Table I. Epoxidation of α,β-Unsaturated Acids

starting materials		reaction scale, mol	reaction time, h	products	
R^1	R^2			yield, %	mp, °C
Ph	H	0.75	2.0	92[a]	
Ph	CH_3	0.50	2.5	92	67-68[b]
Ph	Ph	0.37	2.25	90	121-123[c]
CH_3	H	0.75	2.75	62	87-88[d]

[a] Isolated as the potassium salt. [b] Reference 8; lit. mp 68-69 °C. [c] Reference 8; lit. mp 121-122 °C. [d] Reference 9; lit. mp 84.5-85.0 °C.

the reaction to be run at 24-27 °C without need to actively control pH and with no effect on yield.

This modification makes the epoxidation of unsaturated acids with potassium peroxymonosulfate simpler to perform and affords consistent yields, regardless of scale, from grams to kilograms.

Table I summarizes the results for four unsaturated acids.

Experimental Section

All materials were obtained from commercial suppliers and were used without further purification. Oxone monopersulfate compound (Du Pont, Co.) was obtained from Aldrich Chemical Co. Melting points were determined on a Buchi oil-immersion apparatus and are uncorrected.

Epoxidation Procedure. The general method is illustrated by the preparation of *trans*-β-phenylglycidic acid (isolated as the potassium salt) from *trans*-cinnamic acid.

A stirred slurry of *trans*-cinnamic acid (111.0 g; 0.75 mol) in acetone (515 mL) was treated first with $NaHCO_3$ (274 g; 3.26 mol) and then carefully with water (515 mL). The resulting thick mixture was treated dropwise, over 1.5 h, with a solution of Oxone monopersulfate compound[5] (421 g; contains 1.825 equiv of $KHSO_5$) in 4×10^{-4} M aqueous disodium EDTA[6] (1610 mL). During this addition, the reaction temperature was maintained at 24-27 °C by using a water bath and the reaction pH at ca. 7.4. After the addition was complete the mixture was stirred an additional 0.5 h and then cooled to ca. 10 °C. The reaction was acidified with concentrated HCl (ca. 140 mL) to pH 2 while the temperature was maintained at 10 °C and then treated with EtOAc (1.0 L) followed by rapid stirring. The mixture was filtered to remove insoluble salts, and the organic layer was removed. The aqueous layer was extracted with EtOAc (500 mL), and the combined organic layers were washed once with saturated aqueous NaCl (200 mL), dried over $MgSO_4$, and concentrated in vacuo from a 40 °C bath. Toward the end of the concentration, absolute EtOH was added (to keep the acid from crystallizing out), and concentration was continued until most of the solvent was removed. The yellowish oily residue was dissolved in absolute EtOH (500 mL), cooled on ice, and treated with a solution of KOH (56 g; 1.0 mol) in absolute EtOH (250 mL). The resulting thick slurry was filtered, and the solids were washed with EtOH. The filter cake was resuspended in fresh absolute EtOH (750 mL), filtered, washed with EtOH, and dried in a 50 °C oven to give the title compound (139 g; 92%) as a white powder, identical with that prepared by Harada[7] from ethyl β-phenylglycidate.

Anal. Calcd for $C_9H_7O_3K$: C, 53.44; H, 3.49. Found: C, 53.36; H, 3.74.

(5) Oxone monopersulfate compound (DuPont Co.) is $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Excess oxidant is used due to competing peroxide autodecomposition.

(6) Na_2EDTA is used to prevent trace-metal-catalyzed peroxide decomposition.

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Registry No. $KHSO_5$, 10058-23-8; (*E*)-PhCH=$CHCO_2H$, 140-10-3; (*E*)-PhCH=$C(CH_3)CO_2H$, 1895-97-2; (*E*)-PhCH=C-$(Ph)CO_2H$, 833-81-8; (*E*)-H_3CCH=$CHCO_2H$, 107-93-7; *trans*-3-phenyloxiranecarboxylic acid potassium salt, 19190-78-4; *trans*-2-methyl-3-phenyloxiranecarboxylic acid, 82812-97-3; *trans*-2,3-diphenyloxiranecarboxylic acid, 53884-88-1; *trans*-3-methyloxiranecarboxylic acid, 96150-05-9.

Cyclopropylidene Formation during Lithium Aluminum Hydride Reduction of Some Ethyl 2,2-Dibromocyclopropanecarboxylates and Their Corresponding Acids

Evy Jørgensen and Leiv K. Sydnes*

Department of Chemistry, University of Tromsø, N-9001 Tromsø, Norway

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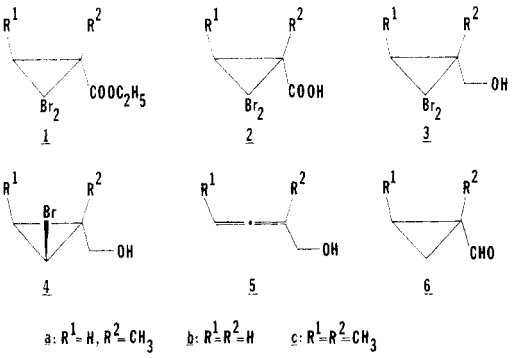
In connection with another study we needed fair amounts of (2,2-dibromo-1-methylcyclopropyl)methanol (**3a**). To make this compound we treated ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate (**1a**) with an excess of lithium aluminum hydride (LAH) as previously described,[1] but to our surprise a complex reaction mixture was obtained rather than essentially one product. Since LAH gradually loses its reducing power when exposed to light and air,[2] the formation of the complex mixture was possibly due to the fact that our previous experiments were carried out with LAH from an old, frequently used sample,[3] whereas the recent reaction involved fresh hydride.[4] This prompted us to investigate the reduction of some ethyl 2,2-dibromocyclopropanecarboxylates and their corresponding acids with a fresh sample of LAH and led to the discovery of cyclopropylidene generation during treatment of *gem*-dihalocyclopropanes with LAH.



a: R^1=H, R^2=CH_3 b: R^1=R^2=H c: R^1=R^2=CH_3

Treatment of ester **1a** with fresh hydride gave reaction mixtures whose composition varied with the specific condition employed (Table I). The highest yield of alcohol **3a** (>90% based on consumed starting material) was obtained with an LAH/substrate ratio of 0.50; higher ratios increased the yields of other products, viz., monobromo alcohol **4a** and allene alcohol **5a**, at the expense of the dibromo alcohol. The product distribution is sensitive to the mode of addition as alcohols **4a** and **5a** are formed in higher yields when LAH is added as a homogeneous, eth-

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(2) (a) Brown, W. G. *Org. React. (N.Y.)* **1951**, *6*, 469. (b) Finholt, A. E.; Jacobson, E. C. *J. Am. Chem. Soc.* **1952**, *74*, 3943.

(3) The sample, purchased from Koch-Light Laboratories, England, was about 2 years old and had been used regularly when the research reported in ref 1 was initiated.

(4) The LAH used in the present study was from a new sample purchased from Aldrich.

0022-3263/86/1951-1926$01.50/0

Table I. Product Distribution in Reactions of Ester 1a with LAH[a]

molar ratio LAH/substrate	mode of addition[b]	product mixture composition, %[c]			
		1a	3a	4a	5a
0.50	A	42	52	6	
0.50	B	41	54	5	
0.50	C	25	27	42	6
1.00	A		55	41	44
1.00	B		54	44	2
1.00	C		15	69	16
2.25	B		20	71	9

[a] The amounts of compounds **1a**, **3a**, **4a**, and **5a** accounted for more than 95% of the starting material. [b] A: The substrate added to an LAH slurry. B: LAH powder added portionwise to a substrate solution. C: A clear, etheral solution of LAH added dropwise to a substrate solution. [c] % as determined by a combination of GC and ^{1}H NMR analyses (see Experimental Section).

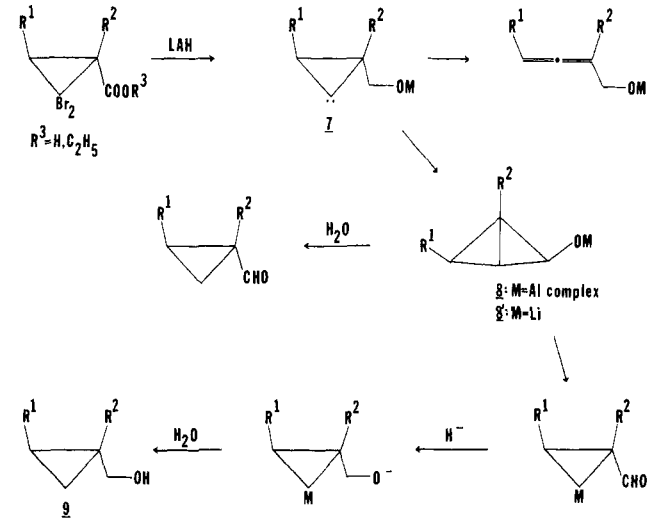
eral solution than as a powder or a slurry. However, the reaction mixtures afforded by inverse addition of LAH powder was essentially identical to those obtained by adding **1a** to an LAH slurry. Similar results were obtained by LAH reduction of esters **1b** and **1c**, but in these cases the secondary reactions were less pronounced (Table II). This was particularly the case with ester **1b** which gave (2,2-dibromocyclopropyl)methanol (**3b**) in almost 90% yield when the LAH/substrate ratio was 0.75.

The general pattern followed by the esters was also observed when the corresponding acids (**2**) were treated with fresh LAH. However, the acids seem to be more reactive than the esters and more prone to undergo secondary reactions. Particularly striking is the formation of cyclopropanecarbaldehydes **6**, which were not obtained when the esters reacted with LAH.

Alcohols **3** and **4** are the expected products from LAH reduction of **1** and **2**.[1] However, the formation of allene **5a** and aldehydes **6b** and **6c** can be accounted for by invoking the cyclopropylidene intermediate **7** (Scheme I). The most general reaction of such a species is ring opening to yield the corresponding allene,[5] but the carbene can also undergo intramolecular insertion into one of the C–H bonds adjacent to the oxygen function and form bicyclo[1.1.0]butan-2-olate **8**, which suffers ring opening and ultimately yields aldehyde **6**.[6] Since alcohol **9** was not formed in any of the reactions the ring opening of **8** (M = Al complex) conceivably takes place during and not prior to hydrolysis. This is in contrast to intermediate **8′** (M = Li), resulting from reactions of **3** with methyllithium, which rearranges prior to hydrolysis.[6] The difference in stability between **8** and **8′** probably reflects that the O–M bond is stronger when oxygen is attached to aluminum than when it is bonded to lithium.[7] In spite of the larger stability of **8** attempts to trap the intermediate have so far been unsuccessful.

Whereas ester **1a** and acid **2a** gave reaction mixtures that contained the same products, albeit in different proportions, acids **2b** and **2c** each gave one more product, viz., aldehyde **6**, than their corresponding esters. The reason for this difference is far from clear but the different aluminum species generated during the primary reduction of the two kinds of substrates is likely to be a part of the explanation. This is supported by a recent report of Yates

Scheme I



and Winnik who observed that the course of reaction of a steroid *gem*-dibromocyclopropane was very sensitive to the aluminum hydride employed.[8] Primary reductions of **1** and **2** furnish the complex hydrides **10** and **11**, respectively. Since **11** is more electrophilic than **10** the former hydride should be more apt to facilitate nucleophilic attack[9] on the cis bromo atom in the *gem*-dibromo moiety, i.e., to facilitate cyclopropylidene generation. Why **11a** is transformed into an allene whereas **11b** and **11c** furnish **8b** and **8c** and finally aldehydes **6b** and **6c**, respectively, is difficult to rationalize.

Experimental Section

Gas chromatographic (GC) analyses were carried out on a Varian 3700 gas chromatograph with a thermal conductivity detector. The column was 2 m long and was packed with 3% OV17 on Chromosorb W-HP, 80/100. The infrared (IR) spectra were recorded on a Shimadzu IR 420 spectrometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on JEOL PMX 60SI and JEOL FX 90Q spectrometers; $CDCl_3$ was used as solvent and tetramethylsilane as internal standard. Mass spectra (MS) were taken on a Micromass 7070H spectrometer, operated in an EI mode with an ionization potential of 70 eV.

Starting Materials. Esters **1a** and **1c** and acids **2a** and **2c** were prepared as described in the literature.[10] 2,2-Dibromocyclopropanecarboxylic acid (**2b**) was synthesized in 89% yield by ruthenium tetraoxide oxidation of 1,1-dibromo-2-phenylcyclopropane[11] by using the method of Chakraborti and Ghatak,[12] mp 93–95 °C (lit.[13] mp 94–95 °C). Ethyl 2,2-dibromocyclopropanecarboxylate (**1b**) was obtained in 83% yield by esterification of **2b** according to Marshall et al.[14] and Kugelrohr distillation at 55 °C (0.20 mm): IR 1735, 1340, 1035, 755, 680 cm^{-1}; ^{1}H NMR δ 1.28 (t, J = 7.8 Hz, 3 H), 1.85–2.10 (m, 3 H), 4.23 (q,

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Table II. Product Distribution in Reactions of *gem*-Dibromocyclopropanes 1b, 1c, and 2 with LAH[a]

substrate	molar ratio LAH/substrate	mode of addition[b]	product mixture composition, %[c]				
			substrate	3	4	5	6
1b	0.75	A	12	88			
1b	0.75	B	13	87			
1c	0.50	A	50	49	1		
1c	0.50	B	54	45	1		
2a	0.75	A		79	14	7	
2a	0.75	B		78	15	7	
2a	1.50	B		47	44	9	
2b	0.75	A	20	52	17		11
2b	0.75	B	33	52	3		12
2c	0.75	A	45	29	21		5
2c	0.75	B	42	41	14		3

[a] The amounts of substrate and compounds 3–6 accounted for more than 95% of the starting material. [b] See Table I. [c] % as determined by a combination of GC and ^{1}H NMR analyses (see Experimental Section).

J = 7.8 Hz, 2 H). Anal. Calcd for $C_6H_8Br_2O_2$: C, 26.50; H, 2.95. Found: C, 26.19; H, 3.07.

General Procedures for the Reductions with Lithium Aluminum Hydride (LAH). The reactions were carried out under pure nitrogen with 2–10 mmol of substrate. Three methods were used. **Method A.** Ester or acid, dissolved in dry ether (5 mL/mmol substrate), was added dropwise to a cold (ice/water) suspension of LAH in dry ether (5 mL/mmol LAH). The resulting mixture was stirred at 35 °C for 1 h and was then poured into ice/water (100 mL). The products were extracted with ether (3 × 25 mL), and the combined extracts were dried ($MgSO_4$). When the substrate was an acid the aqueous phase was then acidified (2 M HCl, pH ~1) and extracted with ether (3 × 25 mL) to recover any unreacted acid; the combined extracts were dried ($MgSO_4$). Separate workup of the extracts gave pale yellow residues which were analyzed prior to purification. **Method B.** LAH powder was added in small portions to a cooled (ice/water) solution of ester or acid in dry ether (7 mL/mmol substrate). The reaction was then performed and completed as described for method A. **Method C.** An etheral solution of LAH (0.99 M) was added dropwise to a cooled (ice/water) solution of ester or acid in dry ether (5 mL/mmol substrate). The reaction was then carried out as described for method A.

The compositions of the product mixtures were determined by GC analyses prior to separation of the products. The relative detector responses were taken into consideration; they were determined for each type of reaction mixtures by comparing GC analyses and ^{1}H NMR analyses of several mixtures of the appropriate compounds.

The products were isolated by a combination of distillation and column chromatography (SiO_2/$CHCl_3$). In most cases the samples thus obtained had a purity of better than 95%. The individual products were identified on the basis of IR and ^{1}H NMR spectra and for compounds **3**–**5**, by comparing their GC retention times with those of authentic samples.[1,6,15]

The following compounds were treated with LAH according to several of the methods mentioned above. The relative amount of LAH used in each case is evident from Tables I and II.

Ethyl 2,2-Dibromo-1-methylcyclopropanecarboxylate (1a). Reduction of **1a** gave three products, (2,2-dibromo-1-methylcyclopropyl)methanol (**3a**),[1] (*trans*-2-bromo-1-methylcyclopropyl)methanol (**4a**),[15] and 2-methyl-2,3-butadien-1-ol (**5a**).[6]

Ethyl 2,2-dibromocyclopropanecarboxylate (1b) furnished one product, (2,2-dibromocyclopropyl)methanol (**3b**).[13]

Ethyl 2,2-Dibromo-1,*trans*-3-dimethylcyclopropanecarboxylate (1c). Reduction of **1c** afforded one major product, (2,2-dibromo-1,*trans*-3-dimethylcyclopropyl)methanol (**3c**),[1] and one minor product, (*trans*-2-bromo-1,*trans*-3-dimethylcyclopropyl)methanol (**4c**). Monobromide **4c** was identical with an authentic sample prepared in 86% yield by LAH reduction of *trans*-2-bromo-1,*trans*-3-dimethylcyclopropanecarboxylic acid[16] (molar ratio LAH/acid = 0.75) according to method B. The product was isolated by Kugelrohr distillation at 55–58 °C (0.60 torr): IR (film) 3380, 1450, 1025, 750 cm^{-1}; ^{1}H NMR δ 0.95–1.32 (m, 4 H), 1.10 (s, 3 H), 3.04 (d, J = 7 Hz, 1 H), 3.20 (br s, 1 H), 3.38 (br s, 2 H). Anal. Calcd for $C_6H_{11}BrO$: C, 40.24; H, 6.19. Found: C, 40.01; H, 5.95.

2,2-Dibromo-1-methylcyclopropanecarboxylic acid (2a) gave the same products that were formed during reduction of **1a**.

2,2-Dibromocyclopropanecarboxylic Acid (2b). The products formed during reduction of **2b** were **3b**, (*trans*-2-bromocyclopropyl)methanol (**4b**), and cyclopropanecarbaldehyde (**6b**).[17] Monobromide **4b** was identical with and authentic sample prepared in 85% yield by LAH reduction (molar ratio LAH/acid = 0.75) of *trans*-2-bromocyclopropanecarboxylic acid[16] according to method B. The product was isolated by Kugelrohr distillation at 50–55 °C (9 torr): IR 3350, 1070, 1045, 950 cm^{-1}; ^{1}H NMR δ 0.65–1.9 (m, 3 H), 2.30 (br s, 1 H), 2.75 (m, 1 H), 3.65 (m, 2 H).

2,2-Dibromo-1,*trans*-3-dimethylcyclopropanecarboxylic Acid (2c). When **2c** was reduced the products were **3c**, **4c**, and 1,*trans*-2-dimethylcyclopropanecarbaldehyde (**6c**).[17]

Registry No. **1a**, 58683-49-1; **1b**, 101696-97-3; *trans*-**1c**, 65655-79-0; **2a**, 5365-21-9; **2b**, 5365-17-3; *trans*-**2c**, 72957-64-3; **3a**, 64670-28-6; **3b**, 22084-99-7; **3c**, 64670-31-1; *trans*-**4a**, 66078-07-7; *trans*-**4b**, 101696-98-4; **4c**, 101696-99-5; **5a**, 22742-89-8; **6b**, 1489-69-6; *trans*-**6c**, 1605-36-3; LAH, 16853-85-3; 1,1-dibromo-2-phenylcyclopropane, 3234-51-3; 2-bromo-1,3-dimethylcyclopropanecarboxylic acid, 101758-93-4; *trans*-2-bromocyclopropanecarboxylic acid, 60212-40-0.

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