) of ethyl 2-keto-3-ethylpentanoate (**3d**) and 99% of a mixture of *cis*- and *trans*-ethyl 2-hydroxy-3-ethyl-3-pentenoate (**2d**): nmr δ 0.90 (t, 3 H, J = 7 Hz), 1.20 (t, 3 H, J = 7 Hz), 1.59 and 1.63 (two d, J = 6 and 7 Hz, respectively, relative areas *ca.* 2:1, 3 H total, allylic CH_3), 1.92 (t, 2 H, J = 7 Hz), 3.33 (broad d, OH), 4.03 (q, 2 H, J = 7 Hz), 4.28 and 4.82 (broadened singlets, relative areas *ca.* 2:1, 1 H total, carbinol CH), 5.35 ppm (broad q, J = 6–7 Hz, vinyl H); ir 1730, 3150–3650 cm^{-1}. *Anal.* Calcd for $CH_{16}O_3$ (*cis*- and *trans*-**2d**): C, 62.77; H, 9.36. Found: C, 63.09; H, 9.16.

Glycidic ester **1b**, 10.1 g (0.06 mol), gave 8.3 g (82%) of a mixture, bp 105–107° (10 Torr), consisting of 90% ethyl 2-hydroxy-2-(1-cyclopentenyl)acetate (**2b**) and 10% ethyl 2-keto-2-cyclopentylacetate (**3b**); pure samples were obtained by preparative vpc.

Compound **2b** had nmr δ 1.20–2.70 (multiplet, 9 H), 3.17 (s, OH), 4.15 (q, 2 H, J = 7 Hz), 4.57 (s, 1 H), 5.62 ppm (broad s, 1 H). *Anal.* Calcd for $C_9H_{14}O_3$: C, 63.50; H, 8.29. Found: C, 63.31; H, 8.12.

Glyoxylic ester **3b** had nmr δ 1.32 (t, 3 H, J = 7 Hz), 1.60–2.10 (m, 8 H), 3.10–3.75 (m, *tert*-CH), 4.19 ppm (q, 2 H, J = 7 Hz); ir 1730 cm^{-1}. *Anal.* Found: C, 63.76; H, 8.65.

Glycidic ester **4** gave in essentially quantitative yield (vpc) ethyl 2-hydroxy-2,3-dimethyl-3-butenoate (**5**), identified by its spectral characteristics: nmr δ 1.22 (t, 3 H, J = 7 Hz), 1.42 (s, 3 H), 1.70 (s, 3 H), 3.40 (broad s, OH), 4.08 (q, 2 H, J = 7 Hz), 4.72 and 4.92 ppm (broad singlets, 1 H each, vinyl); ir 1730, 3200–3650 cm^{-1}. *Anal.* Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.69; H, 8.97.

Overall conversion of glycidate to glyoxylate is illustrated by the reaction of **1c**; 19.8 g (0.10 mol) in 5 min in refluxing benzene with $LiClO_4$ gave 17.0 g (86%) of distillate, bp 89° (0.5 Torr). This was nearly pure **2c**, with *ca.* 1% **3c**. The distillate had nmr δ 1.20–2.35 (m, 13 H), 2.99 (s, OH), 4.12 (q, 2 H, J = 7 Hz), 4.23 (s, 1 H), 5.78 ppm (t, 1 H, J = 6 Hz); ir 1730, 3150–3700 cm^{-1}.

A portion, 13.8 g (0.07 mol), of the distillate was reduced on a Parr shaker, 3 atm H_2, using PtO_2 catalyst and absolute ethanol solvent. Distillation gave 11.5 g (83%) of ethyl cycloheptylglycolate, which was contaminated by the *ca.* 1% of **3c** present in the starting material: bp 124–127° (9 Torr); nmr δ 1.12–2.10 (m, 16 H), 3.23 (broad s, OH), 3.88–4.02 (m, 1 H), 4.15 ppm (q, 2 H, J = 7 Hz); ir 1730, 3150–3650 cm^{-1}.

A portion, 7.5 g (0.038 mol), of this material was subjected to Jones oxidation (CrO_3, aqueous acid, acetone, 0°) to give 6.1 g g (82%) of pure **3c**: bp 127–128° (10 Torr); nmr δ 1.23–2.00 (m, 16 H), 2.82–3.27 (m, *tert*-CH), 4.12 ppm (q, 2 H, J = 7 Hz); ir 1730, shoulder at 1750 cm^{-1}. *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 66.64, H, 9.15. Found: C, 66.36; H, 8.88.

Similarly **2b** was reduced to give ethyl 2-hydroxy-2-cyclopentylacetate: nmr δ 1.27 (t, 3 H, J = 7 Hz), 1.20–2.30 (m, 9 H), 3.47 (s, OH), 3.95–4.33 ppm (m, 3 H, containing ester quartet, J = 7 Hz); ir 1730, 3150–3600 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.84; H, 9.57. Oxidation gave **3b**, confirming its structure.

The mixture of **2d** and **3d** described earlier was similarly reduced and gave ethyl 2-hydroxy-3-ethylpentanoate: bp 88° (11 Torr); δ 0.7–1.70 (m, 14 H), 3.21 (s, OH), 4.10 (s, 1 H), 4.17 ppm (q, 2 H, J = 7 Hz); ir 1730, 3150–3650 cm^{-1}. *Anal.* Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.26; H, 10.63. Oxidation as above furnished **3d**: bp 79–81° (10 Torr); nmr δ 0.90 (t, 6 H, J = 7 Hz), 1.05–1.82 (m, 7 H, containing t, J = 7 Hz), 2.80 (quintet, 1 H, J = 6 Hz), 4.17 ppm (q, 2 H, J = 7 Hz); ir 1730 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 63.10; H, 9.35.

Attempted Base-Catalyzed Rearrangement of 2a.—A mixture of 0.2 g of sodium ethoxide and 1 g of **2a** in 25 ml of absolute ethanol was refluxed under nitrogen for 44 hr. Vpc analysis after neutralization and isolation showed a mixture consisting of 83% of starting material and 17% of ethyl cyclohexylglycolate,[29] which had an ir spectrum identical with that of the material obtained on catalytic reduction of **2a**.

Compound **3a** was similarly treated with sodium ethoxide; after 14 hr 32% had been converted to ethyl cyclohexylglycolate.

Registry No.—**1c**, 6975-19-5; **2a**, 33487-17-1; **2b**, 33487-18-2; **2c**, 33487-19-3; *cis*-**2d**, 33495-64-6; *trans*-**2d**, 33495-65-7; **2e**, 33537-17-6; **3b**, 33537-18-7; **3c**, 33487-20-6; **3d**, 33487-21-7; **3e**, 20201-24-5; **5**, 33487-23-9; ethyl 2-hydroxy-2-cyclopentylacetate, 33487-24-0; ethyl 2-hydroxy-3-ethylpentanoate, 33487-25-1.

(27) Analyses by C. F. Geiger, 312 E. Yale St., Ontario, Calif.

(28) Although the $LiClO_4$ is catalytic, the reaction exhibits autoinhibition, making advisable the use of relatively large amounts of the salt. In general a $LiClO_4$ to glycidate mole ratio of 0.25 gave satisfactory results.

(29) I. I. Lapkin and N. A. Karavanov, *Zh. Obshch. Khim.*, **30**, 1638 (1960).