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A rearrangement of 1-hydroperoxy-2-oxabicycloalkanes into lactones of ω-acyloxy-(ω-3)-hydroxyalkanoic acids related to the Criegee reaction

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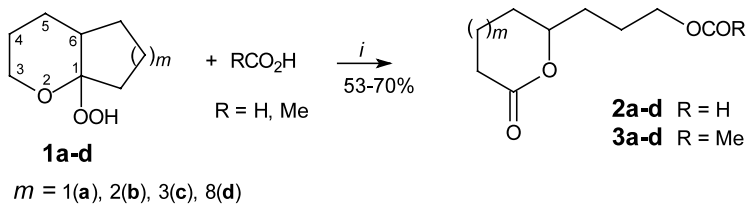
Abstract—1-Hydroperoxy-2-oxabicyclo[*n*.4.0]alkanes ($n=3$, 4, 5 and 10) on heating with formic or acetic acid containing a catalytic amount of sulfuric acid undergo a rearrangement into lactones of ω-acyloxy-(ω-3)-hydroxyalkanoic acids by a mechanism related to the Criegee reaction. © 2002 Published by Elsevier Science Ltd.

The Criegee rearrangement was originally performed using 9-acylperoxydecalin as an example.[1] On heating, this compound was converted into 9-acyloxy-11-oxabicyclo[4.4.1]undecane resulting from the heterolytic cleavage of the bridging C–C bond. This reaction is a typical rearrangement involving a 1,2-shift of a substituent from a carbon atom to an adjacent electron deficient oxygen atom. The electron deficiency on the oxygen atom in this type of reaction is generally achieved by employing protic or aprotic acids as catalysts.[2,3] These reactions are the basis for a phenol synthesis according to Hock,[4] the preparation of esters and lactones by the Baeyer–Villiger oxidation of ketones,[5] the rearrangement of α-methoxyhydroperoxides representing ozonolysis products of certain olefins under the action of acetic or trifluoroacetic anhydride in the presence of triethylamine and DMAP into esters and lactones[6] and other transformations of organic and organoelement hydroperoxides.[2,3]

In this communication, we report a new type of rearrangement related to the Criegee reaction of 1-hydroperoxy-2-oxabicycloalkanes **1a–d**† involving a 1,2-shift of a substituent from a carbon atom to an adjacent the electron deficient oxygen atom resulting in the formation of lactones of ω-acyloxy-(ω-3)-hydroxyalkanoic acids (**2a–d** or **3a–d**) on heating in formic or acetic acid containing a catalytic amount of sulfuric acid (Scheme 1, Table 1).‡



1a-d

m = 1(**a**), 2(**b**), 3(**c**), 8(**d**)

Scheme 1. (i) 0.15 equiv. H_2SO_4, 70–80°C, 20–90 min.

Keywords: oxabicyclic hydroperoxides; acylation; rearrangement; Criegee and Baeyer–Villiger reactions; hydroxy acid derivatives.

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† The starting materials were prepared by hydroperoxidation of the corresponding 2-oxabicycloalkenes-cyclization products of 2-(3-acetoxypropyl)cycloalkanones[7,8] in yields of 83–95%.[9]

‡ *Typical procedure*. A solution of H_2SO_4 (0.15 equiv.) in formic or acetic acid (1.5 ml) was added to a cooled (0–5°C) solution of the hydroperoxide **1** or peroxy ester **4** (2–3 mmol) in HCO_2H or AcOH (3 ml), and the resulting mixture was kept at 0–5°C for 1–2 h then heated at 70–80°C until complete decomposition of the hydroperoxide (0.5–1.5 h, TLC). After the usual work-up, the mixture was distilled using a Hickman flask (the distillation causes thermal depolymerization of oligomers formed along with the lactones) and the distillate was purified by flash chromatography on neutral Al_2O_3 (eluent-light petroleum/EtOAc).

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Table 1. Synthesis of lactones of ω-acyloxy-(ω-3)-hydroxyalkanoic acids from 1-hydroperoxy-2-oxabicycloalkanes (**1a–d**) (0.15 equiv. H_2SO_4, 70–80°C)

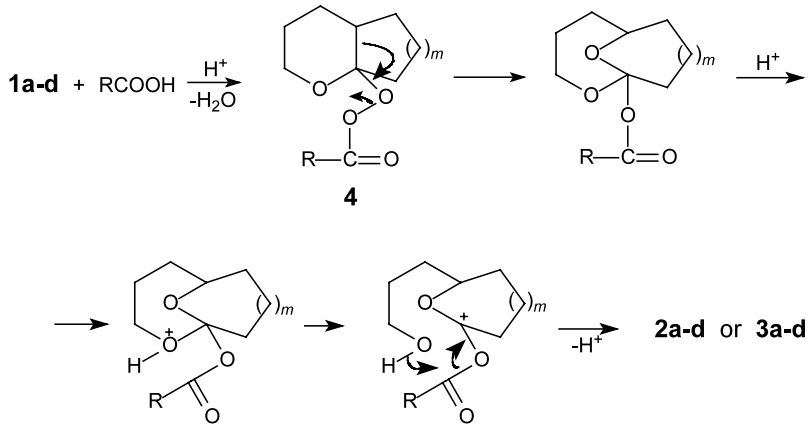
Substrate	RCOOH	Time (min)	Lactone[a]	Yield (%)[b]
1a	HCOOH	20	**2a**	64
1a	AcOH	20	**3a**	65
1b	HCOOH	20	**2b**	68
1b	AcOH	20	**3b**	70
1b	AcOH + Ac_2O (1:1)	20[c]	**3b**	70
1b	AcOH + Ac_2O (1:1)	60[d]	**3b**	45
1c	HCOOH	30	**2c**	57
1c	AcOH	30	**3c**	65
1d	HCOOH	90	**2d**	68
1d	AcOH	90	**3d**	53
4a	AcOH	10	**3a**	69
4b	AcOH	15	**3b**	64
4b	AcOH	15[c]	**3b**	75
4b	AcOH	60[d]	**3b**	50
4d	AcOH	15	**3d**	71

[a] All new lactones gave satisfactory IR, NMR and mass spectral as well as elemental analysis data.
[b] GLC data.
[c] 20–45°C (spontaneous warming).
[d] Without H_2SO_4, 110°C.

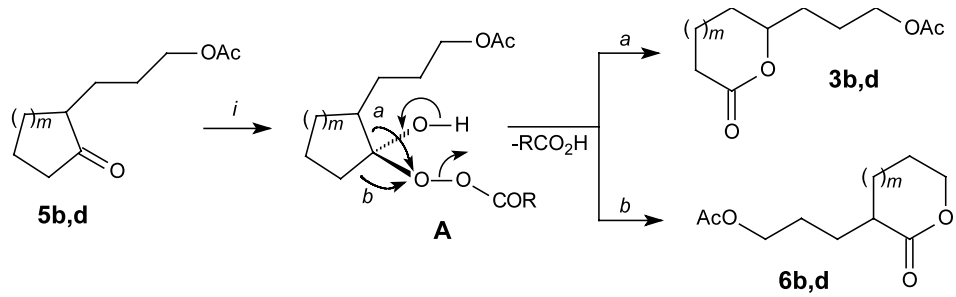
In the absence of H_2SO_4, the transformation of hydroperoxides **1a–d** into lactones **2a–d** or **3a–d** was not observed. It is known that sulfuric acid catalyses the acylation of hydrogen peroxide with carboxylic acids,[10] while carboxylic acids and esters acylate *tert*-butyl hydroperoxide on heating even in the absence of an acidic catalyst.[11] These data give grounds to assume that the transformation of hydroperoxides **1** into lactones **2** and **3** proceeds via the intermediate peroxy esters **4** (Scheme 2). Selective rearrangement of model peroxy esters **4a**, **4b** and **4d** (R = Me) into the corresponding lactones **3** on heating in acetic acid in the presence of sulfuric acid (Table 1) is yet another argument in favour of this assumption. Judging from the facts that in the absence of H_2SO_4 the transformation of hydroperoxides **1** into lactones **2** and **3** does not take place and the rearrangement of peroxy esters **4** into lactones occurs substantially more slowly, the acid catalyses both the acylation of hydroperoxides **1** by the carboxylic acids and the rearrangement of peroxy esters **4**. The latter reaction appears to proceed in a manner similar to the Criegee rearrangement of 9-acylperoxydecalins into 9-acyloxy-11-oxabicyclo[4.4.1]undecane[2] and the transformation of α-alkoxy hydroperoxides into lactones.[5]

The structures of lactones **2** and **3** were established from ^1H and ^{13}C NMR, IR and mass spectra,[§] and

[§] Spectral data. 8-Formyloxyoctan-5-olide (**2a**), IR (KBr): 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ (ppm) 1.30–1.95 (8H, m, CH_2), 2.25–2.50 (2H, m, CH_2C=O), 3.97–4.15 (2H, m, CH_2O), 4.17–4.32 (1H, m, HC-O), 7.95 (1H; m, HC=O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.1, 23.8, 27,5, 29.1, 31.9 (CH_2), 63.1 (CH_2O), 79.5 (HC-O), 160.8 (HC=O), 171.6 (CH_2C=O); *m/z* (EI): 186 (M^+, 3.2), 140 (36.1), 139 (12.1), 136 (56.1), 131 (22.9), 126 (42.6), 114 (18.7), 113 (78.2), 111 (13.1), 109 (13.3), 108 (18.6), 102 (22.6), 101 (17.6), 97 (20.1), 95 (62.5), 94 (65.5), 85 (62.4), 84 (65.2), 81 (56.0), 73 (66.8), 71 (80.55), 67 (66.1), 56 (70.0), 55 (100), 45 (45.2); found: C, 57.94; H, 8.02%. $C_9H_{14}O_4$ requires C, 58.05; H, 7.58%. 9-Formyloxynonan-6-olide (**2b**), IR (KBr): 1715. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.25–1.85 (10H, m, CH_2), 2.20–2.32 (2H, m, CH_2C=O), 4.04–4.13 (2H, m, CH_2O), 4.15–4.28 (1H, m, HC-O), 7.96 (1H, s, H-C=O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.6, 24.09, 24.3, 27.9, 30.0, 33.5 (CH_2), 63.2 (CH_2O), 79.5 (H-C-O), 160.9 (H-C=O), 175.7 (CH_2-C=O); *m/z* (EI): 200 (I^+, 2.43), 183 (4.13), 155 (10.7), 154 (17.53), 137 (24.5), 136 (56.1), 131 (22.9), 126 (42.6), 114 (18.7), 113 (78.2), 111 (13.1), 109 (13.3), 108 (18.6), 102 (22.6), 101 (17.6), 97 (20.1), 95 (62.5), 94 (65.5), 85 (62.4), 84 (65.2), 81 (56.0), 73 (66.8), 71 (80.55), 67 (66.1), 56 (70.0), 55 (100), 45 (45.2); found: C, 60.41; H, 8.33%. $C_{10}H_{16}O_4$ requires C, 59.98; H, 8.05%. 10-Formyloxydecan-7-olide (**2c**), IR (KBr): 1720. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.10–1.95 (12H, m, CH_2), 2.31–2.51 (2H, m, CH_2C=O), 4.19–4.28 (2H, m, CH_2O), 5.03–5.17 (1H, m, HC-O), 8.03 (1H, s, HC=O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.9, 21.3, 22.7, 26.5, 27.9, 29.2, 35.1 (CH_2), 64.5 (CH_2O), 72.6 (HC-O), 160.1 (H-C=O), 173.9 (CH_2C=O). 15-Formyloxypentadecan-12-olide (**2d**), IR (KBr): 1720; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.15–1.8 (22H, m, CH_2), 2.2.–2.4 (1H, m, CH_2C=O), 4.05–4.18 (2H, m, CH_2O), 4.93–5.09 (1H, m, HC-O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.7 (O-C=O), 160.7 (H-C=O), 73.1, 63.3 (C-O), 34.7, 32.2, 29.3, 27.6, 26.6, 26.2, 26.0, 25.9, 24.7, 24.5, 24.3, 22.6 (CH_2); found: C, 67.92; H, 9.71%. $C_{16}H_{28}O_4$ requires C, 67.57; H, 9.92%). 8-Acetoxyoctan-5-olide (**3a**), IR (KBr): 1710; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.40–1.98 (8H, m, CH_2), 2.03 (3H, s, CH_3), 2.25–2.60 (2H, m, CH_2C=O), 3.95–4.11 (2H, m, CH_2O), 4.15–4.35 (1H, m, CHO); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.1, 20.6, 23.9, 27.5, 29.1, 32.0 (CH, CH_3), 63.6 (CH_2O), 79.6 (CHO), 170.8, 171.5 (C=O); *m/z* (EI): 200 (I^+, 3.7), 157 (6), 144 (24.8), 141 (11.4), 140 (18.5), 139 (13), 128 (18.7), 115 (13.8), 114 (13.3), 112 (60.9), 110 (23.3), 102 (14.5), 100 (30.8), 99 (87.7), 97 (50.0), 87 (40.1), 84 (70.7), 81 (38.2), 73 (30.1), 71 (83.8), 68 (76.6), 55 (100), 45 (26.7); found: C, 60.31; H, 8.12%. $C_{10}H_{16}O_4$ requires C, 58.98; H, 8.05%. 9-Acetoxynonan-6-olide (**3b**),[12] IR (KBr): 1710; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.35–1.78 (10H, m, CH_2), 1.97 (3H, s, CH_3), 2.20–2.35 (2H, m, CH_2C=O), 3.93–4.07 (2H, m, CH_2O), 4.15–4.24 (1H, m, CHO); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.7, 24.5, 24.6, 24.8, 33.2, 34.2, 36.6 (CH_2), 64.4 (CH_2O), 70.8 (CHO), 171.3, 178.6 (C=O); *m/z* (EI): 205 (2.5), 171 (16), 170 (27), 153 (6.8), 142 (8.1), 129 (13.7), 113 (14.5), 112 (16.1), 111 (43.8), 100 (36.2), 85 (47.4), 84 (83.6), 71 (45.2), 69 (49.1), 55 (69.8), 54 (100), 45 (46.6), 43 (68.5); found: C, 61.83; H, 8.25%. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%. 10-Acetoxydecan-7-olide (**3c**), IR (KBr): 1715; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.10–2.05 (15H, m, CH_2, CH_3), 2.25–2.50 (2H, m, CH_2C=O), 4.09–4.20 (2H, m, CH_2O), 4.76–4.90 (1H, CHO); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.8, 21.1, 21.9, 22.5, 25.9, 27.7, 28.9, 34.8 (CH_2), 64.3 (CH_2O), 72.4 (CHO), 170.2, 173.6 (C=O); found: C, 63.41; H, 8.65%. $C_{12}H_{20}O_4$ requires C, 63.14; H, 8.83%. 15-Acetoxypentadecan-12-olide (**3d**), IR (KBr): 1715; ^1H NMR ($CDCl_3$, 250 MHz): δ 1.15–1.8 (22H, m, CH_2), 2.03 (3H, s, CH_3), 2.2.–2.4 (2H, m, CH_2C=O), 3.99–4.15 (2H, m, CH_2O), 4.82–4.98 (1H, m, HC-O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.4, 170.7 (O-C=O), 73.3, 63.7 (C-O), 34.1, 33.0, 31.9, 29.2, 29.0, 26.7, 26.0, 25.9, 25.9, 24.6, 24.5, 22.3, 22.2 (CH_2, CH_3); found: C, 68.67; H, 9.93%. $C_{17}H_{30}O_4$ requires C, 68.42; H, 10.13%. 1-Acetoperoxy-2-oxabicyclo[4.3.0]nonane (**4a**), ^1H NMR ($CDCl_3$, 250 MHz): δ 1.59–2.01 (11H, m, CH_2, CH), 2.05 (3H, s, CH_3), 4.03–4.25 (2H, m, CH_2O); found: C, 59.61; H, 7.82%. $C_{10}H_{16}O_4$ requires C, 59.98; H, 8.05%. 1-Acetoperoxy-2-oxabicyclo[4.4.0]decane (**4b**), ^1H NMR ($CDCl_3$, 250 MHz): δ 1.55–1.95 (13H, m, CH_2, CH), 2.04 (3H, s, CH_3), 4.01–4.28 (2H, m, CH_2O); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 17.1, 21.8, 24,5, 24.9, 25.1 (CH_2, CH), 60.1 (CH_2O), 115.7 (O-C-O), 167.8 (C=O); found: C, 61.39; H, 8.23%. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%. 1-Acetoperoxy-2-oxabicyclo[4.10.0]hexadecane (**4d**), ^1H NMR ($CDCl_3$, 250 MHz): δ 1.11–1.92 (25H, m, CH_2, CH), 2.08 (3H, s, CH_3), 3.69–3.82 (2H, m, CH_2O); found: C, 68.12; H, 10.35%. $C_{17}H_{30}O_4$ requires C, 68.42; H, 10.13%.



Scheme 2.



Scheme 3. (i) CH_2Cl_2, MCPBA (1.5 equiv.), CF_3CO_2H (0.2 equiv.), 40°C, 1 h.

those of lactones **3b**,**d** were also confirmed by their independent syntheses from 2-(acetoxypropyl)cy clo-alkanones **5b**,**d** using the Baeyer–Villiger reaction (Scheme 3).[13]

The seven-membered lactone **3b** was obtained by this manner in 34% yield as a mixture with an isomeric lactone **6b** (yield 20%), while the 13-membered lactone **3d** was similarly obtained in only 7% yield along with the lactone **6d** (3%). Similar remote substituent effects on the regioselectivity of the Baeyer–Villiger oxidation of 5α-cholestan-6-one derivatives were observed earlier by Japanese chemists.[14]

Thus, this approach to lactones of ω-substituted ω-hydroxy alkanoic acids from 2-substituted cycloalkanones via 2-oxabicycloalkenes and 1-hydroperoxy-2-oxabicycloalkanes is far better than the Baeyer–Villiger oxidation of 2-substituted cycloalkanones with regard to selectivity and efficiency. This difference in regioselectivity between the processes results from the fact that the key intermediates ('Criegee' intermediates) differ considerably from each other in their structures. Bicyclic peroxy esters **4** are the intermediates in the rearrangement of hydroperoxides **1** into lactones **2** or **3** and monocyclic peroxy esters **A**—in the Baeyer–Villiger oxidation of cycloalkanones **5**. As a result of the remote effect of the acetoxy group similar to that observed in the above cited work,[14] the rearrangement of **A** occurs less selectively than **4**.

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References

1. (a) Criegee, R. *Ber*. **1944**, *77*, 722; (b) Criegee, R. *Lieb. Ann*. **1948**, *560*, 127.
2. Yablokov, V. A. *Usp. Khim*. **1980**, *49*, 1711; *Chem. Abst*. **1981**, *94*, 3324.
3. *Organikum. Organische-chemisches Grundpraktikum*; Rearrangements. 18. Aufg., VEB Deutscher Verlag Wissenschaften: Berlin, 1990; pp. 299–325.
4. (a) Hock, H.; Lang, S. *Ber*. **1944**, *77*, 257; (b) Hock, H.; Kropf, H. *Angew. Chem*. **1957**, *69*, 319.
5. Hassall, C. H. In *The Baeyer–Villiger Oxidation of Aldehydes and Ketones*; Adams, R., Ed. Organic reactions; John Wiley: New York, London, 1957; Vol. IX, pp. 73–106.
6. Schreiber, S. L. F.; Liew, W. *Tetrahedron Lett*. **1983**, *24*, 2363.
7. Ogibin, Yu. N.; Terent'ev, A. O.; Nikishin, G. I. *Izv. Akad. Nauk, Ser. Khim*. **1998**, 1197 [*Russ. Chem. Bull*. **1998**, *47*, 1166 (Engl. Transl.)].

8. Ogibin, Yu. N.; Terent'ev, A. O.; Nikishin, G. I. *Izv. Akad Nauk, Ser. Khim.* **1999**, 2115 [*Russ. Chem. Bull.* **1999**, *48*, 2091 (Engl. Transl.)].
9. Ogibin, Yu. N.; Terent'ev, A. O.; Ananikov, V. P.; Nikishin, G. I. *Izv. Akad Nauk, Ser. Khim.* **2001**, No. 11 2052 [*Russ. Chem. Bull.* **2001**, *50*, No. 11 (Engl. Transl.)].
10. (a) Smit, W. C. *Rec. Trav. Chim.* **1930**, *49*, 675; (b) Fernholz, H. *Chem. Ber.* **1951**, *84*, 110.
11. (a) Nikishin, G. I.; Ogibin, Yu. N.; Palanuer, I. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2478; *Chem. Abst.* **1968**, *68*, 114008; (b) Ogibin, Yu. N.; Palanuer, I. A.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 592 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1970**, *19*, 545 (Engl. Transl.)].
12. Deslongchamps, P.; Guay, D.; Chenevert, R. *Can. J. Chem.* **1985**, *63*, 2493.
13. Koch, S. S.; Chamberlin, A. R. *Synth. Commun.* **1989**, *19*, 829.
14. Takatsuto, S.; Ikekawa, N. *Tetrahedron Lett.* **1983**, *24*, 917.