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Tetrahedron
Tetrahedron 60 (2004) 3717–3729

Unusual selectivity in the oxidative functionalization of *gem*-dibromocyclopropanes

Alexey V. Nizovtsev,[a] Mark S. Baird[b,*] and Ivan G. Bolesov[a]

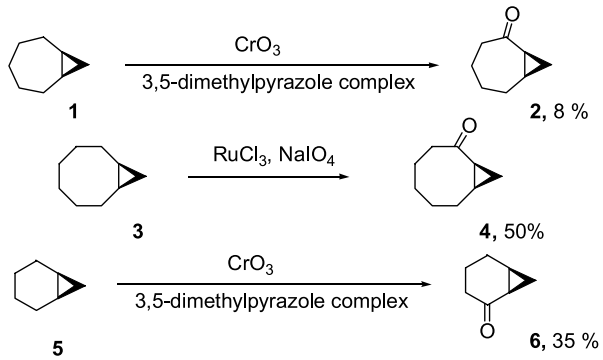
[a]*Department of Chemistry, State University of Moscow, Leninskie gory, 1, Bld.3, Moscow, 119992, GSP-2, Russian Federation*
[b]*Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*

Received 17 October 2003; revised 19 January 2004; accepted 12 February 2004

Abstract—Oxidation of *gem*-dibromocyclopropanes with chromium trioxide in acetic acid or a number of other reagents is generally slower than that of the corresponding cyclopropane; in a number of cases moderate yields of products are obtained but these show unexpected oxidation patterns.

1. Introduction

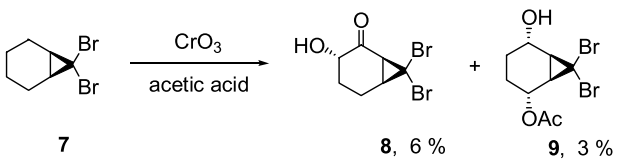
Functionalized dihalocyclopropanes are of considerable interest in view of their importance in the synthesis of a range of natural cyclopropane containing compounds or synthetic analogues.[1] Although there are many approaches to such compounds, one of the most effective starting points is the dihalocyclopropanation of an alkene using haloform and base, a reaction which generally, but not always proceeds through the formation and trapping of a dihalocarbene. Although simple alkenes are efficiently trapped in this way, more complex alkenes are either less readily available or undergo alternative reactions. In some cases this problem may be overcome by an appropriate use of protecting groups. However, an alternative approach would be to introduce carbonyl or hydroxy groups into a simple alkyldibromocyclopropane by oxidation of one or more C–H bonds. There is ample precedent for this reaction in the case of alkylcyclopropanes themselves. Such an oxidation has been used for many years in determining the structure of long chain cyclopropane containing fatty acids, oxidation with chromium trioxide occurring adjacent to the ring and allowing structure assignment by mass spectrometry.[2,3] Oxidation has also been applied to bicyclo[n.1.0]alkanes, as in the conversion of **1** into **2**,[4] **3** into **4**[5] and **5** into **6**[4] (Scheme 1).



Scheme 1.

The oxidation of such bicyclic systems with ozone is also reported. Compound **3** leads almost exclusively to the 2-one **4**, although a minor amount of the corresponding 4-one is also observed; none of the 3-one was isolated.[6] Highly selective oxidations of cyclopropanes leading to α-cyclopropyl ketones have been performed with the use of other oxidants, ruthenium tetroxide,[5,7] dimethyldioxirane,[8] and ozone in the presence of silica.[6,9] Oxidation of bicyclo[4.1.0]heptane with cytochrome P450[10] or with oxometalloporphinates and iodosylbenzene[11] leads predominantly to *endo*- and *exo*-bicyclo[4.1.0]heptan-2-ol.

In contrast, oxidation of dihalocyclopropanes is reported generally to be less effective. Thus chromium trioxide oxidation of 7,7-dibromobicyclo[4.1.0]heptane **7** leads to compounds **8** and **9** in low yields (Scheme 2).[12]



Scheme 2.

Keywords: Dibromocyclopropane; Oxidation.
* Corresponding author. Tel.: +44-1248-382-374; fax: +44-1248-370-528; e-mail address: chs028@bangor.ac.uk

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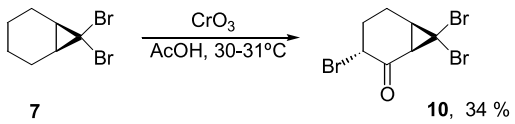
doi:10.1016/j.tet.2004.02.024

Other *gem*-dihalocyclopropanes have also been converted into the corresponding α-cyclopropylketones using chromium trioxide in glacial acetic acid[12,13] or dry ozonolysis,[14] but also in yields from low to modest. We now report the oxidation of a number of *gem*-dibromocyclopropanes, primarily using chromium trioxide in glacial acetic acid.

2. Results and discussion

We could not reproduce the results of oxidation of 7,7-dibromobicyclo[4.1.0]heptane **7** described above.[12] On reaction of **7** with chromium trioxide in glacial acetic acid, an unexpected tribromoketone **10** was obtained with a yield of 34% instead of **8** and **9** (Scheme 3).



Scheme 3.

The yield of **10** depended on the amounts of chromium trioxide and acetic acid (Table 1). It was necessary to use not less than 15 mol. equiv. of oxidant for complete conversion of starting material. Acid products were not obtained under these conditions. The reaction did not proceed when ether was used as a solvent instead of acetic acid.

Table 1. Oxidation of **7** with chromium trioxide in glacial acetic acid

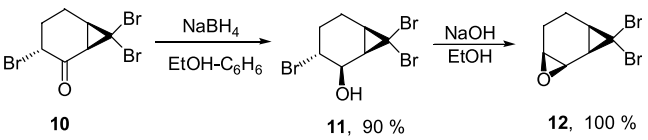
Amount of **7** (mmol)	CrO_3 (mol. equiv.)	AcOH (mL)	Unreacted **7**[a] (%)	Yield of **10**[b] (%)
3	5	8	78	—
3	10	15	32	—
3	15	15	0.5	—
3	20	60	0	36
10	15	100	8	—
10	15	50	0.5	34

[a] By GLC.
[b] Isolated yield.

Formation of **10** possibly occurs through replacement of hydrogen at C(3) in the proposed intermediate 7,7-dibromobicyclo[4.1.0]heptan-2-one by a bromine atom; the source of the bromine is not clear, but may be explained by the low yield of this product—presumably decomposition of the remainder leads to a species that is a brominating agent. Alternatively **8** may actually be an intermediate and again be brominated under the reaction conditions. The yield of **10** was not increased by addition to the reaction mixture of sodium bromide or dibromomethane, but when the reaction was carried out in the presence of carbon tetrabromide (10 mol. equiv.), product **10** was obtained in 38% yield.

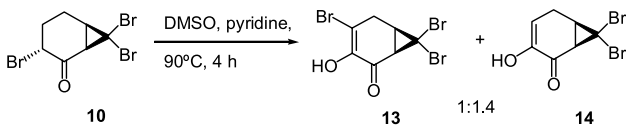
Attempts to dehydrobrominate the ketone **10** with potassium *tert*-butoxide in dichloromethane or ether, with sodium hydroxide under phase transfer conditions or with 1,5-diazabicyclonon-5-ene led to the consumption of starting material, but no products were isolated, while on reaction of **10** with phenylmagnesium bromide followed by water, 7,7-dibromobicyclo[4.1.0]heptan-2-one was formed.

For proof of structure, the tribromoketone **10** was reduced with sodium borohydride to the *trans*-alcohol **11** which on treatment with base gave the *syn*-3-oxatricyclo[5.1.0.0^{2,4}]-octane **12** (Scheme 4), suggesting that the tribromide **11** has the configuration shown. Epoxide **12**, which could be distinguished clearly from the *anti*-isomer by ^{1}H NMR,[15] represents the first example of such a *gem*-dihalogeno *syn*-ring system.



Scheme 4.

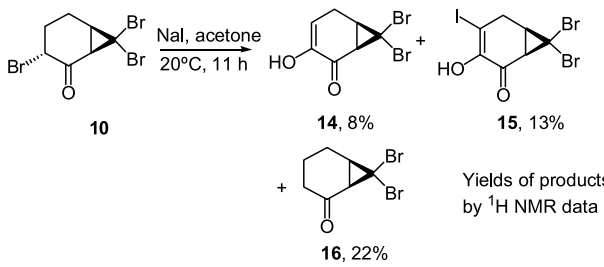
Attempts to ring-open the epoxide **12** using either phenyl magnesium bromide and copper (I) iodide in THF or benzylamine in the presence of $Yb(CF_3SO_3)_2$ were not successful. The alcohol **11** was readily converted into the corresponding acetate; attempts to dehydrobrominate this were largely unsuccessful, reaction with dimethylaminopyridine in DMSO for 3 h at 100 °C leading to the recovery of starting material; however, reaction with 1,5-diazabicyclo-undec-5-ene in DMSO for 3 h at 125 °C did lead to 2-acetoxy-7,7-dibrombicyclo[4.1.0]hept-3-ene, albeit only in 19% yield. Attempts to prepare an enamine by reaction of **10** with morpholine or a silyl enol ether by reaction with trimethylchlorosilane in the presence of triethylamine were not successful and starting material was recovered. Reaction with pyridine in DMSO, led unexpectedly to the formation of two enones **13** and **14** (Scheme 5).



Scheme 5.

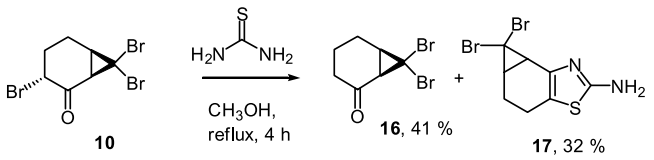
The mechanism of formation of enone **14** is probably similar to that involved in the oxidation of α-bromoketones with DMSO to α-dicarbonyl compounds,[16,17] and includes S_N2 attack of the sulfoxide oxygen at the brominated carbon (CHBr fragment) with subsequent elimination of dimethyl sulfide and then enolization. The mechanism of formation of **13** is not clear. When tribromoketone **10** was treated with potassium iodide and potassium carbonate in DMSO (reported conditions for a similar oxidation[17]), the product did not contain any **13** or **14**, but probably the α-iodoketone, 3-iodo-7,7-dibromobicyclo[4.1.0]heptan-2-one, related to **10** was formed. This was concluded based on the appearance of a new double doublet at lower field in the ^{1}H NMR spectrum compared to starting material (4.48 compared to 4.39 ppm for **10**) and a new carbonyl signal in the ^{13}C NMR (192.5 compared to 192.8 ppm for **10**). By TLC the product showed just one spot with the same R_f as starting material. An attempt to prepare this α-iodoketone by reaction of **10** with sodium iodide in acetone was not successful and the product of reduction—dibromoketone

16—was formed instead (Scheme 6), similar to reduction of α-bromoketones with NaI/Me_3SiCl[18] or HI.[19] As by-products enones **14** and **15** were formed. Unfortunately compounds **15** and **16** could not be separated and were analyzed as a mixture. The assignment of structure **15** was based on ^1H and ^{13}C NMR spectra, which had signals similar to those for **13** except one for the carbon next to the iodine, which was at higher field compared with **13** (93.1 ppm for **15** and 116.6 ppm for **13**). The mechanism of formation of **14** and **15** is again not understood.



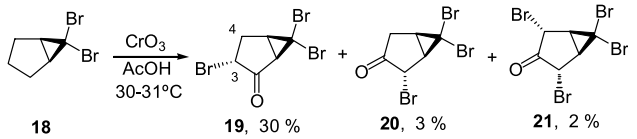
Scheme 6.

Treatment of **10** with thiourea in refluxing methanol, a standard procedure for thiazole formation from α-bromoketones,[20] led after 4 h to a mixture of **16** and thiazole **17** in modest yields (Scheme 7).



Scheme 7.

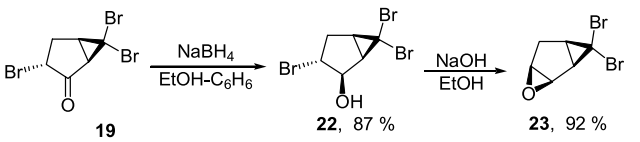
In a similar manner to 7,7-dibromobicyclo[4.1.0]heptane **7**, 6,6-dibromobicyclo[3.1.0]hexane **18** reacted with chromium trioxide in glacial acetic acid to give **19** as the major product albeit in poor yield, together with a mixture of tri- and tetrabromoketones **20**, **21** (Scheme 8).



Scheme 8.

The *exo*-ketone **19** was characterized on the basis of the larger coupling of H-3 to *endo*-H-4 than to *exo*-H-4. Isomer **20** showed an ABX pattern for the H-4, H-4′ and H-5, only the *endo*-H-4 coupling to H-5; in the same way H-1 was not split by H-2, suggesting an *exo*-configuration for the bromine at C-2. Compound **21** showed just two singlets in the ^1H NMR, (δ_H: 2.87 and 4.17) and four carbon signals; on the basis of the lack of coupling between H-1 and H-2 and the symmetry, it was assigned as the *exo*,*exo*-isomer. Once again, the tribromide **19** could be reduced to a single alcohol **22**, and this was dehydrobrominated to give the *syn*-epoxide **23** (Scheme 9).

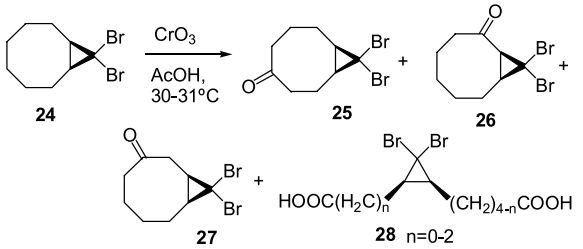
Chromium trioxide in acetic acid reacts with 9,9-dibromobicyclo[6.1.0]nonane **24** to give γ-cyclopropylketone **25** as



Scheme 9.

the major product (Table 2). The best yield of **25** was obtained when 8 mol. equiv. of oxidant were used (Table 2), but even in this case a small amount of the starting material (4%) remained unreacted. Among the other products isolated were the 2-one **26** (13%), the 3-one **27** (<0.5%),[21] and a mixture of (dibromomethano)suberic acids **28** (7%).

Table 2. Oxidation of **24** with chromium trioxide in glacial acetic acid[a]



CrO_3 (equiv.)	Product, isolated yield (%)				
	24	**25**	**26**	**27**	**28**[b]
5	20	39	14	1	—[c]
7	5	41	12	<0.5	7
8	4	48	13	<0.5	7
9	1	48	11	<0.5	9
15	—	33[d]	1	<0.5	—[c]

[a] All experiments were performed with 3 mmol of starting material in 20 mL of glacial acetic acid at 30–31 °C for 1 h.
[b] Isolated as dimethyl diester after treatment with diazomethane.
[c] Acid products were not worked-up.
[d] Also isolated as a 2,4-dinitrophenyl-hydrazone (21%).

It is interesting to note that oxidation of *exo*-9-bromobicyclo[6.1.0]nonane with dimethyldioxirane is reported to lead to the corresponding 4-one, although only in 4% yield and that the dibromide **24** does not react with this reagent.[8] A number of other dihalocyclopropanes are also reported to be inert to this reagent.[8]

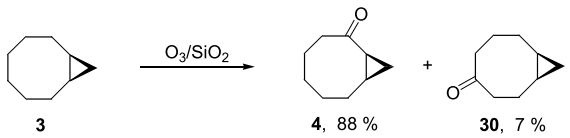
Similar results to those with chromium trioxide were obtained on oxidation of **24** with ruthenium tetroxide or ozone (Table 3) suggesting that the regioselectivity of the oxidation depends mostly on the electron withdrawing properties of the *gem*-dibromocyclopropane fragments.

Table 3. Yields of products in oxidation of **24** with different oxidants

Oxidant	Product (%)				
	24	**25**	**26**	**27**	**28**[a]
CrO_3 (8 mol. equiv.), AcOH	4	48	13	<0.5	7
H_5IO_6 (8 mol. equiv.), $RuCl_3$ (5 mol.%), 70–75 °C, 52 h	9	37	7	2	17
Ozone/SiO_2	31[b]	48[b]	6[b]	5[b]	—[c]

[a] Isolated as dimethyl diester after treatment with diazomethane.
[b] Yield by GLC data.
[c] Acid products were not worked-up.

It is necessary to note that oxidation of **24** with periodic acid required vigorous conditions, refluxing the reaction mixture for 52 h (at room temperature conversion of starting material was less 5%). By comparison oxidation of bicyclo[6.1.0]nonane **3** with 3 equiv. sodium metaperiodate in the presence of ruthenium trichloride proceeds at room temperature giving after 18 h bicyclo[6.1.0]nonan-2-one with an yield of 50%.[5] Dry ozonolysis of dibromocyclopropane **24** on silica also proceeds more slowly than the oxidation of the non-halogenated compound. Thus even when the ozonolysis was repeated three times, conversion of starting material was only 69%. Full conversion of the non-brominated analogue of **24**, bicyclo[6.1.0]nonane was observed even after one ozonolysis cycle,[6,22] and led primarily to a different regioselectivity, the α-cyclopropyl ketone **4** being obtained in a yield of 88% together with a small amount only of **30** (7%) (Scheme 10).[6]

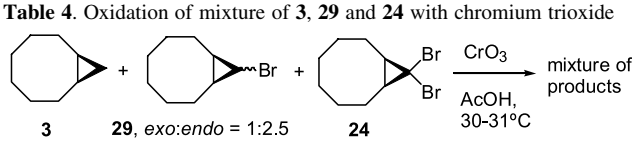


Scheme 10.

The bicycloalkane **3** is also oxidized with dimethyldioxirane, and in this case both the above ketones are isolated again in a ratio of 88:7.[8] 9,9-Dibromobicylo[6.1.0]nonane **24** does not react with dimethyldioxirane.[8] It is interesting to note that, unlike **24**, dibromide **7** was essentially unreactive to periodic acid (10 mol. equiv.) in the presence of ruthenium tetroxide (5 mol%) at 70 °C over 92 h. *gem*-Dibromocyclopropane **24** did not react with chromium trioxide in acetone or in dichloromethane in the presence of 3,5-dimethylpyrazole even when the reaction mixture was refluxed for 18 h. By comparison non-halogenated cyclopropanes react with chromium trioxide–3,5-dimethylpyrazole complex in dichloromethane even at −20 °C to give, after 3 h, α-ketones with modest yields.[4]

In order to examine the relative rates of oxidation of brominated and nonbrominated cyclopropanes, a mixture of **3**, **24** and 9-bromobicyclo[6.1.0]nonane (**29**, *exo*–*endo*=1:2.5) was treated with 8 equiv. of chromium trioxide in glacial acetic acid and the consumption of starting materials was followed by GLC (Table 4). At the start of the reaction the relative peaks areas for **3**, **29** and **24** were 37:32:31. The peak for **3** had disappeared after 10 min. Those for the two monobromides **29** had essentially disappeared after 45 min (it is interesting to note that ratio of remaining monobromides **29** did not significantly change during the experiment. This suggests that the position of bromine in the substrate does not influence the rate of oxidation). After 60 min, ca. 45% (by GC/MS data) of the dibromide **24** remained.

Table 4. Oxidation of mixture of **3**, **29** and **24** with chromium trioxide



Time of reaction	Contents of starting bicyclo[6.1.0]nonanes in the neutral fraction of the reaction mixture by GLC or GC/MS (%)		
	3	**29**	**24**
0	37[a]	32[a]	31[a]
5	4[a]	<19[a]	33[a]
10	—[a]	<7[a]	31[a]
15	—[b]	<3[b]	24[b]
60	—[b]	0[b]	14[b]

[a] By GLC.
[b] by GC/MS.

The selective oxidation of C–H bonds adjacent to cyclopropanes is usually considered to be due to activation by the ring of the neighboring methylene group. The two bromine atoms instead of hydrogen at C(9) of compound **3** seem to lead to a redistribution of the electron density in the bicyclo[6.1.0]nonane skeleton. Because of this, the propensity of an α-methylene group to be oxidized appears to be decreased. From an MO point of view, the oxidant removes an electron from the HOMO of the substrate. Optimization of geometries of both compounds **24** and **3** by ab initio methods using the STO-3G basis set followed by calculation of the HOMO location has shown, that in **24** this is located on the bromines and the quaternary carbon (energy −7.86 eV, Fig. 1), but in **3** it is located on positions 1, 2, 7 and 8 of the eight membered ring (energy −9.33 eV, Fig. 2). This suggests that oxidation of the dibromide begins

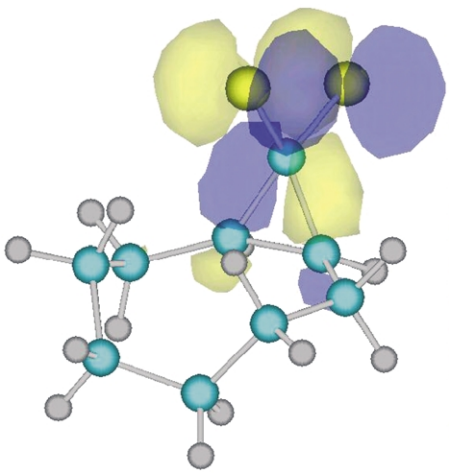


Figure 1. HOMO of 9,9dibromobicyclo-[6.1.0]-nonane **24**.

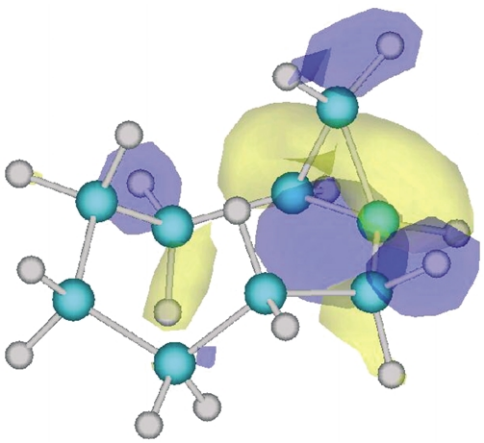
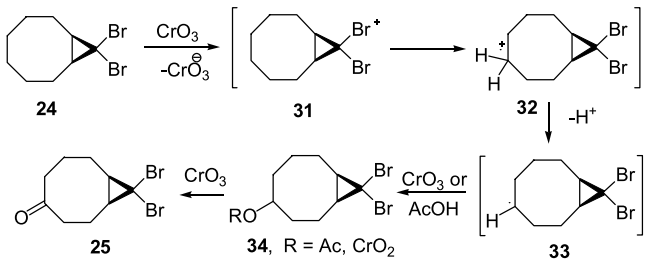


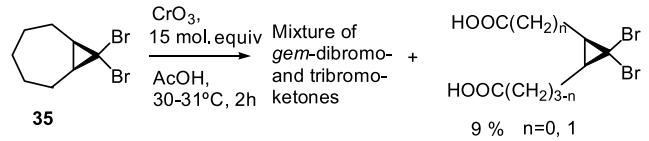
Figure 2. HOMO of bicyclo[6.1.0]nonane **3**.

by coordination of the oxidant to the bromine atoms followed by removal of an electron from the HOMO of substrate. Interaction of the derived cyclopropyl cation-radical **31** with a nearby γ-methylene group possibly produces the cation-radical **32** (Scheme 11). This loses a proton giving radical **33**. Reaction of this with solvent (AcOH) or chromium trioxide would give the ester **34**, this reacting with another molecule of oxidant forming γ-ketone **25**. The isolation of the corresponding alcohols from the ozonolysis of cyclopropane and *gem*-dichlorocyclopropane derivatives[9,14,23] can serve as evidence for participation in the reaction of intermediates of type **34**. The formation of 9,9-dibromobicyclo[6.1.0]nonan-2-one **26** can proceed by a similar process but the difference is in the redistribution of electrons in the intermediate **31** from the α-methylene groups (not from γ-links). A similar oxidation involving cation-radicals and radicals was suggested for reaction of 3,6-dehydrohomoadamantane with chromyl derivatives.[24]



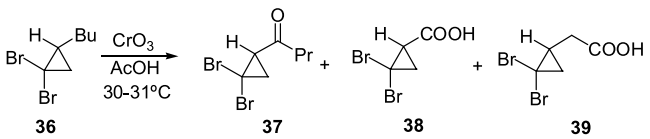
Scheme 11.

Oxidation of 8,8-dibromobicyclo[5.1.0]octane **35** with chromium trioxide in glacial acetic acid proceeds more slowly than for the other bicyclic *gem*-dibromocyclopropanes (full conversion of starting material with 15 of CrO_3 under the conditions of oxidation of 7,7-dibromobicyclo[4.1.0]heptane required 2 h at 30–31 °C instead of 1 h) and afforded a complex mixture of at least four dibromo- and tribromoketones which were not identified, together with a mixture provisionally characterized as (dibromomethano)pimelic acids (Scheme 12). The formation of tribromoketones was assumed based on the ^{1}H NMR spectrum which contained signals in the region 4.2–4.5 ppm, corresponding to the α-bromoketone CHBr fragment. The major *gem*-dibromo-ketone was not 8,8-dibromobicyclo[5.1.0]octan-4-one.[25] The reason for the lower rate of oxidation of this *gem*-dibromocyclopropane compared with reactions described above remains unclear.



Scheme 12.

Monocyclic *gem*-dibromocyclopropanes react with chromium trioxide less selectively than the bicyclic compounds above. The *gem*-dibromocyclopropylketones formed easily oxidize to carboxylic acids. Thus, e.g. 1,1-dibromo-2-butyl cyclopropane **36** reacted with chromium trioxide in acetic acid giving the ketone **37** together with acids **38** and **39** (Scheme 13). Changing the amount of oxidant from 10 to



Scheme 13.

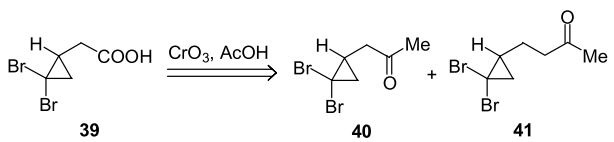
20 mol. equiv. did not change the yield of compound **37**, just the degree of conversion of starting material and the yield of acid products (Table 5). Increasing the amount of chromium trioxide to 30 mol. equiv. and the reaction time to a week led to the disappearance of neutral compounds in the reaction mixture. The acid **38** was isolated with a yield of about 36% as a single product under these conditions.

Table 5. Oxidation of **36** with chromium trioxide in glacial acetic acid

CrO_3 (mol. equiv.)	Time of stirring (h)	**36**	**37**	**38**+**39**[a]	Ratio **38**:**39**[b]
8	1	34	20	>12	1:2.6
10	1	23	24	>18	1:2.2
14	1	12	25	>24	1:2.1
20	1	0	26	>32	1:1.5
30	72	0	0	>36	100:0

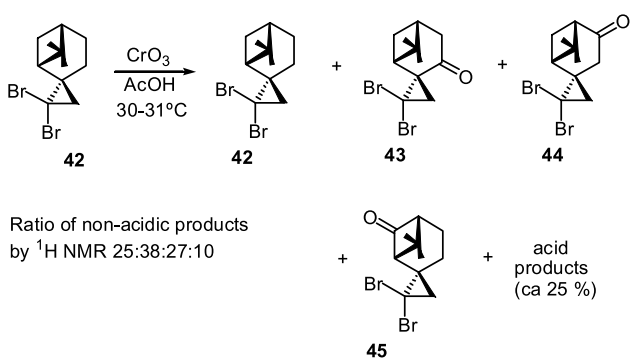
[a] Isolated as mixture of methyl esters after treatment with diazomethane.
[b] By GLC.

The formation of acid **39** is possible just from ketones **40** or **41** (Scheme 14), but not from **37**. The presence of **39** in the reaction mixture is an indirect proof of oxidation not only of an α-methylene group, but also of β- and (or) γ-groups in the chain. By comparison dry ozonolysis of butylcyclopropane led to oxidation of only the α-methylene group giving the butanoylcyclopropane with a yield of 87%.[6]



Scheme 14.

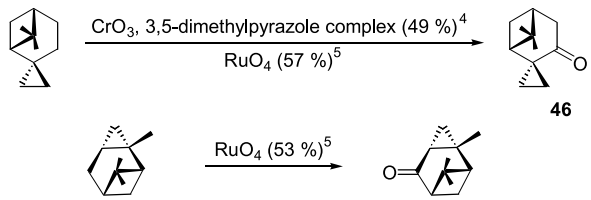
The oxidation of the tricycle **42** derived from (1*S*)-β-pinene can be used as an example of a reaction of a 1,1-dibromo-2,2-dialkylcyclopropane (Scheme 15).



Scheme 15.

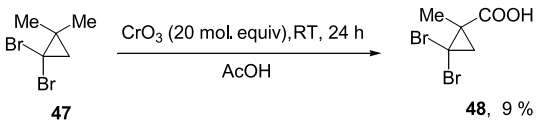
Just as in the case of 1,1-dibromo-2-butylcyclopropane **36**, oxidation occurs relatively equally at both the α- and

β-carbons to give a mixture of ketones **43**–**45**. Products of oxidation of the bridgehead carbons were not found. This can be contrasted to the non-halogenated system where oxidation occurs just at the CH_2-group next to the cyclopropane and a similar oxidation of the cyclopropane derived from β-pinene (Scheme 16).



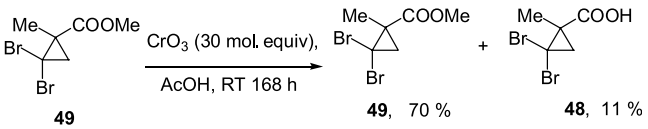
Scheme 16.

The oxidation of a methyl group is also possible under the conditions used in the present work. Thus, for example, reaction of 1,1-dibromo-2,2-dimethylcyclopropane **47** with 20 mol. equiv. chromium trioxide in glacial acetic acid led after 24 h to acid **48** in low yield (Scheme 17). The neutral fraction contained only starting material. Reaction of cyclopropane **47** with 30 mol. equiv. of oxidant for one week led to complete conversion of substrate but did not lead to an increased yield of acid **48**.



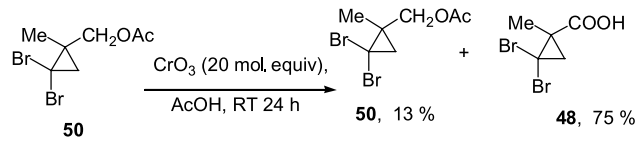
Scheme 17.

Introduction of a methoxycarbonyl group instead of one of methyl group leads to an increased stability to oxidation by chromium trioxide. Thus, in the reaction of ester **49** with 30 mol. equiv. of oxidant, 70% of the starting material was isolated from the reaction mixture even after one week (Scheme 18). The products of oxidation of the methyl group were not observed in this reaction.



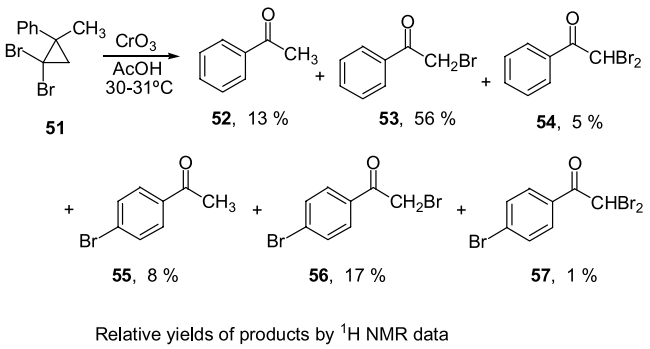
Scheme 18.

Oxidation of the methyl group was also not observed in the reaction of acetate **50**. Acid **48** was isolated in ca. 75% yield and almost 13% starting material was recovered (Scheme 19).



Scheme 19.

An unexpected result was found in the reaction of 1,1-dibromo-2-methyl-2-phenylcyclopropane **51** with chromium trioxide. Instead of oxidation of methyl or phenyl groups, opening of the cyclopropane ring was observed and a mixture of acetophenone and *p*-bromoacetophenone derivatives **52**–**57** was isolated (Scheme 20). It is necessary to note that oxidation of 1-bromo-2-methyl-2-phenylcyclopropane or of a homologue of **51**—1,1-dibromo-2-propyl-2-phenylcyclopropane—with ruthenium tetroxide led to the corresponding cyclopropanecarboxylic acids in good yields.[26,27]



Scheme 20.

3. Conclusion

Oxidation of *gem*-dibromocyclopropanes with chromium trioxide in acetic acid or a number of other reagents is found to be generally slower than that of the corresponding cyclopropane; in a number of cases moderate yields of products are obtained but these show unexpected oxidation patterns. Despite the yields, the products of these simple reactions may have synthetic potential.

This work was carried out as a part of a project supported by the INTAS programme.

4. Experimental

4.1. General

Commercial reagents were used without further purification unless stated. The dibromides (**7**),[28] (**18**),[29] (**24**),[28] (**35**),[30] (**36**),[31] the dibromocarbene adduct of (1*S*)-β-pinene (**42**),[32] and dibromides (**49**),[33] and (**51**)[34] were prepared from alkenes and bromoform in two phase reactions with cetrimide as a phase transfer catalyst using standard procedures. Bicyclo[6.1.0]nonane (**3**)[35] was prepared from (**24**) by reduction with lithium in a mixture of THF and *t*-butanol.[36] 9-Bromobicyclo[6.1.0]nonane (**29**)[37] was prepared from (**23**) by reduction with ethylmagnesium bromide in the presence of titanium isopropoxide.[26] 1,1-Dibromo-2,2-dimethylcyclopropane (**47**)[34] was prepared from isobutene and bromoform in pentane at −25 °C using potassium *tert*-butoxide as a base. The acetate of (2,2-dibromo-1-methylcyclopropyl)methanol (**50**) was prepared from **49** as described.[38] Diethyl ether and tetrahydrofuran were distilled over sodium wire. Petroleum was of boiling point 40–60 °C. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under either dry nitrogen or argon; experiments were conducted under a positive atmosphere

of argon. Unless stated, organic solutions were dried over anhydrous magnesium sulfate and evaporated at 14 mm Hg; yields quoted are for purified compounds and any ratios given are calculated by comparing integrals in the ^{1}H NMR spectrum or by GLC data.

New compounds were homogenous by GLC or TLC. GLC was conducted using a Carlo Erba HRGC 5300 F.I.D. on a capillary column (30 m×0.32 mm id Phase, DB5 split ratio of 50:1) with nitrogen carrier gas. TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualized by examination under an ultraviolet source, by exposure to iodine vapor or by contact with phosphomolybdic acid hydrate (2% in ethanol) followed by heating to 180 °C. Column chromatography was conducted with Matrex Silica 60 (Fisher Scientific Int.Co.) under medium pressure. Melting points are uncorrected. Unless stated, infrared spectra were obtained as solutions in $CHCl_3$ or as liquid films on a Perkin–Elmer 1600 FTIR spectrometer. Low-resolution mass spectra were measured using a Finnigan 8430 spectrometer using EI 70 eV unless stated. Accurate mass measurements refer to ^{79}Br isotopes unless stated and were carried out on a Micromass™ GCT spectrometer. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyzer. NMR spectra were recorded in $CDCl_3$, using Bruker AC250 or A500 spectrometers at 250 or 500 MHz (^{1}H) and 62.9 or 125 MHz (^{13}C). ^{13}C spectra were broad-band decoupled and in most cases corresponding DEPT spectra were also recorded. The results of DEPT spectra are quoted in the form of signs + (corresponding to CH and CH_3 groups) and − (corresponding to CH_2 groups), signals which appear with no sign correspond to quaternary carbons. All previously described compounds were characterized by IR, ^{1}H and ^{13}C NMR and gave data identical to those in the literature.

All calculations were performed using Hyperchem Pro 6.0. Optimization of geometries was achieved by ab initio methods using an STO-3G basis set. The starting MO was the core Hamiltonian. Calculations were continued until the RMS (root-mean-square) gradient became less than 0.1 kcal/A mol. Conformations of all compounds were calculated in vacuo. At the beginning the conformations were calculated using the molecular-mechanics method MM+and then using ab initio methods. The displayed surfaces were generated for orbital contour value 0.06.

4.1.1. Oxidation of 7,7-dibromobicyclo[4.1.0]heptane (7). (a) *With chromium trioxide in acetic acid*. 7,7-Dibromobicyclo[4.1.0]heptane (**7**) (2.540 g, 10 mmol) was added to a suspension of chromium trioxide (15.00 g, 150 mmol) in glacial acetic acid (50 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into a mixture of water (200 mL) and dichloromethane (100 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (2×30 mL), water (30 mL), dried and concentrated in vacuo to give an oil (1.716 g). Chromatography on Silica (100 g) eluting with petrol–ether 10:1 gave *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (**10**) (1.164 g, 34%, R_f 0.42) as a viscous oil which slowly solidified to give white crystals (mp 92–93 °C (hexane)) which showed δ_H: 2.13 (2H, m), 2.46 (3H, m), 2.77 (1H, d, J=9.3 Hz, H-1), 4.39 (1H, dd, J=6.5, 3.4 Hz, H-3); δ_C: 18.3−, 27.7, 30.2−, 32.5+, 36.9+, 49.5+, 192.8 (C=O); IR (cm^{-1}, film): 1711s (C=O), 1444m, 1312m, 1206m, 1181s, 1098m, 1020m, 993m, 944m, 808m, 785m, 736m, 695m, 677m; MS: 350 (0.1), 348 (0.6), 346 (0.6), 344 (0.1), 269 (10), 267 (19), 265 (10), 71 (100); calcd C 24.24, H 2.03%, found C 24.3, H 2.4%.

The combined sodium bicarbonate layers were washed with dichloromethane (2×10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with water (10 mL), dried, filtered and concentrated in vacuo to give a yellow viscous oil (40 mg), which was not identified.

The product above could be also isolated by slow crystallization of the reaction mixture from hot hexane (7 mL per 1 g of mixture), compound (**10**) precipitating as slightly yellow sticks with mp 92–93 °C. If the melting point of product was below 90 °C purification could be achieved by slow crystallization from 10:1 hexane–ethanol (10 mL per 1 g of reaction mixture), giving shiny plates with mp 93–95 °C. The yield obtained by this method was 17–22%.

(b) *With chromium trioxide in ether*. Dibromide (**7**) (762 mg, 3 mmol) was added to a suspension of chromium trioxide (3.00 g, 30 mmol) in dry ether (20 mL) at 0 °C. A strong exothermic effect was observed. The mixture was stirred at 25–30 °C for 1 h, then poured into a mixture of water (100 mL) and ether (50 mL). The aqueous layer was extracted with ether (3×30 mL). The combined organic layers were extracted with sat. aq. sodium bicarbonate (3×10 mL), brine (3×10 mL), dried and concentrated in vacuo to give starting material (676 mg, 89%).

(c) *With periodic acid*. A mixture of dibromide (**7**) (762 mg, 3 mmol), carbon tetrachloride (10 mL), acetonitrile (10 mL), water (15 mL), periodic acid (6.84 g, 30 mmol) and ruthenium trichloride (42 mg, 0.15 mmol, 5 mol%) was stirred at 70–75 °C. After 92 h, the black mixture was cooled, poured in water (20 mL) and extracted with dichloromethane (3× L). The combined organic layers were washed with water (10 mL), sat. aq. sodium bicarbonate (2×10 mL) and water (10 mL), dried and concentrated in vacuo to give an oil (574 mg) which contained by GLC and ^{1}H NMR data starting material (76%), *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (**10**) (7%) and two unidentified compounds.

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (3×5 mL). The combined organic layers were washed with water (10 mL), dried, filtered and concentrated in vacuo to give a yellow viscous oil (1 g), which was not identified.

4.1.2. *exo*-3,7,7-Tribromobicyclo[4.1.0]heptan-*endo*-2-ol (11). Sodium borohydride (73 mg, 1.93 mmol) was added to *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (**10**) (67 g, 1.93 mmol) in dry ethanol (6 mL) and benzene (3 mL), stirred at 15–20 °C for 1 h, then poured in water (30 mL)

and extracted with dichloromethane (4×10 mL). The combined organic layers were washed with water (15 mL), dried and concentrated in vacuo to give an oil (712 mg). Chromatography on Silica (20 g) eluting with 3:2 petrol–ether gave exo-3,7,7-tribromobicyclo[4.1.0]heptan-endo-2-ol (**11**) (608 mg, 90%, R_f 0.40) as white crystals (mp 76.5–79 °C) which showed δ_H: 1.63 (1H, dddd, J=14.7, 13.7, 5.5, 3.2 Hz, H-5^{endo}), 1.73–1.86 (1H, m), 2.09–2.15 (1H, m), 2.15 (1H, ddd, J=10.6, 10.2, 3.2 Hz, H-6), 2.24 (1H, dddd, J=14.7, 10.2, 5.0, 2.2 Hz, H-5^{exo}), 2.31 (1H, dd, J=10.6, 7.5 Hz, H-1), 2.59 (1H, d, J=4.9 Hz, O*H*), 4.19–4.34 (2H, m); δ_C: 23.0−, 31.5+, 33.5, 33.7−, 34.4+, 54.5+, 74.3+; IR (cm^{-1}, $CHCl_3$): 3441br.s (OH), 2949s, 2926s, 2864s, 1443s, 1387m, 1344s, 1289m, 1262s, 1225s, 1191m, 1174s, 1129m, 1112s, 1058s, 1023s, 973m, 959m, 911s, 858m, 820s, 804s, 754s, 718s; calcd C 24.10, H 2.60%, found C 24.4, H 2.4%.

4.1.3. *endo*-8,8-Dibromo-3-oxatricyclo[5.1.0.0^{2,4}]octane (12). Ethanolic sodium hydroxide (1.0 mL, C 0.44 M, 0.44 mmol) was added to *exo*-3,7,7-tribromobicyclo[4.1.0]-heptan-*endo*-2-ol (**11**) (106 mg, 0.3 mmol), stirred for 4 h at ambient temperature, then poured in water (5 mL), extracted with dichloromethane (4×2 mL), dried and concentrated in vacuo to give an oil (99 mg). This was purified on Silica (5 g) eluting with petrol–ether 10:1 to give endo-8,8-dibromo-3-oxatricyclo[5.1.0.0^{2,4}]octane (**12**) (81 mg, 100%, R_f 0.31) as white crystals (mp 75.5–76 °C) which showed δ_H: 1.25–1.41 (1H, m), 1.59–1.75 (2H, m), 1.90–2.05 (3H, m), 3.00 (1H, dd, J=3.7, 3.5 Hz), 3.46 (1H, ddd, J=4.0, 3.7, 0.8 Hz); δ_C: 16.3−, 21.2−, 24.4+, 26.6+, 31.2, 46.8+, 47.7+; IR (cm^{-1}, in $CHCl_3$): 3013m, 2940m, 1416m, 1349m, 1081s, 1053s, 984m, 893m, 834m, 818s, 622m; calcd C 31.38, H 3.01%, found C 31.6, H 2.7%.

4.1.4. Reaction of *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (10) with pyridine. A solution of pyridine (87 mg, 1.098 mmol, 3 mol. equiv.) and *exo*-3,7,7-tribromide (**10**) (127 mg, 0.366 mmol) in dry DMSO (3 mL) was stirred at 90–95 °C. After 4 h the mixture was cooled to room temperature, diluted with dichloromethane (10 mL) and extracted with 1 M hydrochloric acid (15 mL). The water layer was extracted with dichloromethane (3×5 mL). The combined organic layers were washed with water (2×10 mL), dried and concentrated in vacuo to give a yellow solid (108 mg). Chromatography on Silica (25 g) eluting with 3:1 petrol–ether gave 4,7,7-tribromobicyclo-[4.1.0]hept-3-en-2-on-3-ol (**13**) (24.6 mg, R_f 0.31) as white crystals which showed δ_H: 2.49 (1H, dd, J=9.5, 8.5 Hz, H-6), 2.91 (1H, d, J=9.5 Hz, H-1), 3.19 (1H, d, J=20.2 Hz, H-5^{endo}), 3.36 (1H, dd, J=20.2, 8.5 Hz, H-5^{exo}), 6.37 (1H, br.s, O*H*); δ_C: 25.0, 31.7+, 32.4−, 36.7+, 116.6, 145.1, 182.2 (C=O); IR (cm^{-1}, in $CHCl_3$): 3382s, 3040m, 1667s, 1633s, 1375s, 1321s, 1284m, 1189s, 1077m, 944m; MS: 364 (1.3), 362 (4.5), 360 (4.5), 358 (1.3), 283 (29), 281 (100), 279 (36), 255 (1.3), 253 (3.2), 251 (1.3), 202 (7), 200 (7), 174 (11), 172 (11); found M^+ 359.7825; calcd for $C_7H_5O_2^{79}Br^{81}Br_2$ 359.7819; and 7,7-dibromobicyclo[4.1.0]-hept-3-en-2-on-3-ol (**14**)[39] (R_f 0.22) in a mixture with enone (**13**) (40.1 mg) as a white solid which showed δ_H: 2.47–2.52 (1H, m), 2.76–2.85 (2H, m), 2.92 (1H, ddd, J=21.1, 8.5, 4.1 Hz, H-5^{exo}), 5.85 (1H, ddd, J=4.7, 4.1, 0.9 Hz, H-4), 5.95 (1H, br.s, O*H*); δ_C: 22.6−, 25.9, 32.2+, 37.3+, 115.4+, 145.9, 185.5 (C=O). In the reaction mixture, the ratio (**13**): (**14**) was 1:1.4.

4.1.5. Reaction of *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (10) with sodium iodide in acetone. A solution of *exo*-3,7,7-tribromide (**10**) (100 mg, 0.29 mmol) and sodium iodide (96 mg, 0.64 mmol, 2.2 mol. equiv.) in acetone (HPLC grade, 3 mL) was stirred at ambient temperature in the dark. After 11 h, the mixture was poured into water (15 mL), extracted with dichloromethane (4×5 mL), decolorized with aq. sodium thiosulfate, dried and concentrated in vacuo to give an oil (86 mg), which contained by ^{1}H NMR starting material (57%), (**14**) (8%), (**15**) (13%) and (**16**) (22%). Chromatography of this oil (60 mg) on Silica (20 g) eluting with petrol–ether 3:1 gave starting material (26 mg, R_f 0.68) as a colorless viscous oil with spectral data identical to those above, a mixture of 7,7-dibromobicyclo-[4.1.0]heptan-2-one (**16**) (for data see reaction of (**10**) with thiourea) and 4-iodo-7,7-dibromobicyclo[4.1.0]hept-3-en-2-on-3-ol (**15**) (16 mg, R_f 0.46, as a colorless oil with yellow crystals) which showed δ_H: 2.42–2.48 (1H, m), 2.91 (1H, d, J=9.5 Hz), 3.28 (1H, d, J=20.2 Hz), 3.44 (1H, dd, J=20.2, 8.5 Hz), 6.57 (1H, br.s); δ_C: 25.0, 34.1+, 36.1−, 37.1+, 93.1, 148.7, 179.8; MS (CI, 70 eV, methane): 410 (14), 409 (11), 408 (32), 407 (21), 406 (15), 405 (9), 329 (96), 327 (100), 301 (5), 299 (5); found $[M-H]^+$ 408.7596; calcd for $C_7H_4O_2^{81}Br_2I$ 408.7582; and 7,7-dibromobicyclo[4.1.0]hept-3-en-2-on-3-ol (**14**)[39] (3 mg, R_f 0.31) as a colorless viscous oil with spectral data identical to those above (this contained by ^{1}H NMR about 50% unidentified impurities).

4.1.6. Reaction of *exo*-3,7,7-tribromobicyclo[4.1.0]heptan-2-one (10) with thiourea. *exo*-3,7,7-Tribromobicyclo-[4.1.0]heptan-2-one (**10**) (173 mg, 0.5 mmol) and thiourea (114 mg, 1.5 mmol) were refluxed in methanol (1.5 mL) for 4 h. The mixture was cooled to room temperature, then poured into a mixture of dichloromethane (9 mL), water (4 mL) and sat. aq. sodium bicarbonate (1.5 mL). The water layer was extracted with dichloromethane (4×3 mL). The combined organic layers were washed with water (34 mL), dried, filtered and concentrated in vacuo to give mixture of a yellow oil with a yellow solid (149 mg). This was separated on Silica (20 g) eluting with 1:2 petrol–ether to give (**17**) (51 mg, 32%, R_f 0.36) as white solid with mp 138.5–139 °C (dec.) which showed δ_H: 2.13–2.27 (3H, m), 2.61 (1H, ddd, J=16.4, 8.7, 7.6 Hz), 2.70 (1H, dddd, J=16.4, 7.6, 5.4, 1.3 Hz), 2.77 (1H, d, J=10.4 Hz), 4.70–5.10 (2H, br.s); δ_C: 20.0−, 20.3−, 29.3+, 30.7+, 37.1, 120.0, 141.6, 164.7; IR (cm^{-1}, $CHCl_3$): 1621s, 1583m, 1540s, 1524s, 1431m, 1400m, 1364m, 1308s, 1113m, 1090m, 1070m; calcd C 29.65, H 2.49, N 8.65%, found C 30.0, H 2.7, N 8.8%. A mixture of other products (96 mg) was also isolated as white solid together with a colorless oil. This was again separated on Silica (15 g) eluting with 4:1 petrol–ether to give 7,7-dibromobicyclo-[4.1.0]heptan-2-one (**16**) (55 mg, 41%, R_f 0.38) as a colorless oil which showed δ_H: 1.72–1.82 (2H, m), 1.94–2.00 (1H, m), 2.20–2.28 (2H, m), 2.31–2.38 (1H, m), 2.40–2.47 (1H, m), 2.50 (1H, d, J=9.5 Hz); δ_C: 21.1−, 23.9−, 31.2, 35.0+, 38.1+, 38.4−, 202.2; IR (cm^{-1}, film): 2947m, 2867m, 1702s, 1445m, 1412m, 1354m, 1323s, 1306m, 1232m, 1179m, 1148s, 951m, 737s; calcd C 31.38, H 3.01%, found C 31.7, H 3.0%.

4.1.7. Oxidation of 6,6-dibromobicyclo[3.1.0]hexane (18) with chromium trioxide in acetic acid. 6,6-Dibromobicyclo[3.1.0]hexane (**18**) (2.399 g, 10 mmol) was added to a suspension of chromium trioxide (15.00 g, 150 mmol) in glacial acetic acid (50 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into mixture of water (200 mL) and dichloromethane (100 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (2×30 mL), water (30 mL), dried, filtered and concentrated in vacuo to give an oil (1.74 g). This was separated on Silica (100 g) eluting with 20:1 petrol–ether to give starting material (84 mg, 4%, R_f 0.91), *exo*-3,6,6-tribromobicyclo[3.1.0]hexan-2-one (**19**) (984 mg, 30%, R_f 0.30) as white crystals (mp 44.5–46.5 °C) which showed δ_H: 2.65 (1H, ddd, *J*=15.5, 6.7, 5.3 Hz, H-4^{exo}), 2.80 (1H, dd, *J*=6.7, 6.7 Hz, H-5), 2.88 (1H, dd, *J*=15.5, 8.2 Hz, H-4^{endo}), 2.90 (1H, d, *J*=6.7 Hz, H-1), 4.27 (1H, dd, *J*=8.2, 5.3 Hz, H-3); δ_C: 27.2, 25.5−, 37.9+, 42.7+, 44.8+, 200.42 (C=O); IR (cm^{-1}, $CHCl_3$): 1748s (C=O), 974m; MS: 255 (28), 253 (56), 251 (28), 55 (100); calcd C 21.65, H 1.51%, found C 21.8, H 1.7%; *exo*-2,6,6-tribromobicyclo-[3.1.0]hexan-3-one (**20**) (100 mg, 3%, R_f 0.39) as white crystals (mp 101–105 °C (dec.)) which showed δ_H: 2.48 (1H, d, *J*=19.5 Hz, H-4^{endo}), 2.54 (1H, dd, *J*=8.3, 6.4 Hz, H-5), 2.65 (1H, d, *J*=8.3 Hz, H-1), 2.87 (1H, dd, *J*=19.5, 6.4 Hz, H-4^{exo}), 4.08 (1H, s, H-2); δ_C: 31.2+, 33.9, 37.7−, 37.8+, 44.3+, 206.4 (C=O); IR (cm^{-1}, $CHCl_3$): 1753s (C=O), 1137m, 1034m; MS: 255 (31), 253 (62), 251 (31); calcd C 21.65, H 1.51%, found C 22.0, H 1.3%; exo,exo-2,4,6,6-tetrabromo-bicyclo[3.1.0]hexan-3-one (**21**) (64 mg, 2%, R_f 0.48) as white crystals (mp 110.0–115.0 °C (dec.)) which showed δ_H: 2.87 (2H, s, H-1, H-5), 4.17 (2H, s, H-2, H-4); δ_C: 30.2, 37.9+, 39.0+, 203.3 (C=O); IR (cm^{-1}, $CHCl_3$): 1761s (C=O); MS: 293 (4), 291 (12), 289 (12), 287 (4), 255 (36), 253 (72), 251 (36), 227 (25), 225 (50), 223 (25), 65 (100); calcd C 17.51, H 0.98%, found C 18.0, H 0.7%.

The combined sodium bicarbonate layers were washed with dichloromethane (2×10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give a yellow viscous oil (103 mg), which was not identified.

4.1.8. *exo*-3,6,6-Tribromobicyclo[3.1.0]hexan-*endo*-2-ol (22). Sodium borohydride (19.0 mg, 0.50 mmol) was added to a solution of (**19**) (167.5 mg, 0.50 mmol) in dry ethanol (4 mL) and benzene (0.8 mL) and stirred at ambient temperature. After 10 min, TLC showed no starting material. The mixture was poured in water (20 mL) and extracted with dichloromethane (4×5 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give white solid (170 mg). This was purified on Silica (40 g) eluting with 3:1 petrol–ether to give *exo*-3,6,6-tribromobicyclo[4.1.0]heptan-endo-2-ol (**22**) (146 mg, 87%, R_f 0.33) as white crystals (mp 111.5–112 °C) which showed δ_H: 2.30 (1H, d, *J*=8.1 Hz, O*H*), 2.33 (1H, dd, *J*=7.9, 6.3 Hz, H-1), 2.49 (1H, dd, *J*=8.4, 6.3 Hz, H-5), 2.52 (1H, ddd, *J*=15.1, 8.4, 6.3 Hz, H-4^{exo}), 2.74 (1H, dd, *J*=15.1, 8.5 Hz, H-4^{endo}), 4.28 (1H, ddd, *J*=8.5, 6.9, 6.9 Hz, H-3), 4.86 (1H, ddd, *J*=8.1, 7.9, 6.9 Hz, H-2); δ_C: 31.0, 37.0+, 38.1−, 40.2+, 50.2+, 85.4+; IR (cm^{-1}, $CHCl_3$): 3300br.s (OH), 3050m, 1438m, 1329m, 1266m, 1083s, 1070s, 1028m, 932m, 904m, 856m, 806m, 790s, 720m; calcd C 21.52, H 2.11%, found C 21.4, H 2.2%.

4.1.9. *endo*-7,7-Dibromo-3-oxatricyclo[4.1.0.0^{2,4}]heptane (23). Ethanolic sodium hydroxide (1.78 mL, C 0.21 M, 0.366 mmol) was added to (**22**) (30.6 mg, 0.091 mmol) and stirred for 96 h at ambient temperature, then poured into water (25 mL), extracted with dichloromethane (4×5 mL), dried and concentrated in vacuo to give endo-7,7-dibromo-3-oxatricyclo[4.1.0.0^{2,4}]heptane (**23**) (21.4 mg, 92%) as a yellow oil which showed δ_H: 1.94 (1H, ddd, *J*=16.1, 7.6, 2.5 Hz), 2.04 (1H, dd, *J*=16.1, 2.5 Hz), 2.25 (1H, dd, *J*=8.3, 2.9 Hz), 2.73–2.76 (1H, m), 3.78–3.80 (2H, m); δ_C: 29.4−, 33.6+, 34.8, 47.4+, 58.2+, 68.3+; IR (cm^{-1}, film): 3031m, 2922m, 1424m, 1306m, 1232m, 1193m, 1053m, 1019s, 957m, 873m, 841s, 788m, 724m, 705m, 681m; MS (CI, 70 eV, methane): 257 (9), 255 (18), 253 (6), 176 (22), 175 (63), 174 (27), 173 (53), 147 (97), 145 (100); found $[M+H]^+$ 252.8858; calcd for $C_6H_7OBr_2$ 252.8864.

4.1.10. Oxidation of 9,9-dibromobicyclo[6.1.0]nonane (24) with chromium trioxide. (a) *In acetic acid*. 9,9-Dibromobicyclo[6.1.0]nonane (**24**) (846 mg, 3 mmol) was added to a suspension of chromium trioxide (2.40 g, 24 mmol) in glacial acetic acid (20 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into a mixture of water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×30 mL), extracted with sat. aq. sodium bicarbonate (2×15 mL), brine (2×20 mL), dried, filtered and concentrated in vacuo to give an oil (680 mg). This was separated on Silica (70 g) eluting with petrol–ether 5:1 to give starting material (31 mg, 4%), 9,9-dibromobicyclo[6.1.0]nonan-4-one (**25**)[21] (424 mg, 48%, R_f 0.20) as white crystals (mp 55–56 °C), 9,9-dibromobicyclo[6.1.0]nonan-2-one (**26**) (116 mg, 13%, R_f 0.36) as white crystals (mp 66–69 °C from hexane) which showed δ_H: 1.05–1.27 (1H, m), 1.32–2.0 (6H, m), 2.05–2.43 (3H, m), 2.5–2.65 (1H, m), 2.58 (1H, d, *J*=11.7 Hz); δ_C: 24.4−, 27.0−, 27.3−, 28.1, 37.2+, 39.3+, 45.9−, 205.6; IR (cm^{-1}, in $CHCl_3$): 2930s, 2858m, 1708s, 1452m, 1355m; calcd C 36.52, H 4.09%, found C 36.9, H 4.0%; and 9,9-dibromobicyclo[6.1.0]nonan-3-one (**27**)[21] (7 mg, 1%, R_f 0.27) as a yellow viscous oil.

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (3×5 mL). The combined organic layers were washed with water (10 mL), dried, filtered and concentrated in vacuo to give colorless oil (79 mg), which was dissolved in ether (1.5 mL), treated with diazomethane and evaporated in vacuo to give a mixture (77 mg, 7%) of dimethyl 2,3-(dibromomethano)suberate, dimethyl 3,4-(dibromomethano)-suberate and dimethyl 4,5-(dibromomethano)-suberate (analyzed as mixture of isomers) as a slightly yellow oil which showed δ_H: 1.15–2.15 (6H, m), 2.25–2.65

(4H, m), region 3.6–3.75 contained 5 singlets at 3.65, 3.66, 3.69, 3.71, 3.72 with ratio 9:7:4:7:9 respectively by ^{1}H NMR.

(b) *In dichloromethane in the presence of 3,5-dimethylpyrazole*. Chromium trioxide (6.00 g, 60 mmol) and dichloromethane were mixed and the resulting suspension was cooled to −20 °C when 3,5-dimethylpyrazole (5.768 g, 60 mmol) was added. The mixture was stirred at −15 to −20 °C for 15 min to give a dark solution, then (**24**) (846 mg, 3 mmol) was added. The mixture was stirred at −15 to −25 °C for 1 h, at 20 °C for 1 h, then refluxed for 18 h, cooled to room temperature and washed with 15% hydrochloric acid (3×20 mL), water (2×15 mL), dried and concentrated in vacuo to give starting material (810 mg, 96%).

(c) *In acetone*. Chromium trioxide (6.00 g, 60 mmol) was added in portions to acetone (20 mL) at 1 °C over 15 min at below 15 °C. Then (**24**) (846 mg, 3 mmol) was added in one batch. No exothermic effect was observed. The mixture was stirred at 19–20 °C for 1 h and analyzed by GLC. No products of oxidation were formed.

4.1.11. Oxidation of 9,9-dibromobicyclo[6.1.0]nonane (24) with periodic acid. A mixture of dibromide (**24**) (846 mg, 3 mmol), carbon tetrachloride (10 mL), acetonitrile (10 mL), water (15 mL), periodic acid (5.47 g, 24 mmol) and ruthenium trichloride (42 mg, 0.15 mmol, 5 mol%) was stirred at 70–75 °C. After 52 h the black mixture was cooled, poured into water (20 mL) and extracted with dichloromethane (3×10 mL). The combined organic layers were washed with water (10 mL), extracted with sat. aq. sodium bicarbonate (2×10 mL), washed with water (10 mL), dried, filtered and concentrated in vacuo to give an oil (574 mg). This was separated on Silica (70 g) eluting with 5:1 petrol–ether to give starting material (75 mg, 9%) as a colorless oil, **25**[21] (325 mg, 37%) as white crystals, **26** (61 mg, 7%) as white crystals and **27**[21] (18 mg, 2%) as a yellow oil with spectral and analytical data identical to those above.

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), then acidified with hydrochloric acid to pH 1. The mixture was extracted with dichloromethane (5×5 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give a colorless oil (386 mg), which was dissolved in ether (1.5 mL), treated with diazomethane and evaporated in vacuo to give a mixture (192 mg, 17%) of dimethyl 2,3-(dibromomethano)suberate, dimethyl 3,4-(dibromomethano)suberate and dimethyl 4,5-(dibromomethano)-suberate as a slightly yellow oil with spectral data identical to those above.

4.1.12. Dry ozonolysis of 9,9-dibromobicyclo[6.1.0]-nonane (24). Silica gel (34 g) was added to a solution of (**24**) (846 mg, 3 mmol) in pentane (100 mL) and the solvent was evaporated in vacuo. The resulting powder was placed in a U-tube, cooled to −80 °C and a stream of ozone (2.5 g/h) was then passed through it for 20 min. It was then allowed to warm slowly, over 3 h, to room temperature and this cycle was repeated three times followed by elution of the organic material using ether. The resulting solution was concentrated in vacuo and analyzed by GLC (see Table 3).

4.1.13. Oxidation of bicyclo[6.1.0]nonane (3), 9-bromobicyclo[6.1.0]nonane (29) and 9,9-dibromobicyclo-[6.1.0]nonane (24) with chromium trioxide. A solution of a mixture of (**3**) (124 mg, 1 mmol), (**29**) (203 mg, 1 mmol, *exo*–*endo*=1:2.5) and (**24**) (282 mg, 1 mmol) in glacial acetic acid (2 mL) was added to a suspension of chromium trioxide (2.40 g, 24 mmol) in glacial acetic acid (18 mL). The mixture was stirred at 30–31 °C for 1 h. Aliquots (about 0.5 mL) were taken after each 5 min, quenched with sat. aq. sodium bicarbonate (20 mL) which was added until the formation of CO_2 was complete. This was extracted with ether (2 mL) and the organic layer was analyzed by GLC and GC/MS. The results of this are presented in Table 4.

4.1.14. Oxidation of 8,8-dibromobicyclo[5.1.0]octane (35) with chromium trioxide in acetic acid. 8,8-Dibromobicyclo[5.1.0]octane (**35**) (804 mg, 3 mmol) was added to a suspension of chromium trioxide (4.50 g, 45 mmol) in glacial acetic acid (15 mL). The mixture was stirred at 30–31 °C for 2 h and poured into a mixture of water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×30 mL), extracted with sat. aq. sodium bicarbonate (2×20 mL), brine (2×20 mL), dried and concentrated in vacuo to give an oil (409 mg), which contained at least four main products with retention time 7.55 (6%), 8.50 (30%), 10.65 (33%) and 11.65 min (25%). Starting material had retention time 4.55 min and it was fully converted after 2 h, but after 1 h the reaction mixture contained approximately 50% of dibromide (**35**). Chromatography on Silica (200 g) eluting with 5:1 petrol–ether gave 7 fractions (the reaction mixture showed on TLC at least 5 spots with R_f 0.46, 0.40, 0.35, 0.20, 0.15). One of the major products (with R_t 8.50 min) was isolated nearly pure; according to ^{1}H and ^{13}C NMR spectra, it was not 8,8-dibromobicyclo[5.1.0]octan-4-one[25] and showed δ_H: 1.03–1.26 (1H, m), 1.37–1.71 (3H, m), 1.82–2.06 (3H, m), 2.43–2.55 (3H, m); δ_C: 24.0−, 25.0−, 29.4−, 30.1, 32.0+, 41.2+, 44.4−, 202.2. The structure of this compound is unknown. According to ^{1}H NMR data some products contained the CHBr fragment (signals at 4.2–4.5 ppm), some of them not. According to ^{13}C NMR data all products contained a C=O fragment (δ_C: 200–202 ppm).

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (5×10 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give a yellow oil (109 mg), which was dissolved in ether (2 mL), treated with diazomethane, dried and evaporated in vacuo to give a mixture (95 mg, 9%) of, presumably, dimethyl 2,3-(dibromomethano)pimelate and dimethyl 3,4-(dibromomethano)pimelate in 54:36 ratio by GLC (attribution of peaks unknown) as a slightly yellow oil which showed δ_H: 1.62–2.12 (5H, m), 2.30–2.65 (3H, m), region 3.6–3.73 contained 4 singlets at 3.66, 3.68, 3.716, 3.723 with ratio 4:3:3:4 respectively by ^{1}H NMR; δ_C: 22.8−, 23.5−, 26.0−,

28.5, 29.2+, 32.0−, 32.2−, 32.3+, 33.4−, 33.8, 34.5+, 37.2+, 51.6+, 51.7+, 52.1+, 53.2+, 167.0, 171.5, 172.9, 173.5.

4.1.15. Oxidation of 1,1-dibromo-2-butylcyclopropane (36) with chromium trioxide in acetic acid. 1,1-Dibromo-2-butylcyclopropane (**36**) (768 mg, 3 mmol) was added to a suspension of chromium trioxide (3.00 g, 30 mmol) in glacial acetic acid (20 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aq. layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (3×20 mL), brine (2×20 mL), dried and concentrated in vacuo to give oil (606 mg). This was separated on Silica (70 g) eluting with petrol–ether 20:1 to give (**36**) (176 mg, 23%) and 1-(2,2-dibromocyclopropyl)-butan-1-one (**37**) (196 mg, 24%, R_f 0.35) as a colorless oil which showed δ_H: 1.00 (3H, t, J=7.4 Hz), 1.73 (2H, m), 1.93 (1H, dd, J=9.1, 7.4 Hz), 2.23 (1H, dd, J=7.8, 7.4 Hz), 2.68 (2H, m), 2.83 (1H, dd, J=9.1, 7.8 Hz); δ_C: 13.4+, 16.6−, 21.0, 27.0−, 38.5+, 46.4−, 201.5; IR (cm^{-1}, film): 2962m, 2874m, 1716s, 1370s, 1105m, 1069m; found M^+ 271.9047; calcd for $C_7H_{10}^{81}Br_2$ 271.9057.

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), acidified with hydrochloric acid to pH 1, then extracted with dichloromethane (4×10 mL). The combined organic layers were washed with water (20 mL), dried and concentrated in vacuo to give a colorless oil (151 mg) which was dissolved in ether (2 mL), treated with diazomethane and evaporated in vacuo to give a mixture (143 mg, ca. 18%) of methyl 2,2-dibromocyclopropanecarboxylate and methyl (2,2-dibromocyclo-propyl)-acetate[40] (ratio 1:2, respectively by ^1H NMR and GLC) as a colorless oil. Methyl (2,2-dibromocyclopropyl)acetate showed δ_H: 1.36 (1H, dd, J=7.1, 7.1 Hz), 1.85–2.02 (2H, m), 2.50 (1H, dd, J=17.0, 7.0 Hz), 2.73 (1H, dd, J=17.0, 6.8 Hz), 3.75 (3H, s); GC/MS: 274 (0.5), 272 (1), 270 (0.5), 243 (1), 241 (2), 239 (1), 53 (100); found M^+ 273.8846; calcd for $C_6H_8O_2^{81}Br_2$ 273.8850.

4.1.16. Oxidation of dibromocarbene adduct of (1*S*)-β-pinene (42) with chromium trioxide in acetic acid. *gem*-Dibromocyclopropane (**42**) (924 mg, 3 mmol) was added to a suspension of chromium trioxide (3.00 g, 30 mmol) in glacial acetic acid (20 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into a mixture of water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×30 mL), extracted with sat. aq. sodium bicarbonate (2×15 mL), brine (2×20 mL), dried and concentrated in vacuo to give an oil (680 mg), which contained by ^1H NMR starting material (**42**) (25%), α-ketone (**43**) (38%), β-ketone (**44**) (27%) and cyclobutanone derivative (**45**) (10%). This oil was separated on Silica (70 g) eluting with 5:1 petrol–ether to give (**42**) (72 mg, 8%, R_f 0.95), α-ketone (**43**) (31 mg, R_f 0.56) as a colorless oil which showed δ_H: 0.92 (3H, s), 1.37 (3H, s), 1.63 (1H, d, J=7.3 Hz), 1.65 (1H, d, J=10.7 Hz), 2.17 (1H, dd, J=6.0, 6.0 Hz), 2.28 (1H, dddd, J=6.0, 5.0, 3.9, 2.5 Hz), 2.51 (1H, d, J=7.3 Hz), 2.61 (1H, dd, J=18.8, 2.5 Hz), 2.77–2.80 (2H, m) (for confirmation of structure of (**43**), a comparison of the ^1H NMR of this compound with spectra for the non-brominated ketone (**46**) and pinocarvone were made (supplementary information available)); δ_C: 21.5+, 25.4+, 30.6, 32.8−, 34.6−, 38.4+, 40.0, 44.5−, 44.8, 49.0+, 204.5; IR (cm^{-1}, film): 2950m, 1714s, 1463m, 1410m, 1388m, 1371m, 1336m, 1256m, 1123m, 1064m, 1020m, 911m, 705m; MS (CI, 70 eV, methane): 325 (55), 324 (26), 323 (100), 322 (14), 290 (7), 289 (10), 287 (10), 281 (7), 279 (18), 277 (9); found $[M+H]^+$ 324.9448; calcd for $C_{11}H_{15}O^{81}Br_2$ 324.9449; a mixture of α-ketone (**43**) with at least four unidentified compounds (170 mg, R_f 0.56, 0.49, 0.46, 0.39 and 0.34), one of them containing a COCHBr fragment based on the ^1H NMR data (dd at 4.85 ppm) and, as a colorless oil, a mixture of β-ketone (**44**) which showed in $CDCl_3$ δ_H: 1.07 (3H, s), 1.25 (3H, s), 1.66 (1H, d, J=7.4 Hz), 1.90–1.93 (1H, m), 2.02 (1H, d, J=7.4 Hz), 2.13–2.16 (2H, m), 2.36–2.39 (1H, m), 2.53 (2H, d, J=2.4 Hz); δ_C: 21.6+, 21.8+, 33.0, 35.7−, 37.8−, 39.3, 40.5−, 48.7, 54.0+, 61.0+, 215.6 and in C_6D_6 δ_H: 0.64 (3H, s), 0.66 (3H, s), 1.00 (1H, d, J=7.3 Hz), 1.31 (1H, dd, J=4.4, 1.6 Hz), 1.40 (1H, d, J=7.3 Hz), 1.50 (1H, dd, J=14.5, 4.7 Hz), 1.96 (1H, d, J=14.5 Hz), 2.03 (1H, dd, J=4.7, 1.6 Hz), 2.20 (1H, dd, J=18.3, 4.4 Hz), 2.48 (1H, d, J=18.3 Hz) (signals for this ketone were distinguished from crude NMR data by 2D spectra {COSY and HNQC} and selective decoupling experiments); GC/MS (R_t 15.75 min, EI, 70 eV): 324 (0.6), 322 (1.8), 320 (1), 243 (9), 242 (3), 241 (9), 240 (3), 214 (6), 212 (12), 210 (6); found M^+ 319.9411; calcd for $C_{11}H_{14}O^{79}Br_2$ 319.9425; with cyclobutanone derivative (**45**) which showed δ_H: two methyl groups at 0.97 and 1.40 ppm and two doublets for one proton each at 1.63 and 1.71 ppm with J=7.8 Hz; δ_C: for C=O bond 209.9 ppm (other signals were not distinguished from crude NMR); GC/MS (R_t 15.88 min, EI, 70 eV): 243 (5), 242 (2), 241 (5), 240 (2); found $[M-HBr]^+$ 240.0150; calcd for $C_{11}H_{13}O^{79}Br$ 240.0152. Assignment of structure for cyclobutanone derivative (**45**) is based on the MS spectrum, which was similar to that of β-ketone (**44**), and the IR spectrum for the mixture which showed signals for C=O bonds at 1750 cm^{-1}, attributed to (**45**) and 1717 cm^{-1}, attributed to (**44**). Treatment of this mixture (170 mg) in dry ethanol (2 mL) at 5 °C with 2,4-dinitrophenylhydrazine (123 mg, 0.62 mmol) in dry ethanol (2 mL) and sulfuric acid (0.26 mL) afforded after 5 min an orange precipitate, which was filtered after 2 h, washed with cold ethanol (2×5 mL), dried in vacuo over calcium chloride and recrystallized from 2:1 hexane–benzene (6 mL) to give the 2,4-dinitrophenylhydrazone of (**44**) (16 mg) as orange crystals (mp 168–169 °C (dec.)) which showed δ_H: 0.95 (3H, s), 1.43 (3H, s), 1.70 (1H, d, J=11.0 Hz), 1.73 (1H, d, J=7.9 Hz), 1.78 (1H, d, J=7.9 Hz), 2.17 (1H, dd, J=5.7, 5.4 Hz), 2.51 (1H, d, J=18.6 Hz), 2.73 (1H, ddd, J=11.0, 5.7, 5.4 Hz), 2.92 (1H, dd, J=5.4, 5.4 Hz), 3.37 (1H, d, J=18.6 Hz), 7.97 (1H, d, J=9.5 Hz), 8.31 (1H, dd, J=9.5, 2.5 Hz), 9.13 (1H, d, J=2.5 Hz), 11.04 (1H, s); δ_C: 23.3+, 25.5+, 27.4−, 30.7, 32.7−, 36.1, 36.5−, 42.3, 50.5+, 50.8+, 116.3+, 123.5+, 129.2, 130.0+, 137.9, 145.0, 160.7; IR (cm^{-1}, in $CHCl_3$): 3302m, 2964m, 1618s, 1584s, 1538m, 1517m, 1497s, 1426s, 1368m, 1338s, 1309s, 1273s, 1256s, 1129m, 1066m, 695m, 669m; calcd C 40.66, H 3.61, N 11.16%, found C 40.8, H 3.7, N 11.5%.

The combined sodium bicarbonate layers were washed with dichloromethane (2×10 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (3×10 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give a colorless oil, which was dissolved in ether (3 mL), treated with diazomethane and evaporated in vacuo to give a mixture (191 mg) of unidentified methyl esters.

Oxidation of *gem*-dibromocyclopropane (**42**) (3.081 g, 10 mmol) as above with subsequent addition of 2,4-dinitrophenylhydrazine (1.183 g, 5.97 mmol) in dry ethanol (15 mL) and sulfuric acid (2.5 mL) to a solution of the neutral fraction of the reaction mixture (1.988 g) in dry ethanol (5 mL) and stirring over 24 h, afforded an orange precipitate. This was washed with cold water–methanol (1:1) and recrystallized from isopropanol (precipitation was very slow) to give 2,4-dinitrophenylhydrazone of α-ketone (**43**) (65 mg) as orange crystals (mp 180–183 °C (dec.)) which showed δ_H: 0.98 (3H, s), 1.23 (3H, s), 1.58 (1H, d, *J*=7.6 Hz), 1.87 (1H, m), 1.96 (1H, d, *J*=7.6 Hz), 2.09 (1H, d, *J*=13.9 Hz), 2.18 (1H, dd, *J*=13.9, 4.4 Hz), 2.68 (1H, dd, *J*=4.4, 1.6 Hz), 2.70 (2H, m), 7.88 (1H, d, *J*=9.6 Hz), 8.24 (1H, dd, *J*=9.6, 2.6 Hz), 9.08 (1H, d, *J*=2.6 Hz), 10.79 (1H, s); δ_C: 21.4+, 21.8+, 31.0−, 33.0, 38.0−, 38.4−, 39.2, 50.4, 54.5+, 55.2+, 116.4+, 123.6+, 129.1, 130.0+, 137.7, 145.1, 166.9; IR (cm^{-1}, in $CHCl_3$): 3308m, 3110m, 2991m, 2958m, 2940m, 1650m, 1613s, 1589s, 1638s, 1513s, 1470m, 1455m, 1420s, 1393m, 1364s, 1336s, 1312s, 1288s, 1268s, 1180m, 1137s, 1070s, 1042m, 1027m, 1015m, 922m, 842m, 833m, 691m; MS: 504 (39), 502 (91), 500 (37), 461 (8), 459 (16), 457 (8), 423 (20), 421 (20), 242 (16), 240 (20); found M^+ 499.9690; calcd for $C_{17}H_{18}N_4O_4Br_2$ 499.9695.

4.1.17. Oxidation of 1,1-dibromo-2,2-dimethylcyclopropane (47) with chromium trioxide. The dibromide (**47**) (684 mg, 3 mmol) was added to a suspension of chromium trioxide (6.00 g, 60 mmol) in glacial acetic acid (20 mL), stirred at room temperature for 24 h, then poured into water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (2×20 mL), brine (2×20 mL), dried and concentrated at normal pressure to give starting material. The combined sodium bicarbonate layers were washed with dichloromethane (20 mL), acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (5×10 mL). The combined organic layers were washed with water (20 mL), dried and concentrated in vacuo to give 2,2-dibromo-1-methylcyclopropanecarboxylic acid (**48**) (67 mg, 9%) as a white solid.[41]

4.1.18. Oxidation of methyl 2,2-dibromo-1-methylcyclopropanecarboxylate (49) with chromium trioxide. Methyl 2,2-dibromo-1-methylcyclopropanecarboxylate (**49**) (816 mg, 3 mmol) was added to a suspension of chromium trioxide (9.00 g, 90 mmol) in glacial acetic acid (20 mL), stirred at room temperature for 168 h, then poured into water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aq. layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×20 mL), extracted with sat. aq. sodium bicarbonate (3×10 mL), brine (2×20 mL), dried and concentrated in vacuo to give starting material (**49**) (570 mg, 70%) as slightly yellow oil.

The combined sodium bicarbonate layers were washed with dichloromethane (20 mL), then acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (4×10 mL). The combined organic layers were washed with water (20 mL), dried and concentrated in vacuo to give 2,2-dibromo-1-methylcyclopropanecarboxylic acid (**48**) (87 mg, 11%) as a white solid.[41]

4.1.19. Oxidation of acetate of (2,2-dibromo-1-methylcyclopropyl)methanol (50) with chromium trioxide. The acetate (**50**) (572 mg, 2 mmol) was added to a suspension of chromium trioxide (4.00 g, 40 mmol) in glacial acetic acid (12 mL). The mixture was stirred at ambient temperature for 24 h, then poured into water (100 mL) and dichloromethane (50 mL). The organic layer was separated and the aq. layer was extracted with dichloro-methane (3×30 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (2×20 mL), water (30 mL), dried and concentrated in vacuo to give starting material (**50**) (74 mg, 13%) as slightly yellow oil.

The combined sodium bicarbonate layers were washed with dichloromethane (10 mL), acidified with hydrochloric acid to pH 1 and extracted with dichloromethane (4×10 mL). The combined organic layers were washed with water (10 mL), dried and concentrated in vacuo to give 2,2-dibromo-1-methylcyclopropancarboxylic acid (**48**) (385 mg, 75%) as a white solid.[41]

4.1.20. Oxidation of 1,1-dibromo-2-methyl-2-phenylcyclopropane (51) with chromium trioxide in glacial acetic acid. Dibromide (**51**) (870 mg, 3 mmol) was added to a suspension of chromium trioxide (6.00 g, 60 mmol) in glacial acetic acid (20 mL). The mixture was stirred at 30–31 °C for 1 h, then poured into water (100 mL) and dichloro-methane (50 mL). The organic layer was separated and the aq. layer was extracted with dichloromethane (3×30 mL). The combined organic layers were washed with water (2×50 mL), extracted with sat. aq. sodium bicarbonate (2×20 mL), water (30 mL), dried and concentrated in vacuo to give a mixture (672 mg) of acetophenone (**52**), α-bromoacetophenone (**53**),[42] α,α-dibromoacetophenone (**54**),[42] *p*-bromoacetophenone (**55**),[43] α,*p*-dibromoacetophenone (**56**)[42] and α,α,*p*-tribromoacetophenone (**57**),[44] in ratio 13:56:5:8:17:1 respectively by ^{1}H NMR. The identity of acetophenone derivatives was confirmed by direct comparison of ^{1}H NMR and GC/MS spectral data with those of authentic samples or by comparison with literature data.

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