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THE BAEYER–VILLIGER REACTION OF STRAINED CAGE COMPOUNDS, 1,3-BISHOMOCUBANONES, VIA CARBOCATIONS

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Abstract—The Baeyer–Villiger oxidation of 1,3-bishomocubanone **1a** in chloroform with *m*-chloroperbenzoic acid (m-CPBA) at room temperature proceeds quite rapidly and gives the ordinary lactone, 10-oxapentacyclo[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]undecan-11-one **2a** and the skeletal rearrangement product, 11-oxapentacyclo[6.3.0.0^{2,4}.0^{3,7}.0^{5,9}]undecan-10-one **4a**. Methyl substituted homologs (**1d**, **1e**, **1f**) of **1a** give the corresponding ordinary and rearranged lactones (**2d**, **2e**, **2f**, **4d**, **4e**, **4f**). In these oxidations, the mechanism via carbocations, cyclobutyl **18** and cyclopropylcarbinyl cations **19**, plays a major role different from the ordinary concerted migration mechanism. Solvent effects, kinetic treatments, and methyl substituent effects on product ratios support this carbocation mechanism. The adduct formation process between a ketone and m-CPBA must be rate-determining.

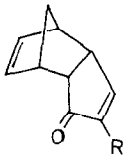
Mechanistic studies from kinetic and theoretical points of view have revealed that the Baeyer–Villiger reaction follows the two-step mechanism, the addition of a peracid to a ketone and the subsequent concerted migration, not involving ionic intermediates, and the latter process is usually rate determining.[1] In reactions of strained cage ring systems, however, unusual mechanisms different from the established one often act predominantly to give new ring systems as represented by the dimerization with diazomethane[2] and the Beckmann rearrangement.[3] We report here another example of reactions with unusual mechanisms in the strained cage system, that is, the Baeyer–Villiger reaction via carbocations.[4]

RESULTS

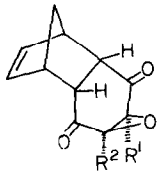
1,3-Bishomocubanone **1a** was synthesized from **5a** by the established method,[5] and the deuterated compound **1b** was similarly obtained from **5b** prepared by the treatment of **5a** with sodium methoxide in deuteromethanol. 1,3-Bishomocubanone-carboxylic acid methyl ester **8a** and its methyl substituted derivatives (**8b**, **8c**, **8d**) were synthesized photochemically from the corresponding dienones (**7a**, **7b**, **7c**, **7d**) in the manner described by Hertz[6] and hydrolyzed to their acids, sodium salt of which were treated with *p*-nitrobenzyl bromide to afford the corresponding *p*-nitrobenzyl esters (**1c**, **1d**, **1e**, **1f**).

When a chloroform solution of **1a** was treated with *m*-chloroperbenzoic acid (m-CPBA) at room temperature, the oxidation proceeded quite rapidly[7] to afford three lactones, **2a**, **3a** and **4a** in yields of 50.4, 1.1 and 13.1%, respectively.

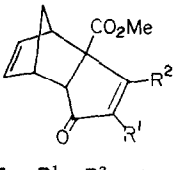
On the basis of mass spectra and elemental analyses, the three lactones have the composition $C_{10}H_{10}O_2$ (mol wt 162). Both **2a** and **3a** have 6-membered lactone (IR) and a quite similar fragmentation pattern (mass). The distinction between **2a** and **3a** was provided by NMR spectra of the corresponding deuterated compounds, **2b** and **3b**, derived from a deuterated starting material (**1b**).



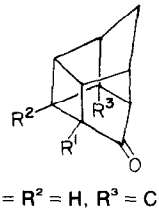
5a: R = H
5b: R = D



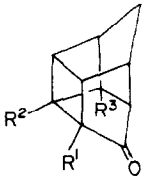
6a: R^1 = R^2 = H
6b: R^1 = H, R^2 = Me
6c: R^1 = R^2 = Me



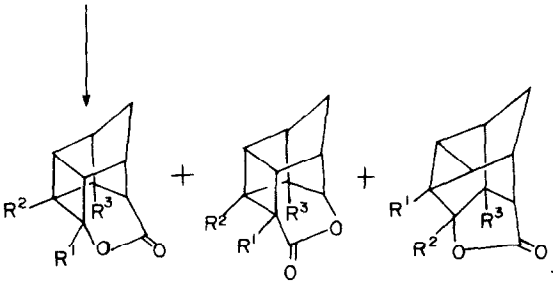
7a: R^1 = R^2 = H
7b: R^1 = H, R^2 = Me
7c: R^1 = Me, R^2 = H
7d: R^1 = R^2 = Me



8a: R^1 = R^2 = H, R^3 = CO$_2$Me
8b: R^1 = H, R^2 = Me, R^3 = CO$_2$Me
8c: R^1 = Me, R^2 = H, R^3 = CO$_2$Me
8d: R^1 = R^2 = Me, R^3 = CO$_2$Me

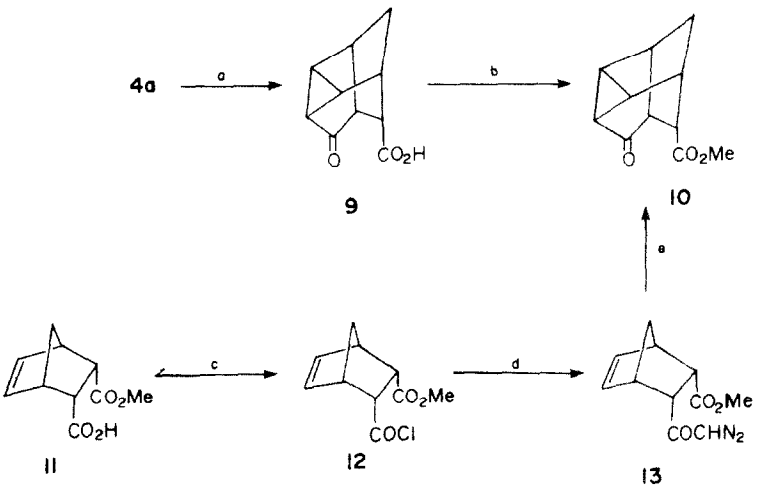


1a: R^1 = R^2 = R^3 = H
1b: R^1 = D, R^2 = R^3 = H
1c: R^1 = R^2 = H, R^3 = CO$_2$CH$_2$C$_6$H$_4$NO$_2$(p)
1d: R^1 = H, R^2 = Me, R^3 = CO$_2$CH$_2$C$_6$H$_4$NO$_2$(p)
1e: R^1 = Me, R^2 = H, R^3 = CO$_2$CH$_2$C$_6$H$_4$NO$_2$(p)
1f: R^1 = R^2 = Me, R^3 = CO$_2$CH$_2$C$_6$H$_4$NO$_2$(p)



2 **3** **4**

In **2b**, the original triplet signal of **2a** at 4.70 ppm disappeared, whereas the multiplet signal of **3a** at 4.64 ppm remained unchanged in **3b**. Compound **4a** has a 5-membered lactone and a fragmentation pattern clearly different from those of **2a** and **3a**. The double doublet signal of **4a** at 5.06 ppm changed to a doublet ($J = 7$ Hz) in the deuterated product (**4b**). These spectral data and mechanistic consideration revealed the structure of **4a**, which was converted to **10** by the treatment with alkaline potassium permanganate followed by esterification with diazomethane. Compound **10** was then confirmed by its unequivocal synthesis from the known half-ester (**11**)[8] as shown in the following scheme.



a, $KMnO_4$, NaOH; b, CH_2N_2; c, $SOCl_2$, pyridine, 30–35°, 4 h; d, CH_2N_2, Et_2O; e, CuI, THF, 40–45°.

Compound **2a** was recovered unchanged by the treatment either with m-CPBA and *m*-chlorobenzoic acid at room temperature for 24 h or with acetic acid at 50° for 12 h, but treatment both with acetic acid under reflux for 48 h and with a stronger acid, trifluoroacetic acid or *p*-toluenesulfonic acid, in chloroform at room temperature for 15 min readily gave **4a** quantitatively.[9]

In order to learn the solvent effect of this peracid oxidation, **1a** was treated with m-CPBA in various solvents and yields of **2a** and **4a** determined by using the NMR integration data[12] were summarized in Table 1, which shows that the ratio of **4a**:**2a** changes with increasing solvent polarity.

A 1,3-bishomocubanone with *p*-nitrobenzyl ester group[13] **1c** in chloroform was oxidized next and readily gave a normal lactone **2c** together with a rearranged lactone **4c** and with a trace of **3c**. Analogous compounds (**1d**, **1e**, **1f**) substituted with mono and dimethyl groups on their bicyclo[2.2.0]hexane rings were also oxidized affording similar results. The structures of all lactones were established spectroscopically.

The normal lactones (**2c**, **2d**, **2e**, **2f**) were easily converted to the corresponding rearranged lactones (**4c**, **4d**, **4e**, **4f**) by the treatment with boron trifluoride[14] and neither with m-CPBA nor with *m*-chlorobenzoic acid.

In order also to learn the effect of methyl groups located at different positions in the bicyclo[2.2.0]hexane ring, the rates of oxidations of the above ketones were measured both by iodometry of m-CPBA and by UV-spectrometry of the *p*-nitrobenzyl chromophore of the ketones using a high-pressure liquid chromatograph with UV-detector, and were found to follow second-order kinetics, first order both in m-CPBA and in the ketones ($v = k_{obs}$[ketone][m-CPBA]) as shown in Table 2 just as those of usual peracid oxidations. Although there is no significant difference among these observed rate constants, the ratio of two-types of lactones (**4**/**2**) varies apparently with the position of methyl substituents.

Two additional and contrastive results are finally shown. Oxidation of **1a** with lead tetraacetate in refluxing acetic acid gave **4a** as a sole product[15] with no traces of **2a** and **3a**. On the other hand, oxidation of **14**, prepared from **1a** by catalytic reduction,[17] with m-CPBA in chloroform gave the normal Baeyer–Villiger oxidation products **15** and **16** in the ratio about 3:1.[18]

Table 1. Oxidation of 1,3-bishomocubanone (**1a**; 0.35 g) in various solvents (16 ml) with m-CPBA (1.5 eq) at room temperature

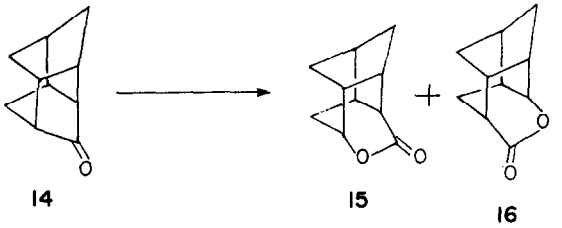
solvent	time (min)	yield,%[a] 4a	2a	ratio 4a/2a
benzene	15	12	56	0.21
dioxane	15	14	55	0.25
chloroform	3	10	35	0.29
	7	13	49	0.27
	15	15	55	0.27
	30	16	57	0.28
	45	17	58	0.29
	60	17	59	0.29
dioxane:H_2O (9:1)	60	15	45	0.33
dioxane:H_2O (1:1)	60	31	46	0.67

[a]Calculated by using the NMR integration data at 4.70 ppm for **2a** and at 5.06 ppm for **4a**. The yield of **3a** was almost nil.

Table 2. Rates and product ratios for the oxidation of methyl-substituted 1,3-bishomocubanones 1 with m-CPBA in chloroform at 30.0°

ketone	k[a] $M^{-1}sec^{-1}$	ratio[b] 4/2
1a	1.04×10^{-2}	0.29[c]
1c	0.95×10^{-2}	0.32
1d	1.04×10^{-2}	0.45
1e	1.26×10^{-2}	0.15
1f	1.00×10^{-2}	0.19

[a]Measured by iodometry. [b]Quantitative yields of 2 and 4 were determined by UV-spectrometry on a high pressure liquid chromatograph. [c]Determined by NMR integration data.



DISCUSSION

There are three features of interest in the m-CPBA oxidation of 1,3-bishomocubanone **1a**. First, the oxidation of **1a** proceeds very rapidly as compared with those of usual 5-membered ketones.[7] Secondly, although there is no significant difference in migratory aptitude between bond a and bond b in the ring expansion reaction with diazomethane,[19] the m-CPBA oxidation takes place almost exclusively at the bond a. Thirdly, the skeletal rearrangement product **4a**, which is the primary product as will be discussed later, as well as the normal products (**2a**, **3a**) is simultaneously formed.

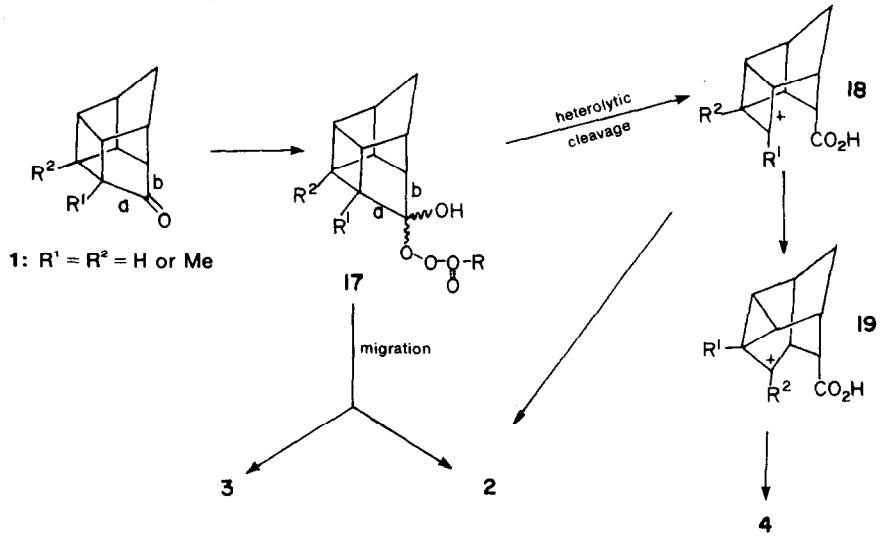
Because the direct formation of **4a** from **1a** cannot be explained in terms of the established concerted migration mechanism, we propose here an alternative mechanism via carbocations as shown in the following scheme.[20] Thus, the oxidation is initiated by the formation of an adduct **17**, usually followed by migration of bonds a and b with synchronous leaving of a carboxylate anion. In the oxidation of **1a**, however, because of a strained bicyclo[2.2.0]hexane ring system, the latter step changes predominantly to a heterolytic cleavage of bond a to form a carbocation **18**, which can rearrange to a more stable cation **19** through the well-known cyclobutylcyclopropylcarbinyl rearrangement.[21] This mechanism is consistent with the above three features and supported by following evidence and discussions.

There are two facts that **4a** is the primary product, not the secondary one formed through an acid-catalyzed rearrangement of the initially formed normal product **2a**. One is that the treatment of **2a** with m-CPBA and *m*-chlorobenzoic acid at room temperature for a long time gave no trace of **4a**, the other that the ratio of **4a**:**2a** was found to be almost constant throughout the oxidation, which was followed by NMR analysis (Table 1).

The solvent effect in this oxidation also supports the carbocation mechanism. Thus, the value of **4a**/**2a** becomes greater in more polar solvents, especially in aqueous organic solvents. Polar solvents, especially water can stabilize the carbocations, in other words, can prolong their life-times, and at the same time can decrease the nucleophilicity of the carboxyl group. Both these effects are apparently favorable for the rearrangement from **18** to **19**, and hence increase the relative yield of **4a**.

If these classical carbocations (**18**, **19**) exist as transient intermediates, introduction of a methyl group to a suitable position to stabilize each cation must accelerate the formation of the corresponding product. This is clearly demonstrated in the oxidation of methyl substituted bishomocubanones (**1d**, **1e**, **1f**).

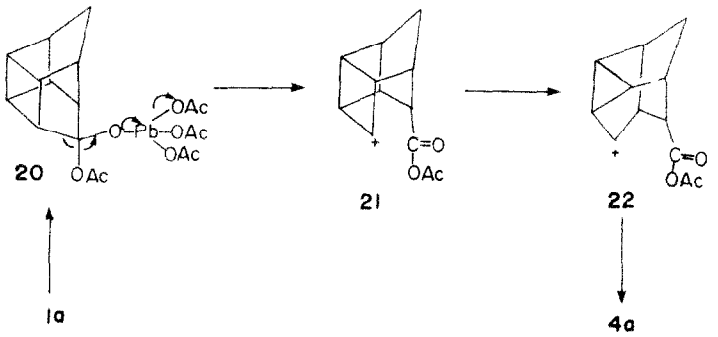
Their relatively large rate constants (Table 2) are almost identical to that of the reference compound **1c**, product ratios (**4**/**2**), however, are quite different from each other and reflect the effect of methyl substituents. Thus, **1e** having a methyl group favorable to stabilize the cyclobutyl cation **18** reduces the ratio **4**/**2** to less than one-half its reference value of the non-substituted compound **1c**, on the contrary, another monomethyl



derivative **1d** favors the formation of the cyclopropylcarbinyl cation **19**, increasing the ratio by a factor of about 1.5. The dimethyl derivative **1f** gives again a smaller ratio near to that of **1e** because the two methyl groups must cross each other on the process from **18** to **19** and this steric interaction probably inhibit the formation of **19**.

No significant difference among the rate constants presented in Table 2 indicates that because both processes of the cation formation and the termination to the products are quite rapid, the rate-determining step lies in the adduct formation between m-CPBA and the ketones in contrast to that in the ordinary Baeyer–Villiger oxidations.[23]

Finally, two contrastive results are discussed. Because **14** no longer has the strained bicyclo[2.2.0]hexane ring system, its oxidation gave two normal products (**15**, **16**) via migration of bond b as well as bond a. On the other hand, when **1a** was oxidized with lead tetraacetate in refluxing acetic acid, only the carbocation mechanism acted as presumably shown in the following scheme. In this case **4a** is the sole product with no traces of **2a** and **3a** because of less nucleophilicity of an anhydride group in an intermediate **21** rather than of the acid-catalyzed rearrangement of the initially formed **2a**.



EXPERIMENTAL

4 - Deuterotricyclo[5.2.1.$0^{2,6}$]*deca - 4,8 - dien - 3 - one* **5b**. A MeOD (15 ml) soln of **5a** (3 g) and NaOMe (0.3 g) was stirred at room temperature for 35 min. After being quenched NaOMe with CO_2-gas, the solvent was evaporated *in vacuo* to leave an oil, which was taken up in CH_2Cl_2, washed with water, and dried over Na_2SO_4. Evaporation of the solvent left 3.0 g of colorless oil; δ ($CDCl_3$) 5.60–6.20 (2H, m), 7.22 (1H, d, J = 3 Hz).

5 - Deuteropentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decan - 6 - one* **1b**. An EtOAc (200 ml) soln of **5b** (3 g) was irradiated with a 400 W high pressure mercury lamp using a Pyrex filter for 3 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column (10 g) eluting with benzene to give 2.2 g (73.5%) of a colorless solid, m.p. 120–125° (hexane); δ ($CDCl_3$) 1.60 (1H, d, J = 12 Hz), 1.74 (1H, d, J = 12 Hz), 2.25 (1H, broad s), 2.7–3.3 (6H, m).

Methyl 5 - oxotricyclo[5.2.1.$0^{2,6}$]*deca - 3,8 - diene - 2 - carboxylate* **7a**. To a stirred MeOH (250 ml)–THF (125 ml) soln of **6a** (5 g, 27.2 mmol) was added *t*-BuOK (10.3 g, 92 mmol), and the stirring at 45° was continued for 1 h. After CO_2-gas was bubbled to quench the base, the soln was concentrated *in vacuo* to leave an oil, which was taken up in $CHCl_3$. The $CHCl_3$ soln was washed with sat. NaCl aq, dried, and evaporated to leave 3.09 g of a pale brown oil, which was chromatographed on silica gel (90 g) eluting with benzene–EtOAc (40:1) to give 1.67 g (34.5%) of **7a** as a pale yellow solid. Recrystallization from benzene–hexane gave colorless prisms, m.p. 67–68°; ν_{max} (Nujol) 1730, 1700, 1580 cm^{-1}; δ ($CDCl_3$) 3.78 (3H, s), 5.2–6.4 (3H, m), 7.38 (1H, d, J = 6 Hz). (Found: C, 70.58; H, 5.98. $C_{12}H_{12}O_3$ requires: C, 70.57; H, 5.92%).

Methyl 10 - oxopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decane - 2 - carboxylate* **8a**. An EtOAc (250 ml) soln of **7a** (1.24 g) was irradiated with a 200 W high pressure lamp using a Pyrex filter for 6.5 h. Evaporation of the solvent left a yellow oil (1.29 g), which was chromatographed on a short column of silica gel (20 g). Elution with benzene–EtOAc (40:1) gave 1.03 g (83.1%) of **8a** as a colorless oil; ν (neat) 1760, 1725, 1240 cm^{-1}; *m/e* (%) 204 (M^+, 19), 176 (19), 145 (32), 117 (100), 116 (33), 115 (38), 91 (17), 66 (25); δ ($CDCl_3$) 1.66 (1H, d, J = 12 Hz), 1.94 (1H, d, J = 12 Hz), 2.40–2.68 (2H, m), 2.80–3.20 (4H, m), 3.38 (1H, s), 3.69 (3H, s).

4' - Nitrobenzyl 10 - oxopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decane - 2 - carboxylate* **1c**. A 10% KOH (1.2 ml)–MeOH (8 ml) soln of **8a** (400 mg, 1.96 mmol) was refluxed for 2 h. After evaporation of the MeOH, to the residue was added H_2O (50 ml), and the soln was acidified with 10% HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with sat. NaCl aq, dried, and evaporated to leave a colorless solid (310 mg) of the carboxylic acid; ν_{max} (Nujol) 1750, 1690 cm^{-1}. The acid (310 mg, 1.63 mmol) in EtOH (4 ml) was converted into Na salt with 10% NaOH using phenolphthalein indicator. To the soln was added 4-nitrobenzyl bromide (208 mg, 1.63 mmol), and the mixture was refluxed for 4 h and then concentrated *in vacuo*. After H_2O (50 ml) was added, the mixture was extracted with $CHCl_3$, the washed and dried extract was evaporated leaving a pale yellow oil (354 mg), which was purified by passing through a short column of silica gel (4 g). Elution with hexane–EtOAc (5:1) gave 274 mg (43%) of **1c**, which was recrystallized from Et_2O to afford colorless prisms, m.p. 68–69°; ν_{max} (Nujol) 1760, 1730, 1600 cm^{-1}; *m/e* (%) 325 (M^+, 8), 297 (11), 189 (25), 161 (50), 145 (34), 137 (21), 117 (100), 115 (40); δ ($CDCl_3$) 1.69 (1H, d, J = 14 Hz), 1.93 (1H, d, J = 14 Hz), 2.50–2.80 (2H, m), 2.84–3.25 (4H, m), 3.36–3.52 (1H, m), 5.20 (2H, s), 7.40 (2H, d, J = 9 Hz), 8.25 (2H, d, J = 9 Hz). (Found: C, 66.42; H, 4.69; N, 4.44. $C_{18}H_{15}NO_5$ requires: C, 66.45; H, 4.65; N, 4.31%).

Methyl 4 - methyl - 5 - oxotricyclo[5.2.1.$0^{2,6}$]*deca-3,8-diene-2-carboxylate* **7c**. To a stirred THF (75 ml)–MeOH (150 ml) soln of **6b** (3.0 g, 14.7 mmol) was added *t*-BuOK (5.1 g, 45.5 mmol), and the stirring was continued for 2 h at 45°. After the base was quenched with CO_2-gas, the solvent was evaporated *in vacuo* and to the residue was added H_2O (100 ml). The mixture was extracted with $CHCl_3$ and the extract was washed with sat. NaCl aq, dried, and evaporated to leave 1.92 g of a pale brown oil, which was chromatographed on a silica gel column (50 g) eluting with benzene–EtOAc (50:1) to afford two fractions. The first was 458 mg (15.7%) of **7c** as a pale yellow oil; ν_{max} (neat) 1730, 1700, 1630 cm^{-1}; δ (CCl_4) 1.60 (3H, s), 3.55 (3H, s), 5.90 (2H, m), 6.90 (1H, s).

Methyl 3 - methyl - 5 - oxotricyclo[5.2.1.$0^{2,6}$]*deca - 3,8 - diene - 2 - carboxylate* **7b**. The second fraction was 997 mg (34.3%) of **7b** as a pale yellow oil; ν_{max} (neat) 1730, 1700, 1620 cm^{-1}; δ (CCl_4) 1.90 (3H, s), 3.60 (3H, s), 5.60 (1H, s), 5.90 (2H, m).

Methyl 3 - methyl - 10 - oxopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decane - 2 - carboxylate* **8b**. An EtOAc (250 ml) soln of **7b** (2.5 g) was irradiated for 20 h with the 200 W lamp and after-treated as described above to give 1.78 g (71.5%) of **8b** as a colorless oil; ν_{max} (neat) 1760, 1720 cm^{-1}; *m/e* (%) 218 (M^+, 16), 196 (34), 159 (31), 131 (100), 115 (25), 91 (29), 66 (39); δ (CCl_4) 1.12 (3H, s), 1.63 (1H, d, J = 11 Hz), 1.85 (1H, d, J = 11 Hz), 2.20–2.32 (1H, m), 2.40–2.50 (1H, m), 3.39 (1H, s), 3.68 (3H, s).

4' - Nitrobenzyl 3 - methyl - 10 - oxopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane - 2 - carboxylate* **1d**. A 10% KOH (1.8 ml)–MeOH (10 ml) soln of **8b** (587 mg) was stirred at 50° for 3 h. Work-up as described above gave 480 mg of the crude acid as a colorless solid: ν_{max} (Nujol) 1750, 1690 cm^{-1}. The acid (480 mg) was converted to its Na salt, which was treated with 4-nitrobenzyl bromide (610 mg) as described above to give 445 mg (48.8%) of **1d**. Recrystallization from EtOH gave colorless prisms, m.p. 125–126°; ν_{max} (Nujol) 1750, 1725 cm^{-1}; *m/e* (%) 339 (M$^+$, 4), 311 (29), 203 (32), 175 (45), 159 (24), 131 (100); δ ($CDCl_3$) 1.08 (3H, s), 1.66 (1H, d, J = 11 Hz), 1.86 (1H, d, J = 11 Hz), 2.26–2.44 (1H, m), 2.46–2.60 (1H, m), 2.76–3.12 (3H, m), 3.43 (1H, s), 5.20 (2H, s), 7.40 (2H, dd, J = 9, 2 Hz), 8.23 (2H, dd, J = 9, 2 Hz). (Found: C, 67.20; H, 5.05; N, 4.20. $C_{19}H_{17}NO_5$ requires: C, 67.25; H, 5.05; N, 4.13%).

Methyl 9 - methyl - 10 - oxopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane - 2 - carboxylate* **8c**. Irradiation of **7c** (1.19 g) in EtOAc (250 ml) for 6 h as described above gave 800 mg (72.7%) of **8c** as a colorless oil; ν_{max} (neat) 1760, 1725 cm^{-1}; δ ($CDCl_3$) 1.21 (3H, s), 1.68 (1H, d, J = 11 Hz), 1.92 (1H, d, J = 11 Hz), 2.40–2.70 (2H, m), 2.80 (1H, t, J = 9 Hz), 2.90–3.18 (2H, m), 3.30–3.44 (1H, m), 3.69 (3H, s); *m/e* (%) 218 (M$^+$, 16), 190 (24), 159 (100), 131 (78), 115 (23), 91 (34), 66 (49).

4' - Nitrobenzyl 9 - methyl - 10 - oxopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane - 9 - carboxylate* **1e**. The ester (**8c**, 500 mg) was converted to the acid (427 mg) [ν_{max} (Nujol) 1760, 1680 cm^{-1}], and then esterified as described above to afford 530 mg (68%) of **1e**. Recrystallization from EtOH gave colorless prisms, m.p. 91–92°; ν_{max} (Nujol) 1750, 1720, 1600 cm^{-1}; *m/e* (%) 339 (M$^+$, 6), 311 (15), 203 (24), 175 (33), 159 (100), 131 (53); δ ($CDCl_3$) 1.23 (3H, s), 1.70 (1H, d, J = 12 Hz), 1.94 (1H, d, J = 12 Hz), 2.50–2.76 (2H, m), 2.83 (1H, t, J = 5 Hz), 2.95–3.22 (2H, m), 3.35–3.52 (1H, m), 5.21 (2H, s), 7.40 (2H, d, J = 11 Hz), 8.24 (2H, q, 11 Hz). (Found: C, 67.27; H, 4.99; N, 3.90. $C_{19}H_{17}NO_5$ requires: C, 67.25; H, 5.05; N, 4.13%).

Methyl 3,4 - dimethyl - 5 - oxotricyclo[5.2.1.0^{2,6}]*deca - 3,8 - diene - 2 - carboxylate* **7d**. To a stirred THF (80 ml)–MeOH (40 ml) soln of **6c** (3.4 g, 15.6 mmol) was added *t*-BuOK (5.39 g, 48.1 mmol) and the stirring was continued for 4.5 h at 50°. Work-up as described above gave 1.41 g (39%) of **7d** as a pale yellow oil: ν_{max} (neat) 1725, 1700, 1640 cm^{-1}; δ (CCl_4) 1.55 (3H, s), 1.84 (3H, s), 3.70 (3H, s).

Methyl 3,9 - dimethyl - 10 - oxopentacyclo-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane - 2 - carboxylate* **8d**. Irradiation of **7d** (1.3 g) in EtOAc (250 ml) for 12 h as described above gave 880 mg (67.7%) of **8d**. Recrystallization from hexane gave colorless prisms, m.p. 49–50°; ν_{max} (neat) 1760, 1720 cm^{-1}; *m/e* (%) 232 (M$^+$, 19), 204 (50), 200 (38), 173 (59), 145 (100), 129 (38); δ ($CDCl_3$) 0.96 (3H, s), 1.06 (3H, s), 1.63 (1H, d, J = 12 Hz), 1.83 (1H, d, J = 12 Hz), 2.40–2.58 (2H, m), 2.72–3.00 (2H, m), 3.35–3.48 (1H, m), 3.65 (3H, s). (Found : C, 72.20; H, 6.89. $C_{14}H_{16}O_3$ requires: C, 72.39; H, 6.94%).

4' - Nitrobenzyl 3,9 - dimethyl - 10 - oxopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decane - 2 - carboxylate* **1f**. The ester (**8d**, 520 mg) was converted to the acid (430 mg) [ν_{max} (Nujol) 1760, 1700 cm^{-1}], which was dissolved in EtOH (4 ml), converted its Na salt, and then refluxed with 4-nitrobenzyl bromide (430 mg) for 2 h. After the soln was cooled, the precipitated crystals were collected by filtration and recrystallized from EtOH–benzene to afford 620 mg (78.4%) of **1f** as colorless prisms, m.p. 145–146°; ν_{max} (Nujol) 1755, 1700, 1600 cm^{-1}; *m/e* (%) 353 (M$^+$, 10), 325 (54), 217 (40), 200 (45), 189 (88), 173 (71), 145 (100), 136 (35); δ ($CDCl_3$) 0.93 (3H, s), 1.07 (3H, s), 1.67 (1H, d, J = 12 Hz), 1.87 (1H, d, J = 12 Hz), 1.44–1.64 (2H, m), 1.76–2.08 (2H, m), 2.34–2.52 (1H, m), 5.20 (2H, s), 7.40 (2H, dd, J = 7, 2 Hz), 8.25 (2H, dd, J = 7, 2 Hz). (Found: C, 67.95; H, 5.33; N, 3.95. $C_{20}H_{19}NO_5$ requires: C, 67.98; H, 5.42; N, 3.96%).

Oxidation of **1a** *with m-chloroperbenzoic acid (m-CPBA).* To a $CHCl_3$ (30 ml) soln of **1a** (700 mg, 4.8 mmol) was added 85% m-CPBA (1.46 g, 7.17 mmol) and the soln was stirred for 1 h at room temperature, then diluted with $CHCl_3$ (100 ml), and washed successively with sat. KI aq, sat. $Na_2S_2O_3$ aq, sat. $NaHCO_3$ aq, and sat. NaCl aq. The dried $CHCl_3$ layer was evaporated to leave 693 mg of a waxy solid, which was chromatographed on a silica gel (30 g) column eluting with benzene–EtOAc (40:1) to give three fractions. The first was 102 mg (13.1%) of *11 - oxapentacyclo*[6.3.0.0^{2,4}.0^{3,7}.0^{5,9}]*undecan - 10 - one* **4a**, m.p. 135–136° (hexane); ν_{max} (CCl_4) 1781, 1348, 1176, 1008 cm^{-1}; *m/e* (%) 162 (M$^+$, 3), 118 (23), 117 (34), 91 (14), 84 (40), 79 (100); δ ($CDCl_3$) 1.4–3.2 (9H, m), 5.06 (1H, dd, J = 7, 3 Hz). (Found: C, 74.05; H, 6.11. $C_{10}H_{10}O_2$ requires: C, 74.02; H, 6.23%). The second was 418 mg (50.4%) of *10 - oxapentacyclo*[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undecan - 11 - one* **2a**, m.p. 145.5–147° (hexane) ν_{max} (CCl_4) 1761, 1368, 1071 cm^{-1}; *m/e* (%) 162 (M$^+$, 1), 118 (3), 117 (10), 105 (10), 97 (55), 91 (13), 66 (100); δ ($CDCl_3$) 1.56 (2H, s), 2.4–3.3 (7H, m), 4.70 (1H, t, J = 6 Hz). (Found: C, 74.08; H, 6.24. $C_{10}H_{10}O_2$ requires: C, 74.02; H, 6.23%). The third was 9 mg (1.1%) of *11 - oxapentacyclo*[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undecan - 10 - one* **3a**, m.p. 127–128.5° (hexane); ν_{max} (CCl_4) 1753, 1372, 1060 cm^{-1}; *m/e* (%) 162 (M$^+$, 2), 118 (3), 117 (8), 105 (5), 97 (36), 91 (9), 66 (100); δ (CCl_4) 1.43 (1H, d, J = 10 Hz), 1.73 (1H, d, J = 10 Hz), 2.4–3.5 (7H, m), 4.64 (1H, m). (Found: C, 74.05; H, 6.25. $C_{10}H_{10}O_2$ requires: C, 74.02; H, 6.23%).

endo - 3 - *Diazoacetyl* - endo - 2 - *methoxycarbonylnorborn* - 5 - *ene* **13**. A dry benzene (10 ml) soln of the half-ester (**11**, 2.3 g, 11.7 mmol), pyridine (1 drop), and $SOCl_2$ (2.8 g, 23.5 mmol) was stirred at 30–35° for 4 h. After the solvent was evaporated, the residue was dissolved in benzene (10 ml) and the benzene was evaporated again to leave a yellow oil (2.46 g) of the chloride **12** [ν_{max} (neat) 1800 (broad), 1740 cm^{-1}]. The benzene soln of the chloride was added dropwise with stirring to the ice-cooled soln (200 ml) of CH_2N_2 (prepared from 21.5 g of *p*-toluenesulfonylmethylnitrosamide) over a 45 min period and the stirring was continued for additional 12 h. After removal of insoluble materials, the filtrate was evaporated *in vacuo* and the residual oil (3.5 g) was chromatographed on a silica gel (30 g) column eluting with EtOAc–benzene (10:1) to give 1.06 g (41%) of **13** as a yellow solid, m.p. ~70° (decomp); ν_{max} (Nujol) 2125, 1730, 1640 cm^{-1}.

7 - *Methoxycarbonyltetracyclo*[4.3.0.0^{2,4}.0^{3,8}]*nonan - 5 - one* **10**. (a) A THF (10 ml) soln of **13** (550 mg, 2.5 mmol) was added dropwise to a stirred suspension of CuI (965 mg, 5.08 mmol) in THF (5 ml) at 40–45° (bath temp.) over a 1.5 h period and the stirring at the same temperature was continued for additional 4 h. After removal of the CuI, the filtrate was evaporated and the residual brown oil (410 mg) was chromatographed on a silica gel (11 g) column eluting with benzene–EtOAc (20:1) to afford 224 mg (47%) of **10** as a colorless solid. Recrystallization from benzene–hexane gave colorless prisms, m.p. 44–45°; ν_{max} (CCl_4) 1730 (broad), 1200 cm^{-1}; *m/e* (%) 192 (M$^+$, 4), 164 (7), 149 (20), 114 (95), 99 (48), 79 (100); δ (CCl_4) 1.56–1.8 (1H, m), 1.86–2.5 (4H, m), 2.52–2.96 (4H, m), 3.58 (3H, s). (Found: C, 68.81; H, 6.32. $C_{11}H_{12}O_3$ requires: C, 68.73; H, 6.29%).

(b) Compound **4a** (3.26 g, 20.1 mmol) in 0.1 n NaOH (212 ml) was stirred at 60° for 1.5 h, and to the soln was added dropwise $KMnO_4$ (7.6 g, 48.1 mmol) in H_2O (150 ml) over a 30 min period. After the stirring was continued for additional 5 h at 60°, the excess $KMnO_4$ was decomposed with $Na_2S_2O_3$ aq, insoluble materials were removed by filtration, and the filtrate was washed with ether, brought to pH 3 with 10% HCl, then extracted with $CHCl_3$. The washed and dried $CHCl_3$ layer was evaporated leaving 1.72 g (48%) of *tetracyclo*[4.3.0.0^{2,4}.0^{3,8}]*nonan - 5 - one - 7 - carboxylic acid* **9** as a colorless solid. Recrystallization from benzene gave colorless prisms, m.p. 128–129°; ν_{max} (Nujol) 3250, 1740–1710 (broad) cm^{-1}. (Found: C, 67.29; H, 5.67. $C_{10}H_{16}O_3$ requires: C, 67.40; H, 5.67%). The acid was esterified with CH_2N_2 in the usual way to yield **10**. Recrystallization from benzene–hexane gave colorless prisms, m.p. 44–45°.

Rearrangement of **2a** *to* **4a** *with trifluoroacetic acid.* Compound **2a** (200 mg, 1.23 mmol) was dissolved in trifluoroacetic acid (5 ml) and stirred for 15 min. The soln was concentrated *in vacuo* and the residue was dissolved in CH_2Cl_2 (50 ml). The washed and dried CH_2Cl_2 layer was evaporated leaving a waxy solid quantitatively, which was recrystallized from hexane to give 180 mg (90%) of **4a**, m.p. 135–136°.

Oxidation of **1c** *with m-CPBA.* A $CHCl_3$ (15 ml) soln of **1c** (260 mg, 0.8 mmol) and 85% m-CPBA (244 mg, 12 mmol) was stirred for 2 h at room temperature. Work-up as described above gave 290 mg of a colorless solid, which was chromatographed on silica gel (9 g) eluting with EtOAc–hexane (1:5) to give two compounds. The first was 44 mg (16.1%) of 8 - (4 - *nitrobenzyl-*

carbonyl) - 11 - *oxapentacyclo*[6.3.0.0^{2,4}.0^{3,7}.0^{5,9}]*undecan* - 10 - *one* **4c**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 102–103°; ν_{max} (Nujol) 1765, 1720, 1610 cm^{-1}; *m/e* 263 (5), 188 (22), 162 (40), 135 (44), 117 (100), 115 (31); δ ($CDCl_3$) 1.6–1.8 (1H, m), 1.9–2.5 (4H, m), 2.8–3.4 (3H, m), 5.22 (2H, s), 5.44 (1H, d, J = 4 Hz), 7.44 (2H, d, J = 9 Hz), 8.20 (2H, d, J = 9 Hz). (Found: C, 63.21; H, 4.45; N, 4.00. $C_{18}H_{15}NO_6$ requires: C, 63.34; H, 4.43; N, 4.10%). The second was 145 mg (54.1%) of 2 - (4 - *nitrobenzyloxycarbonyl*) - 10 - *oxapentacyclo*[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undecan* - 11 - *one* **2c**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 127–128°; ν_{max} (Nujol) 1720 (broad), 1610 cm^{-1}; *m/e* 276 (12), 275 (77), 136 (12), 105 (9), 90 (11), 89 (11), 66 (100); δ ($CDCl_3$) 1.5–1.9 (2H, m), 2.5–2.7 (1H, m), 2.8–3.6 (5H, m), 4.92 (1H, t, 6 Hz), 5.22 (2H, s), 7.28 (2H, d, J = 9 Hz), 8.20 (2H, d, J = 9 Hz). (Found: C, 63.25; H, 4.42; N, 4.22. $C_{18}H_{15}NO_6$ requires: C, 63.34; H, 4.43; N, 4.10%).

Oxidation of **1d** *with m-CPBA*. A $CHCl_3$ (10 ml) soln of **1d** (219 mg, 0.67 mmol) and 85% m-CPBA (175 mg, 0.86 mmol) was stirred for 2 h. Work-up as described above gave two compounds. The first was 61 mg (27.6%) of 1 - *methyl* - 8 - (4 - *nitrobenzylogycarbonyl*) - 11 - *oxapentacyclo*-[6.3.0.0^{2,4}.0^{3,7}.0^{5,9}] *undecan* - 10 - *one* **4d**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 136–137°; ν_{max} (Nujol) 1760, 1740, 1605 cm^{-1}; *m/e* (%) 355 (M$^+$, 3), 277 (44), 175 (18), 147 (16), 141 (90), 137 (100), 131 (79), 106 (15), 79 (37); δ ($CDCl_3$) 1.48 (3H, s), 1.66–2.16 (3H, m), 2.18–2.44 (2H, m), 2.72–3.00 (2H, m), 3.26–3.32 (1H, m), 5.06 (2H, s), 7.48 (2H, d, J = 9 Hz), 8.20 (2H, d, J = 9 Hz). (Found: C, 64.22; H, 4.84; N, 3.84. $C_{19}H_{17}NO_6$ requires: C, 64.22; H, 4.82; N, 3.94%). The second was 128 mg (57.9%) of 3 - *methyl* - 2 -(4 - *nitrobenzyloxycarbonyl*) - 10 - *oxapentacyclo* [5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undecan* - 11 - *one* **2d**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 140–141°; ν_{max} (Nujol) 1730 (broad), 1605, 1345 cm^{-1}; *m/e* (%) 355 (M$^+$, 2), 299 (12), 291 (18), 290 (100), 137 (25), 106 (15), 66 (90); δ ($CDCl_3$) 1.18 (3H, s), 1.3–1.9 (2H, m), 2.44 (1H, t, J = 4 Hz), 2.7–2.84 (1H, m), 2.86–3.12 (2H, m), 3.44–3.64 (1H, m), 4.56 (1H, d, J = 4 Hz), 5.17 (1H, d, J = 14 Hz), 5.25 (1H, d, J = 14 Hz), 7.50 (1H, d, J = 9 Hz), 8.16 (1H, d, J = 9 Hz). (Found: C, 64.02; H, 4.72; N, 3.94. $C_{19}H_{17}NO_6$ requires: C, 64.22; H, 4.82; N, 3.94%).

Oxidation of **1e** *with m-CPBA*. A $CHCl_3$ (6 ml) soln of **1e** (202 mg, 0.56 mmol) and 85% m-CPBA (182 mg, 0.89 mmol) was stirred for 3 h at room temperature. Work-up as described above gave two compounds. The first was 23 mg (11.2%) of 2 - *methyl* - 8 - (4 - *nitrobenzyloxycarbonyl*) - 11 - *oxapentacyclo* [6.3.0.0^{2,4}.0^{3,7}.0^{5,9}]*undecan* - 10 - *one* **4e**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 140–94°; ν_{max} (Nujol) 1770, 1720, 1600 cm^{-1}; *m/e* (%) 355 (M$^+$, 4), 219 (26), 175 (21), 173 (52), 136 (30), 131 (100), 93 (61); δ ($CDCl_3$) 1.24 (3H, s), 1.44–1.74 (1H, m), 1.92–2.35 (3H, m), 2.8–3.3 (3H, m), 5.18 (1H, s), 5.26 (2H, s), 7.48 (2H, d, J = 8 Hz), 8.20 (2H, d, J = 8 Hz). (Found: C, 63.82; H, 4.66; N, 3.80. $C_{19}H_{17}NO_6$ requires: C, 64.22; H, 4.82; N, 3.94%). The second was 155 mg (76%) of 9 - *methyl* - 2 - (4 - *nitrobenzyloxycarbonyl*) - 10 - *oxapentacyclo*[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undecan* - 11 - *one* **2e**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 113–114°; ν_{max} (Nujol) 1740 (broad), 1600 cm^{-1}; *m/e* (%) 291 (17), 290 (100), 191 (10), 136 (19), 131 (12), 106 (12), 66 (62); δ ($CDCl_3$) 1.56 (3H, s), 1.68–1.96 (2H, m), 2.56–3.12 (5H, m), 3.48–3.56 (1H, m), 5.22 (2H, s), 7.48 (2H, d, J = 9 Hz), 8.18 (2H, d, J = 9 Hz). (Found: C, 64.29; H, 4.73; N, 4.06. $C_{19}H_{17}NO_6$ requires: C, 64.22; H, 4.82; N, 3.94%).

Oxidation of **1f** *with m-CPBA*. A $CHCl_3$ (6 ml) soln of **1f** (202 mg, 0.56 mmol) and 85% m-CPBA (182 mg, 0.89 mmol) was stirred for 3 h to give two compounds. The first was 29 mg (13.2%) of 1,2 - *dimethyl* - 8 - (4 - *nitrobenzyloxycarbonyl*) - 11 - *oxapentacyclo*[6.3.0.0^{2,4}.0^{3,7}.0^{5,9}] *undeca* - 10 - *one* **4f**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 133–134°; ν_{max} (Nujol) 1760, 1715 cm^{-1}; *m/e* (%) 369 (M$^+$, 7) 277 (13), 233 (24), 145 (75), 137 (27), 93 (100); δ ($CDCl_3$) 1.12 (3H, s), 1.36 (3H, s), 1.44–1.64 (1H, m, 1.86 (1H, d, J = 9 Hz), 2.02–2.30 (2H, m), 2.72–3.00 (2H, m), 3.10–3.32 (1H, m), 5.25 (2H, s), 7.48 (2H, d, J = 8 Hz), 8.30 (2H, d, J = 8 Hz). (Found: C, 64.79; H, 5.19; N, 3.69. $C_{20}H_{19}NO_6$ requires: C, 65.03; H, 5.19; N, 3.79%). The second was 160 mg (69.6%) of 3,9 - *dimethyl* - 2 - (4 - *nitrobenzyloxycarbonyl*) - 10 - *oxapentacyclo*[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]*undeca* - 11 - *one* **2f**. Recrystallization from EtOAc–hexane gave colorless prisms, m.p. 143–144°; ν_{max} (Nujol) 1730 (broad), 1340, 1050 cm^{-1}; *m/e* (%) 369 (M$^+$, 3), 341 (13), 305 (23), 304 (100), 188 (23), 145 (34), 136 (47), 96 (36); δ ($CDCl_3$) 1.02 (3H, s), 1.44 (3H, s), 1.56–1.90 (2H, m), 2.42 (1H, t, J = 5 Hz), 2.64–2.84 (2H, m), 2.88–3.04 (1H, m), 3.48–3.62 (1H, m), 5.17 (1H, d, J = 14 Hz), 5.25 (1H, d, J = 14 Hz), 7.50 (2H, d, J = 8 Hz), 8.18 (2H, d, J = 8 Hz). (Found: C, 64.88; H, 5.05; N, 3.82. $C_{20}H_{19}NO_6$ requires: C, 65.03; H, 5.19; N, 3.79%).

Oxidation of **14** *with m-CPBA*. A $CHCl_3$ (30 ml) soln of **14** (500 mg, 3.38 mmol) and 85% m-CPBA (688 mg, 3.38 mmol) was stirred for 9 h at room temperature. A waxy solid (530 mg) was chromatographed on silica gel (50 g) eluting with benzene–EtOAc (30:1) to afford two products. The first was 114 mg (20.6%) of 9 - *oxatetracyclo*[5.2.2.0^{2,6}.0^{4,10}]*undecan* - 8 - *one* **16**, m.p. 187–188° (benzene–hexane); ν_{max} (CCl_4) 1760, 1370, 1220, 1050 cm^{-1}; *m/e* (%) 164 (M$^+$, 14), 136 (18), 120 (41), 107 (26), 91 (32), 80 (35), 79 (100), 66 (84); δ ($CDCl_3$) 1.2–1.6 (4H, m), 1.68–2.8 (6H, m), 4.53 (1H, dd, J = 3, 1 Hz). (Found: C, 73.18; H, 7.39. $C_{10}H_{12}O_2$ requires: C, 73.14; H, 7.37%). The second was 369 mg (66.6%) of 8 - *oxatetracyclo*[5.2.2.0^{2,6}.0^{4,10}]*undecan* - 9 - *one* **15**, m.p. 198–199° (benzene–hexane); ν_{max} (CCl_4) 1750, 1350, 1210, 1060 cm^{-1}; *m/e* (%) 164 (M$^+$, 51), 136 (36), 135 (19), 122 (26), 120 (15), 107 (15), 91 (28), 79 (100), 66 (91); δ ($CDCl_3$) 1.15–1.8 (6H, m), 2.0–2.7 (5H, m), 4.70 (1H, t, J = 6 Hz). (Found: C, 73.17; H, 7.34. $C_{10}H_{12}O_2$ requires:C, 73.14; H, 7.37%).

Oxidation of **1a** *with lead tetraacetate*. An AcOH (35 ml) soln of **1a** (1 g, 6.85 mmol) and 70% $Pb(OAc)_4$ (5.2 g, 8.2 mmol) was refluxed for 3 h. The reaction mixture was poured onto H_2O (400 ml) and extracted with CH_2Cl_2. The extract was washed with sat. $NaHCO_3$ aq, dried, and evaporated to leave a waxy solid (1.03 g), which was chromatographed on silica gel (20 g) eluting with benzene–EtOAc (40:1) to afford 210 mg (21%) of the recovered starting material and 610 mg (55%) of **4a**, m.p. 135–136° (from hexane).

Rearrangement of **2c**, **2d**, **2e**, *and* **2f** *with* $BF_3 \cdot Et_2O$. A $CHCl_3$ (1 ml) soln of **2c** (50 mg) and $BF_3 \cdot Et_2O$ (0.1 ml) was allowed to stand at room temperature for 20 min. After dilution with $CHCl_3$, the soln was washed with sat. NaCl aq, dried, and evaporated to give **4c** after recrystallization from EtOAc–hexane, 40 mg (80%), m.p. 102–103°. Under the same conditions, **2d**, **2e**, and **2f** gave **4d** (96%), **4e** (84%) and **4f** (75%), respectively.

Rate measurements and quantitative analyses. Equal volumes of $CHCl_3$ solns of a ketone (0.1 M) and m-CPBA (0.15 M) were mixed and allowed to stand at 30.0°. At intervals, aliquots of the reaction solution were withdrawn and analyzed residual m-CPBA contents by usual iodometry. At the same time, aliquots were quenched with excess KI aq and to the $CHCl_3$ layer *p*-nitrobenzyl acetate as an internal standard was added and analyzed quantitatively the recovered ketone **1** and products (**2**, **3**, **4**) by UV-spectrometry at 254 nm on a high-pressure liquid chromatograph [JASCO FLC-150; JASCO WC-02 500 Corasil 2, elution with EtOAc–hexane saturated with MeCN (1:10)].

Analyses of **2a** and **4a** were performed NMR spectrometrically in CCl_4 using the signals at 4.70 ppm for **2a** and 5.06 ppm for **4a** as compared with the signal (6.76 ppm) of an internal standard, durene.

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[7]The oxidation of **1a** was completed within 1 h at room temperature (see experimental section), but under the same conditions cyclopentanone and norbornan-2-one required 16 and 23 h, respectively.

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[9]The Baeyer–Villiger oxidation of some strained compounds with bicyclo[2.2.0]hex-2-yl ketones[10] and a cyclobutyl ketone[11] gave similar rearranged lactones and their mechanism have been proposed to involve a cyclobutyl-cyclopropyl-carbinyl rearrangement of the first formed ordinary oxidation products.

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[12]The yield of **3a** was almost nil.

[13]The *p*-nitrobenzyl ester group was introduced in order to facilitate quantitative analyses using a high pressure liquid chromatography in kinetic experiments.

[14]This rearrangement also occurs readily by the treatment with trifluoroacetic acid, but is accompanied in some degree by the cleavage of *p*-nitrobenzyl ester groups.

[15]Recently it was reported that oxidation of **1a** with ceric ion gave **3a** as the sole product, while that with m-CPBA gave a mixture of **2a** and **3a**.[16] Oxidation with ceric ammonium sulfate under the described conditions, however, gave only **4a**, and not **3a**.

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[23]The ordinary migration mechanism does apparently not play a major role, but cannot be completely ruled out because **3a** is probably formed in this mechanism.