94. Preparation of α,α-Dibromocyclobutanones from Olefins: A Simple Procedure for the Regioselective Functionalization of Olefins[1])

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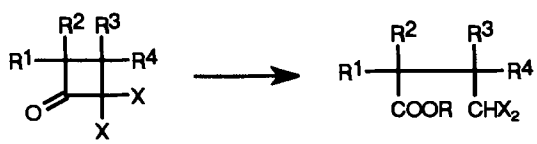
Dibromoketene is prepared by *in-situ* Zn dehalogenation of tribromoacetyl bromide in the presence of $POCl_3$. Under these conditions, the cycloaddition of dibromoketene with olefins **5** yields α,α-dibromocyclobutanones **2**, which are cleaved with alkoxides to yield β-dibromomethyl esters **4**. Several examples are given. For monosubstituted olefins, the functionalization is regioselective, the methoxycarbonyl group being introduced at the terminal C-atom.

Introduction. – The synthetically most useful reaction of ketenes is perhaps their cycloaddition with olefins to yield cyclobutanones. Whereas most ketenes are relatively difficult to obtain, dichloroketene is easily prepared by dehydrohalogenation of dichloroacetyl chloride, or by reduction of trichloroacetyl chloride [2]. Besides, electronegativity effects make haloketenes, and specially dichloroketene, more reactive in this cycloaddition than alkyl- or arylketenes [2]. The α,α-dichlorocyclobutanones **1**, resulting from this cycloaddition, are useful and very reactive synthetic intermediates in which the Cl-atoms can be removed by reduction, substitution, or hydrolysis. However, cleavage of the cyclobutanone ring by treatment of **1** with hydroxides or alkoxides to yield a β-dichloromethyl acid **3** or β-dichloromethyl ester **3′** (*Scheme*) is usually difficult. Rearrangements of diverse types, ring expansion, or ring contraction take often place instead [2] [3]. Interestingly, *Greene* and coworkers [3a] proposed an efficient and general method of

Scheme



1 X = Cl
2 X = Br

3 R = H, X = Cl
3′ R = Alkyl, X = Cl
4 R = Me, X = Br
4′ R = Et, X = Br
4″ R = i-Pr, X = Br

[1]) For a preliminary communication, see [1].

vicinal dicarboxylation of olefins: an intermediate α,α-dichlorocyclobutanone **1** was selectively opened to yield a substituted succinic acid through successive treatment with BuLi, Ac_2O, and $NaIO_4/RuO_2$.

Whereas $RCBr_2$ is a better leaving group than $RCCl_2$, we hoped that the ring cleavage shown in the *Scheme* would be easier and cleaner for an α,α-dibromocyclobutanone **2** than for an α,α-dichlorocyclobutanone **1**. This procedure would then allow the selective addition of the $CHBr_2$ and COOR groups to an olefin, using only simple and inexpensive reagents. The first step is the [2 + 2] cycloaddition of dibromoketene to the olefin. However, few reports on the preparation and use of dibromoketene exist in the literature. To our knowledge, the cycloaddition of dibromoketene had been studied only with two very reactive olefins, cyclopentadiene, and dicyclopentadiene [4] [5]. Besides, it had already been noted that dibromoketene is less reactive than dichloroketene. Dibromoketene had been prepared by dehydrohalogenation of dibromoacetyl chloride with tertiary amines [4], or, occasionally, by reduction of tribromoacetyl bromide [4a] or of trimethylsilyl tribromoacetate [5].

The dehydrohalogenation procedure has the drawback that tertiary amines and/or ammonium salts are known to catalyze the polymerization of haloketenes [2b] [6]. This polymerization is slower than the cycloaddition of dichloroketene to most olefins; however, it seems to compete very efficiently with the cycloaddition of dibromoketene to olefins which requires much longer reaction times (*vide infra*).

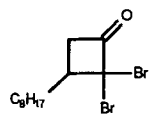
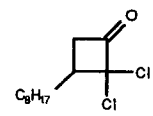
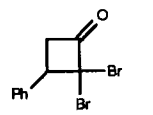
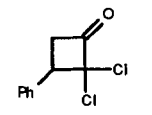
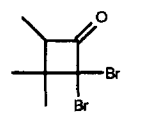
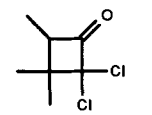
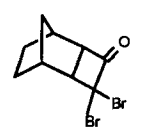
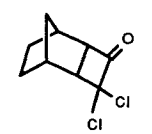
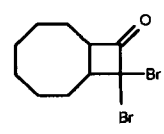
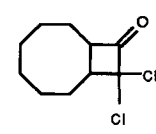
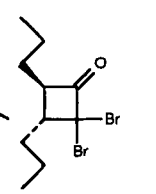
The original procedure for the preparation of dibromoketene by reduction of tribromoacetyl bromide with Zn [4a] faces a similar problem: the produced zinc salts catalyze the cationic polymerization of some conjugated olefins [6]. The original preparation method of dichloroketene by reduction of trichloroacetyl chloride with Zn/Cu couple was modified by *Krepski* and *Hassner*: the addition of phosphorus oxychloride ($POCl_3$) caused the complexation of zinc salts. The yields of the cycloaddition of dichloroketene with some unreactive olefins were then significantly improved [7].

In this paper we will describe an improved method for the preparation of dibromoketene, its cycloaddition with many olefins, and the ring cleavage of the obtained α,α-dibromocyclobutanones **2** to yield a β-(dibromomethyl) acid derivative.

Results and Discussion. – We reproduced the preparation of dibromoketene by dehydrohalogenation of dibromoacetyl chloride with Et_3N [4] and its cycloaddition to the very reactive cyclopentadiene. However, under the same conditions, dec-1-ene was totally inert. The same results were obtained when dibromoketene was prepared by reduction of trimethylsilyl tribromoacetate [5]. These two methods of preparation of dibromoketene were not studied further.

We tried to generate dibromoketene by reduction of tribromoacetyl bromide with Zn/Cu couple in the presence of $POCl_3$ according to a procedure similar to [7]. We found that the reaction with dec-1-ene gave the expected cyclobutanone **2a** in good yield (70%). However, this reaction was slow (20°, *ca.* 14 h): tribromoacetyl bromide was added during 1 h to the mixture of Zn/Cu couple, olefin, and $POCl_3$ (see *Exper. Part*), and GC analysis showed that at the end of the addition, *ca.* 43% of dec-1-ene was still unreacted. This amount decreased slowly to *ca.* 25% after 2 h, and to *ca.* 5% after 18 h. The yield of **2a** was not improved when the addition rate of the acyl bromide was decreased or when a large excess of reagents (more than 1.75 equiv.) was used. To avoid the cationic polymer-

Table 1. *Preparation of Some Dihalogenocyclobutanones*

Olefin	Dibromocyclobutanone	Yield[a])	Dichlorocyclobutanone	Reported yield[d])
	 **2a**	70%[b])	 **1a**	88% [8]
	 **2b**	35%[c])	 **1b**	87% [7]
	 **2c**	65%[b])	 **1c**	87% [3]
	 **2d**	55%[b])	 **1d**	70% [7]
	 **2e**	50%[b])	 **1e**	91% [9]
	 **2f**	40%[b])		

[a]) Yields of isolated products.
[b]) 1.75 equiv. of CBr_3–COBr, 1.75 equiv. of $POCl_3$, and 2 equiv. of Zn/Cu couple were used in Et_2O.
[c]) Only 1.05 equiv. of CBr_3–COBr, 1.05 equiv. of $POCl_3$, and 1.1 equiv. of Zn/Cu couple were used in Et_2O.
[d]) Yields obtained using dichloroketene prepared by reduction of CCl_3–COCl in presence of $POCl_3$.

ization of olefins, only a slight excess of reagents was used with polymerization-sensitive olefins, *e.g.*, styrene. It should be noted that the dibromocyclobutanones are difficult to purify. Decomposition was always observed to some extent during vacuum distillation or column chromatography on various adsorbents. The yields reported in *Table 1* are average yields of purified cyclobutanones **2a–f**, but the yields of the cycloadditions themselves could not be determined exactly. However, it appears that they are significantly lower than the yields reported in the literature for the cycloaddition of dichloroketene with the same olefins. Nevertheless, this procedure seems to be the method of choice for the cycloaddition of dibromoketene with most olefins.

The cleavage of the α,α-dibromocyclobutanone ring according to the *Scheme* was reported in the literature for a few examples, using Na_2CO_3, NaOH, or MeONa [10] [4b] [4c]. The results obtained with **2a** show that the nucleophilicity of the attacking ion is crucial for this reaction. The best results were obtained by the use of a strong or relatively strong base in MeOH (see *Table 2, Entries 9–13*). As a general procedure, we used *t*-BuOK in MeOH. The yield of **4a** was also fair with NaOH in aqueous dioxane, after esterification with CH_2N_2 (*Entry 4*). However, it dropped when *t*-BuOK/EtOH or *t*-BuOK/i-PrOH were used to afford **4'a** and **4''a**, respectively (*Entries 14* and *15*). Under the usual conditions (*t*-BuOK/MeOH or MeONa/MeOH), cleavage of the disubstituted dibromocyclobutanone **2f** yielded **4f** (for structure, see *Table 3*) in a modest yield (35%). Cleavage of the trisubstituted or bicyclic dibromocyclobutanones **2c–e** gave only complex mixtures.

We found that the yield of the ring opening of dibromocyclobutanone **2a** (according to *Table 2, Entries 4* and *13*) was almost independent of the presence of the impurities formed during the synthesis of **2a**. This allowed us to avoid the difficult purification of **2a** by distillation or chromatography. By treatment of crude **2a** (prepared according to *Table 1* and purified only by extraction) with *t*-BuOK/MeOH, the overall yield from

Table 2. *Ring Opening of Cyclobutanone* **2a** *According to the* Scheme

Entry	Base	Solvent	Yield of ester **4a**[a])
1	LiOH	dioxane/H_2O 4:1	24%[b])
2	K_2CO_3	dioxane/H_2O 4:1	28%[b])
3	K_3PO_4	dioxane/H_2O 4:1	56%[b])
4	NaOH	dioxane/H_2O 4:1	61%[b])
5	Na_2CO_3	MeOH/H_2O 4:1	72%
6	Et_3N	anh. MeOH	17%
7	NH_3	anh. MeOH	40%
8	Cs_2CO_3	anh. MeOH	52%
9	MeONa	anh. MeOH	70%
10	DBU[c])	anh. MeOH	66%
11	DBN[d])	anh. MeOH	67%
12	*Proton-Sponge*®[e])	anh. MeOH	71%
13	*t*-BuOK	anh. MeOH	72%
14	*t*-BuOK	anh. EtOH	35%[f])
15	*t*-BuOK	anh. i-PrOH	10%[g])

[a]) For the structure of **4a**, see *Table 3*. [b]) After treatment of the crude acid with CH_2N_2. [c]) 1,8-Diazabicyclo[5.4.0]-undec-7-ene. [d]) 1,5-Diazabicyclo[4.3.0]non-5-ene. [e]) *N,N,N',N'*-Tetramethylnaphthalene-1,8-diamine. [f]) Ethyl ester **4'a**. [g]) Isopropyl ester **4''a**.

dec-1-ene (**5a**) to methyl 3-(dibromomethyl)undecanoate (**4a**) was raised from 50 to 66%. However, this very simple procedure is not exactly a 'one-pot reaction' (see *Exper. Part*).

Different solvents were also tried for the cycloaddition step of dibromoketene with dec-1-ene (**5a**). The crude cyclobutanone **2a**, which contained various amounts of complexed zinc salts, was treated with NaOH in aqueous dioxane and the resulting acid esterified with CH_2N_2. When the cycloaddition was carried out in Et_2O, a 61% yield of ester **4a** was obtained; the yield was slightly higher in CH_2Cl_2 (66%) but significantly lower in other solvents, like 1,2-dimethoxyethane (10%), THF (20%), $ClCH_2CH_2Cl$ (22%), and MeCN (34%).

The cycloaddition was carried out in CH_2Cl_2 with nine olefins (see *Table 3*). The crude cyclobutanones obtained were treated with *t*-BuOK/MeOH. In most cases, the expected β-dibromomethyl esters **4** were obtained in fair-to-good yields. The addition of dibromoketene to monosubstituted olefins is, like the addition of dichloroketene, a regioselective reaction. This allows the introduction of the $CHBr_2$ group at the C(2) atom of the olefin. Most functionalities (*e.g.* alcohol, ether, ester) are tolerated in the starting olefin **5**; however, a disadvantage of this procedure using $POCl_3$ to generate dibromoketene is the acidity of the reaction medium, which prevents the use of olefins bearing acid-sensitive groups (*e.g.* **5l**). Except for the reaction of dec-1-ene (**5a**), the yields of β-dibromomethyl esters **4** were not optimized. The preparation of **4ha**/**4hb** from dicyclopentadiene (**5h**) had already been carried out by *Boland* and *Jaenicke* (*vide supra*), but they obtained only a 32% yield [4c]. Our result confirms that even for a very reactive olefin, the generation of dibromoketene by Zn/Cu reduction in presence of $POCl_3$ is far better than the dehydrohalogenation procedure used by *Boland* and *Jaenicke*.

We expect that this procedure will prove useful, due to the possibility of regioselective introduction of two synthetically interesting groups on a terminal olefin.

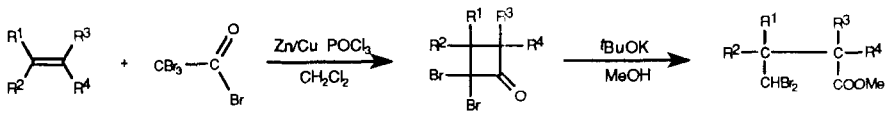
We are grateful to Dr. *A. E. Greene*, Grenoble, for helpful discussions, to the *Centre National de la Recherche Scientifique* (URA 135), for financial support, and to Miss *L. Brand*, undergraduate student, for the performance of some experiments.

Experimental Part

General. All reactions were run under N_2. Et_2O, tetrahydrofuran (THF), and 1,2-dimethoxyethane were freshly distilled from sodium/benzophenone, CH_2Cl_2 and dichloroethane from P_2O_5, MeCN from CaH_2, MeOH, EtOH, and i-PrOH from Mg. $POCl_3$ was distilled immediately prior to use. Tribromoacetyl bromide was synthesized according to [11] and the Zn/Cu couple according to [12]. Microanalyses were performed by the 'Service Central d'Analyse du CNRS'.

α,α-Dibromocyclobutanones **2***: General Procedure.* A soln. of 1.75 equiv. of tribromoacetyl bromide and 1.75 equiv. of $POCl_3$ in dry solvent (2 ml/mmol **5**) was added at 25° during 1 h to a stirred mixture of olefin **5** and 2 equiv. of Zn/Cu couple in dry solvent (2 ml/mmol **5**). The best results were obtained with CH_2Cl_2. The mixture was stirred for 15 h and then filtered through *Celite*. The solvent was evaporated and Et_2O (20 ml/mmol **5**) added to the oily residue. Addition of petroleum ether (10 ml/mmol **5**) caused the precipitation of some tarry material. The supernatant soln. was decanted and the tarry material extracted with petroleum ether. The combined org. phases were successively washed with H_2O, sat. aq. $NaHCO_3$ soln., and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. The yield of the crude α,α-dibromocyclobutanone **2** obtained was not significative (usually 80–100%, slightly more in some experiments), and crude **2** was used directly in the following step. The reaction was usually run with 0.5–3 mmol of olefin **5**. To determine the yield (for cyclobutanones **2a–f**) or for characterization purposes,

Table 3. *Conversion of Olefins to β-Dibromomethyl Esters*



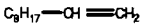
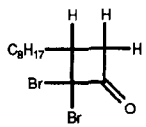
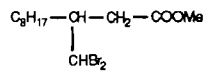
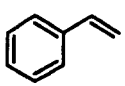
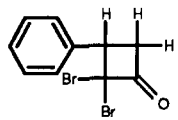
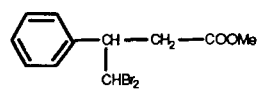
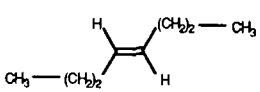
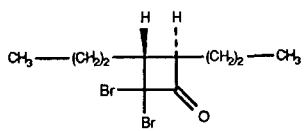
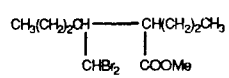
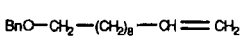
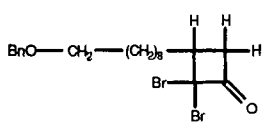
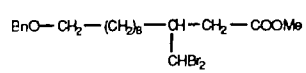
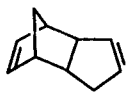
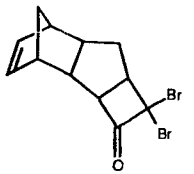
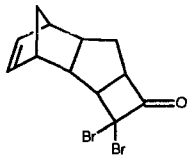
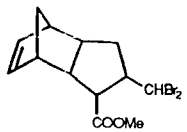
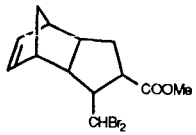
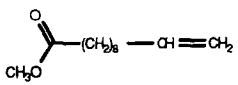
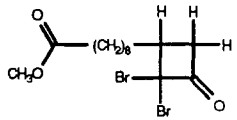
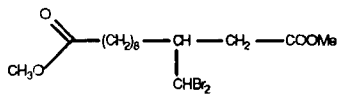
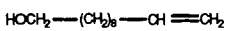
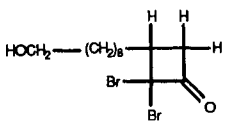
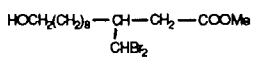
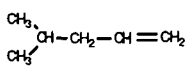
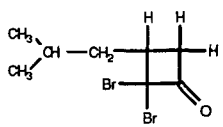
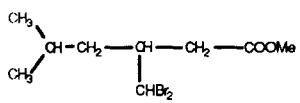
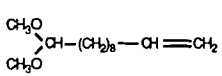
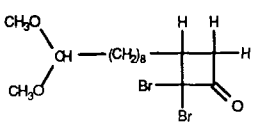
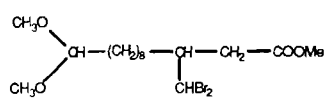
Olefins	α,α-Dibromocyclobutanones	β-Dibromomethyl esters	Overall yield
 **5a**	 **2a**	 **4a**	71%
 **5b**	 **2b**	 **4b**	35%
 **5f**	 **2f**	 **4f**	23%
 **5g**	 **2g**	 **4g**	64%

Table 3 (cont.)

Olefins	α,α-Dibromocyclobutanones	β-Dibromomethyl esters	Overall yield
	 	 	
5h	**2ha** **2hb**	**4ha** **4hb**	50%
			
5i	**2i**	**4i**	47%
			
5j	**2j**	**4j**	34%
			
5k	**2k**	**4k**	28%
			
5l	**2l**	**4l**	10%

crude **2** was occasionally purified by vacuum distillation or CC (silica gel, Et_2O/petroleum ether). Decomposition was always observed, even during vacuum distillation using a *Kugelrohr* or chromatography on *Florisil*. The puritiy of the samples obtained was not sufficient for elemental analysis.

2,2-Dibromo-3-octylcyclobutanone (**2a**): B.p. 114°/0.05 Torr. IR (film): 2980, 2940, 2860, 1810, 670. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.89 (*t*, ^3J = 6.5, 3 H); 1.15–2.00 (*m*, 14 H); 2.80–3.05 (*m*, 2 H); 3.15–3.40 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 14.1 (*q*); 22.7 (*t*); 27.5 (*t*); 29.2 (*t*); 29.38 (*t*); 29.40 (*t*); 31.8 (*t*); 34.1 (*t*); 46.1 (*d*); 46.9 (*t*); 66.2 (*s*); 192.5 (*s*).

2,2-Dibromo-3-phenylcyclobutanone (**2b**): M.p. 73.5–74.7°. IR (KBr): 3030, 2930, 1790, 1600, 1500, 1450, 1080, 760. ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.45 (*dd*, ^2J = 17.3, ^3J = 10, H–C(4)); 3.76 (*dd*, ^2J = 17.3, ^3J = 10, H–C(4)); 4.35 (*t*, ^3J = 10, H–C(3)); 7.30–7.50 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 44.7 (*t*); 50.4 (*d*); 67.1 (*s*); 127.7 (*d*); 128.3 (*d*); 128.5 (*d*); 136.2 (*s*); 191.4 (*s*).

2,2-Dibromo-3,3,4-trimethylcyclobutanone (**2c**): B.p. 50°/0.05 Torr. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.13 (*d*, ^3J = 7, Me–C(4)); 1.22, 1.53 (2*s*, 2 Me–C(3)); 3.60 (*q*, ^3J = 7, H–C(4)).

4,4-Dibromotricyclo[4.2.1.0^{2,5}]nonan-3-one (**2d**): B.p. 80°/0.03 Torr. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.2–1.7 (*m*, 6 H); 2.60–2.67 (*m*, 2 H); 2.98 (*d*, ^3J = 6.5); 3.64 (*dt*, ^3J = 6.5, ^4J = 1.5, H–C(2), H–C(5)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 26.0 (*t*); 27.5 (*t*); 34.8 (*t*); 37.3 (*d*); 41.3 (*d*); 54.2 (*d*); 64.6 (*s*); 65.0 (*d*); 196.3 (*s*).

10,10-Dibromobicyclo[6.2.0]decan-9-one (**2e**): B.p. 85°/0.08 Torr. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.2–2.0 (*m*, 12 H); 3.03 (*ddd*, ^3J = 11.2, 10.8, 2), 3.58 (*ddd*, ^3J = 11.8, 10.8, 2, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 24.0 (*t*); 25.3 (*t*); 25.6 (*t*); 27.5 (*t*); 28.9 (*t*); 29.1 (*t*); 51.1 (*d*); 58.0 (*d*); 66.2 (*s*).

trans-*2,2-Dibromo-3,4-dipropylcyclobutanone* (**2f**): B.p. 104°/0.04 Torr. IR (film): 2970, 2930, 2880, 1800, 1750, 1470, 780. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.92, 1.02 (2*t*, ^3J = 7.2, 2 Me); 1.25–2.10 (*m*, 8 H); 2.56 (*ddd*, ^3J = 9.8, 8.2, 5.8), 3.21 (*dt*, ^3J = 9.8, 7, H–C(3), H–C(4)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 13.8 (*q*); 14.0 (*q*); 20.5 (*t*); 20.8 (*t*); 31.7 (*t*); 36.2 (*t*); 52.5 (*d*); 59.9 (*d*); 64.3 (*s*); 196.1 (*s*).

2,2-Dibromo-3-[(9-benzyloxy)nonyl]cyclobutanone (**2g**): The starting material, olefin **5g**, was prepared by benzylation [13] of alcohol **5j**. *Data of* **2g**: IR (film): 2930, 2855, 1800, 1100, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.20–2.00 (*m*, 16 H); 2.82–3.03 (*m*, 2 H); 3.16–3.33 (*m*, 1 H); 3.47 (*t*, 2 H, ^3J = 6.5); 4.50 (*s*, PhCH_2); 7.24–7.36 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 26.2 (*t*); 27.5 (*t*); 29.33 (*t*); 29.35 (*t*); 29.41 (*t*); 29.45 (*t*); 29.8 (*t*); 34.0 (*t*); 46.2 (*d*); 46.9 (*t*); 66.3 (*s*); 70.5 (*t*); 72.9 (*t*); 127.5 (*d*); 127.6 (*d*); 128.3 (*d*); 138.7 (*s*); 192.4 (*s*).

5,5-Dibromotetracyclo[7.2.1.0^{2,8}.0^{3,6}]dodec-10-en-4-one (**2ha**) *and 4,4-Dibromotetracyclo[7.2.1.0^{2,8}.0^{3,6}]-dodec-10-en-5-one* (**2hb**; 9:1 mixture): IR (film): 3060, 2980, 2940, 2880, 1800, 1450, 750, 720, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): **2ha**: 3.33 (*ddd*, ^3J = 9, 8.5, 5, H–C(6)); 3.70 (*dt*, ^3J = 8.5, J = 0.6, H–C(3)); **2hb**: 3.81 (*ddd*, ^3J = 12, 8, 5, H–C(6)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): **2ha**: 34.1 (*t*); 47.4 (*d*); 47.5 (*d*); 50.7 (*d*); 51.1 (*d*); 51.5 (*t*); 56.9 (*d*); 64.7 (*d*); 66.2 (*s*); 135.4 (*d*); 136.2 (*d*); 197.1 (*s*); **2hb**: 32.6 (*t*); 47.3 (*d*); 47.5 (*d*); 51.0 (*d*); 52.6 (*t*); 55.7 (*d*); 56.8 (*d*); 64.70 (*d*); 66.3 (*s*); 135.9 (*d*); 136.3 (*d*); 197.4 (*s*).

Methyl 2,2-Dibromo-3-oxocyclobutane-1-nonanoate (**2i**): IR (film): 2940, 2860, 1810, 1740, 1440, 1200, 1175, 740. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.20 (*m*, 10 H); 1.48–1.73 (*m*, 4 H); 2.30 (*t*, 2 H, ^3J = 7.6); 2.75–3.05 (*m*, 2 H); 3.15–3.35 (*m*, 1 H); 3.66 (*s*, MeO). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 24.9 (*t*); 27.5 (*t*); 29.06 (*t*); 29.12 (*t*); 29.19 (*t*); 29.26 (*t*); 34.02 (*t*); 34.06 (*t*); 46.1 (*d*); 46.9 (*t*); 51.4 (*q*); 66.2 (*s*); 174.2 (*s*); 192.4 (*s*).

2,2-Dibromo-3-(9-hydroxynonyl)cyclobutanone (**2j**): B.p. 180°/0.08 Torr. IR (film): 3500, 2940, 2860, 1810, 1760, 1740, 1280, 670. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.10–1.60 (*m*, 12 H); 1.60–2.10 (*m*, 4 H); 2.80–3.05 (*m*, 2 H); 3.15–3.35 (*m*, 1 H); 4.25 (*t*, ^3J = 6.5, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 25.6 (*t*); 27.5 (*t*); 28.2 (*t*); 29.0 (*t*); 29.28 (*t*); 29.30 (2*t*); 34.0 (*t*); 46.1 (*d*); 46.9 (*t*); 66.3 (*s*); 67.7 (*t*); 192.4 (*s*).

2,2-Dibromo-3-(2-methylpropyl)cyclobutanone (**2k**): B.p. 83°/0.1 Torr. IR (film): 2970, 2940, 2910, 2870, 1800, 1760, 1740, 1470, 1390, 1375. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.92–1.05 (*m*, 6 H); 1.46 (*dt*, ^2J = 13.4, ^3J = 6.7, 1 H, Me_2CHCH_2); 1.74 (*m*, Me_2CHCH_2); 1.82 (*dt*, ^2J = 13.4, ^3J = 6.7, 1 H, Me_2CHCH_2); 2.97 (*ddt*, ^3J = 12.7, 9, 6.7, H–C(3)); 2.98 (*dd*, ^2J = 20, ^3J = 9, 1 H–C(4)); 3.26 (*dd*, ^2J = 20, ^3J = 12.7, 1 H–C(4)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 22.4 (*q*); 22.7 (*q*); 26.6 (*d*); 42.9 (*t*); 44.4 (*d*); 47.2 (*t*); 66.7 (*s*); 192.5 (*s*).

2,2-Dibromo-3-(9,9-dimethoxynonyl)cyclobutanone (**2l**): The starting olefin **5l** was prepared from alcohol **5j** by oxydation [14] and acetalization [15]. *Data of* **2l**: IR (film): 2930, 2860, 1800, 1760, 1740, 1260, 1230, 670. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.20–2.00 (*m*, 16 H); 2.80–3.05 (*m*, 2 H); 3.15–3.45 (*m*, 1 H); 3.57 (*s*, 3 H); 3.78 (*dd*, ^3J = 8.6, 2.8, $(MeO)_2CH$); 3.89 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 26.5 (*t*); 27.5 (*t*); 29.3 (3*t*); 29.5 (*t*); 33.4 (*t*); 34.0 (*t*); 46.1 (*d*); 46.9 (*t*); 54.5 (*q*); 61.4 (*q*); 66.2 (*s*); 86.7 (*d*); 192.4 (*s*).

β-Dibromomethyl Esters **4**: *General Procedure 1.* A soln. of base (1 mmol) in anh. MeOH (3 ml) was added to a soln. of cyclobutanone **2** (amount obtained from 1 mmol of olefin **5**) in anh. MeOH (5 ml). After stirring for 1 h at 20°, 1M HCl (1.3 ml) and sat. aq. $NaHCO_3$ soln. (1 ml) were successively added. After solvent evaporation, H_2O (10 ml) and Et_2O (20 ml) were added, and the two phases were separated. The aq. layer was extracted with Et_2O

(25 ml, twice), the combined org. phase washed with sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and evaporated, and the residue purified by CC (silica gel, Et_2O/petroleum ether). This procedure was used with cyclobutanones **2a**, **2b**, **2f–l**.

Procedure 2 via *the β-Dibromomethyl Acid.* Base (1.05 mmol) was added to a soln. of cyclobutanone **2a** (amount obtained from 1 mmol of olefin **5a**) in dioxane/H_2O 4:1 (2 ml). After stirring for 1 h at 20°, 1M HCl (1.2 ml) and sat. aq. NaCl soln. (3 ml) were added, and the mixture was extracted with Et_2O (20 ml, 3 times). The combined org. phases were washed with sat. aq. $NaHCO_3$ soln. (5 ml), dried ($MgSO_4$), and evaporated.

The crude acid was dissolved in Et_2O (5 ml), and CH_2N_2 in Et_2O (1 ml) was added. After 5 min, AcOH was added (0.2 ml, amount necessary to discolour the soln.), the solvent evaporated, and the residue purified by CC (silica gel, Et_2O/petroleum ether) to yield ester **4a**.

Methyl 3-(Dibromomethyl)undecanoate (**4a**): IR (film): 3040, 3010, 2970, 2940, 2870, 1740, 1465, 1455, 1430, 1200, 1160, 690. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.88 (*t*, ^3J = 6.5, 3 H); 1.15–1.79 (*m*, 14 H); 2.42 (*dd*, ^2J = 15.3, ^3J = 6.9, H–C(2)); 2.50 (*m*, H–C(3)); 2.73 (*dd*, ^2J = 15.3, ^3J = 4.5, H–C(2)); 3.71 (*s*, MeO); 6.00 (*d*, ^3J = 2.5, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 14.1 (*q*); 22.6 (*t*); 26.7 (*t*); 29.2 (*t*); 29.4 (*t*); 29.5 (*t*); 31.8 (*t*); 32.2 (*t*); 36.6 (*t*); 46.3 (*d*); 51.90 (*q*); 52.2 (*d*); 172.5 (*s*). Anal. calc. for $C_{13}H_{24}Br_2O_2$ (372.15): C 41.96, H 6.50, Br 42.94; found: C 42.24, H 6.57, Br 42.25.

Methyl 4,4-Dibromo-3-phenylbutanoate (**4b**): IR (film): 3140, 3110, 3070, 3000, 2950, 2850, 1740, 1455, 1430, 1225, 1160, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.00 (*dd*, ^2J = 16.4, ^3J = 9.4, H–C(2)); 3.21 (*dd*, ^2J = 16.4, ^3J = 5, H–C(2)); 3.60 (*s*, MeO); 3.91 (*ddd*, ^3J = 9.4, 5, 4.6, H–C(3)); 5.93 (*d*, ^3J = 4.6, $CHBr_2$); 7.27–7.37 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 36.7 (*t*); 50.6 (*d*); 51.9 (*q*); 52.3 (*d*); 128.2 (*d*); 128.6 (*d*); 138.2 (*s*); 162.9 (*s*). Anal. calc. for $C_{11}H_{12}Br_2O_2$ (336.03): C 39.32, H 3.60, Br 47.56; found: C 39.79, H 3.76, Br 46.82.

Methyl 3-(Dibromomethyl)-2-propylhexanoate (**4f**): IR (film): 2960, 2935, 2870, 1735, 1465, 1460, 1435, 1240, 1210, 1195, 1170. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.92, 0.97 (2*t*, ^3J = 7, 2 Me); 1.10–1.90 (*m*, 6 H); 2.20–2.40 (*m*, H–C(3)); 2.55–2.70 (*m*, H–C(2)); 3.70 (*s*, MeO); 5.83 (*d*, ^3J = 2.9, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 14.0 (*q*); 14.2 (*q*); 20.9 (*t*); 22.6 (*t*); 31.7 (*t*); 32.4 (*t*); 49.1 (*d*); 50.4 (*d*); 51.6 (*d*); 51.7 (*q*); 175.1 (*s*). Anal. calc. for $C_{11}H_{20}Br_2O_2$ (344.10): C 38.40, H 5.86; found: C 38.34, H 5.89.

Methyl 12-(Benzyloxy)-3-(dibromomethyl)dodecanoate (**4g**): IR (film): 2930, 2855, 1740, 1435, 1200, 1170, 1100, 735, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.2–1.7 (*m*, 16 H); 2.42 (*dd*, ^2J = 15.2, ^3J = 6.8, 1 H–C(2)); 2.50 (*m*, H–C(3)); 2.74 (*dd*, ^2J = 15.2, ^3J = 4.4, 1 H–C(2)); 3.46 (*t*, ^3J = 6.6, CH_2(12)); 3.71 (*s*, MeO); 4.50 (*s*, $PhCH_2$); 6.00 (*d*, ^3J = 2.4, $CHBr_2$); 7.20–7.40 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 26.2 (*t*); 26.7 (*t*); 29.3 (*t*); 29.42 (2*t*); 29.45 (*t*); 29.8 (*t*); 32.1 (*t*); 36.6 (*t*); 46.3 (*d*); 51.9 (*q*); 52.2 (*d*); 70.5 (*t*); 72.9 (*t*); 127.5 (*d*); 127.6 (*d*); 128.3 (*d*); 138.7 (*s*); 172.5 (*s*). EI-MS (70 eV): 494 (0.2), 492 (0.4), 490 (0.2, $M^{+\cdot}$), 213 (3), 181 (4), 107 (12), 91 (100). HR-MS: 490.0710 ($C_{21}H_{32}Br_2O_3^{+\cdot}$; calc. 490.0718).

*Methyl 2-(Dibromomethyl)-2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-indene-1-carboxylate* (**4ha**) *and Methyl 1-(Dibromomethyl)-2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-indene-2-carboxylate* (**4hb**; 3:1 mixture): IR (film): 3080, 2980, 2940, 2880, 1730, 1210, 1180, 670, 680. ^{1}H-NMR ($CDCl_3$, 250 MHz): **4ha**: 3.68 (*s*, MeO); 5.80 (*d*, ^3J = 9.7, $CHBr_2$); **4hb**: 3.67 (*s*, MeO); 6.05 (*d*, ^3J = 10.0, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): **4ha**: 34.7 (*t*); 45.6 (*d*); 47.4 (*d*); 47.5 (*d*); 47.8 (*d*); 51.0 (*d*); 51.8 (*d*); 52.24 (*d*); 52.27 (*t*); 57.6 (*q*); 135.8 (*d*); 137.4 (*d*); 174.5 (*s*); **4hb**: 32.5 (*t*); 45.5 (*d*); 46.8 (*d*); 47.8 (*d*); 51.7 (*d*); 51.9 (*d*); 53.6 (*t*); 54.3 (*d*); 57.1 (*q*); 136.3 (*d*); 136.5 (*d*); 174.5 (*s*). Anal. calc. for $C_{13}H_{16}Br_2O_2$ (364.09): C 42.89, H 4.43, Br 43.90; found: C 42.94, H 4.53, Br 43.85.

Dimethyl 3-(Dibromomethyl)dodecanedioate (**4i**): IR (film): 2930, 2860, 1740, 1440, 1200, 1170, 680. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.15–1.50 (*m*, 10 H); 1.50–1.75 (*m*, 4 H); 2.30 (*t*, ^3J = 7.6, CH_2(11)); 2.41 (*dd*, ^2J = 15.2, ^3J = 6.7, 1 H–C(2)); 2.51 (*m*, H–C(3)); 2.73 (*dd*, 1 H, ^2J = 15.2, ^3J = 4.5, 1 H–C(2)); 3.66 (*s*, MeO); 3.70 (*s*, MeO); 5.99 (*d*, ^3J = 2.5, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 24.9 (*t*); 26.7 (*t*); 29.07 (*t*); 29.12 (*t*); 29.17 (*t*); 29.3 (*t*); 32.1 (*t*); 34.1 (*t*); 36.5 (*t*); 46.2 (*d*); 51.4 (*q*); 51.9 (*q*); 52.1 (*d*); 172.5 (*s*); 174.3 (*s*). Anal. calc. for $C_{15}H_{26}Br_2O_4$ (430.19): C 41.88, H 6.09, Br 37.15; found: C 42.15, H 6.34, Br 38.92.

Methyl 3-(Dibromomethyl)-12-hydroxydodecanoate (**4j**): IR (film): 3380, 2940, 2860, 1740, 1440, 1220, 1175, 1060, 680. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.20–1.50 (*m*, 12 H); 1.50–1.90 (*m*, 4 H); 2.42 (*dd*, ^2J = 15.3, ^3J = 6.9, 1 H–C(2)); 2.48 (*m*, H–C(3)); 2.73 (*dd*, ^2J = 15.3, ^3J = 4.4, 1 H–C(2)); 3.63 (*t*, ^3J = 6.5, CH_2(12)); 3.70 (*s*, MeO); 5.99 (*d*, ^3J = 2.4, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 25.7 (*t*); 26.6 (*t*); 29.2 (*t*); 29.31 (*t*); 29.34 (*t*); 29.40 (*t*); 32.1 (*t*); 32.7 (*t*); 36.5 (*t*); 46.2 (*d*); 51.9 (*q*); 52.1 (*d*); 62.9 (*t*); 172.5 (*s*). EI-MS (70 eV): 405 (0.1), 403 (0.2), 401 (0.1, $[M + H]^+$), 293 (4), 291 (4), 270 (4), 229 (6), 211 (8), 199 (8), 149 (14), 74 (100). HR-MS: 401.0317 ($C_{14}H_{27}Br_2O_3^+$; calc. 401.0327).

Methyl 3-(Dibromomethyl)-5-methylhexanoate (**4k**): IR (film): 2960, 2940, 2880, 1740, 1470, 1440, 1370, 1310, 1260, 1220, 1175, 690. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.93, 0.94 (2*t*, ^3J = 5.85, 2 Me); 1.28 (*dt*, ^2J = 13.5, ^3J = 6.7, 1 H–C(4)); 1.47–1.63 (*m*, 1 H–C(4), H–C(5)); 2.41 (*dd*, ^2J = 15.9, ^3J = 6.3, 1 H–C(2)); 2.57 (br. *quint. d*, $^3J \approx 6$,

2.5, H–C(3)); 2.71 (*dd*, ^2J = 15.9, ^3J = 5.8, 1 H–C(2)); 3.70 (*s*, MeO); 5.99 (*d*, ^3J = 2.5, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 22.4 (*q*); 22.7 (*q*); 25.1 (*d*); 36.7 (*t*); 41.1 (*t*); 44.0 (*d*); 51.9 (*q*); 52.4 (*d*); 172.4 (*s*). Anal. calc. for $C_9H_{16}Br_2O_2$ (316.04): C 34.21, H 5.10, Br 50.57; found: C 34.44, H 5.13, Br 50.52.

Methyl 3-(Dibromomethyl)-12,12-dimethoxydodecanoate (**4l**): IR (film): 2940, 2860, 1740, 1440, 1260, 1230, 1180, 1120, 1110, 690. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.3–1.95 (*m*, 16 H); 2.41 (*dd*, ^2J = 15.2, ^3J = 6.8, 1 H–C(2)); 2.49 (*m*, H–C(3)); 2.73 (*dd*, ^2J = 15.2, ^3J = 4.4, 1 H–C(2)); 3.57 (*s*, MeO); 3.72 (*s*, MeO); 3.78 (*dd*, ^3J = 8.4, 2.9, H–C(12)); 3.89 (*s*, MeO); 6.0 (*d*, ^3J = 2.4, $CHBr_2$). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 26.6 (*t*); 26.7 (*t*); 29.29 (*t*); 29.35 (*t*); 29.39 (*t*); 32.1 (*t*); 33.4 (*t*); 36.6 (2*t*); 46.2 (*d*); 51.9 (*q*); 52.1 (*d*); 54.5 (*q*); 58.8 (*q*); 86.8 (*d*); 172.5 (*s*). EI-MS (70 eV): 417 (26), 415 (52), 413 (29, $[M - 31]^+$), 383 (14), 335 (13), 333 (13), 80 (100). HR-MS: 413.0330 ($C_{15}H_{27}Br_2O_3^+$; calc. 413.0327).

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