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ON THE QUESTION OF CARBONYL OXIDE INTERMEDIATES IN THE OXYGEN TRANSFER BY FURAN ENDOPEROXIDES AND BICYCLIC OZONIDES: INTRAMOLECULAR TRAPPING EXPERIMENTS

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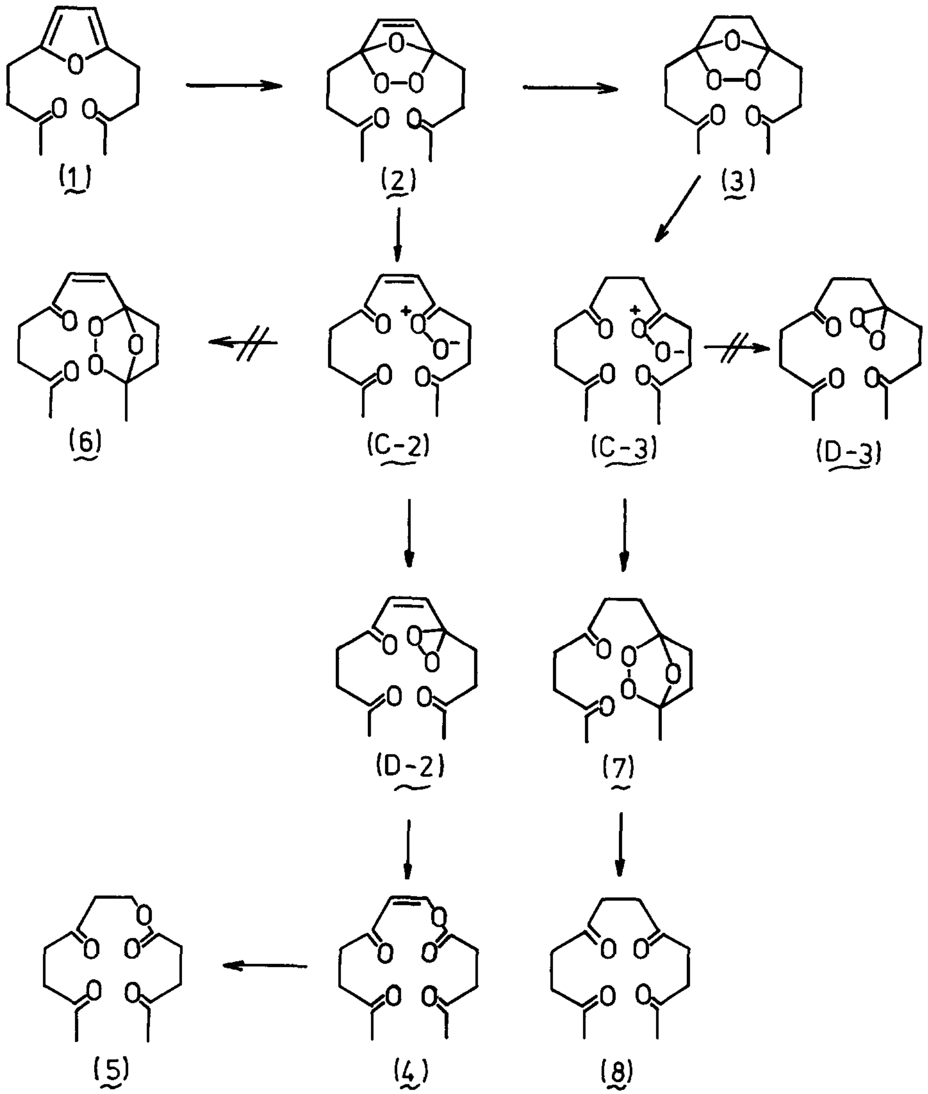
SUMMARY: On heating the furan endoperoxide (2) rearranges into the enol ester (4) and the bicyclic ozonide (3) affords instead the rearranged ozonide (7). The process (2) → (4) represents an intramolecular Baeyer-Villiger rearrangement presumably via the dioxirane (D-2), while the process (3) → (7) represents intramolecular trapping of the carbonyl oxide (C-3).

In the accompanying communication[1] we pointed out that a differentiation between the carbonyl oxide (C) and dioxirane (D) intermediates, which were proposed as the oxygen atom transfering species in the epoxidation of olefins and oxidation of sulfides and aldehydes and ketones by furan endoperoxides and bicyclic ozonides[2], must engage intramolecular trapping experiments as mechanistic probes. For example, Criegee[3] demonstrated that carbonyl oxides can be efficiently trapped intramolecularly by flanking keto groups to give bicyclic ozonides. Yet, dioxirane intermediates rearrange to give the so-called "anamolous ozonolysis" product via intramolecular Baeyer-Villiger rearrangement.[3a] We conducted such an intramolecular trapping experiment by preparing the furan endoperoxide (2) and bicyclic ozonide (3), containing flanking keto groups as internal trapping agents. Our results are presented in Scheme I.

Photooxygenation of a 0.1 M solution of 2,5-di(3-oxobutyl)-furan (1)[4] in $CHCl_3$ at 0°C afforded the endoperoxide (2). Spectral data: ^1H NMR ($CDCl_3$) δ(ppm): 2.20 (6H, s, CH_3), 2.40-2.80 (8H, m, side chain CH_2 groups) and 6.20 (2H, s, -CH=CH-); IR ($CHCl_3$) ν(cm^{-1}) 3020 (olefinic CH), 2980-2900 (aliphatic CH), 1720 (C=O) and 1660 (C=C). On warm-up of the endoperoxide solution in $CHCl_3$ to ca. 30°C (2) was completely consumed within 8 h in the dark, affording the Baeyer-Villiger product (4) (Scheme I).



SCHEME I

Spectral data: ^{1}H NMR ($CDCl_3$)δ(ppm) 2.20 (6H, s, CH_3), 2.60-2.80 (8H, b.s., CH_2), 5.40 (1H, d, J = 8 Hz, -CO-CH=) and 7.50 (1H, d, J = 8Hz, O-CH=); IR ($CHCl_3$)ν(cm^{-1}) 3020 (olefinic CH), 2960 (aliphatic CH), 1780 (-O-$\overset{\text{O}}{\text{C}}$-), 1720 (-CO-), 1680 (-$\overset{\text{O}}{\text{C}}$-C=C-), and 1650 (C=C). Furthermore, catalytic hydrogenation (Pd-C in AcOEt) gave 2,5-dioxoheptyl levulinate (5). Spectral data: ^{1}H NMR ($CDCl_3$)δ(ppm) 2.05 (6H, s, CH_3), 2.50-2.70 (10H, b.s., CH_2) and 4.10-4.30 (2H, t, J = 6 Hz, -CH_2-O-); IR (CCl_4)ν(cm^{-1}) 2995-2920 (aliphatic CH), 1750 (-CO_2-) and 1725 (-CO-). Hydrolysis of (5) gave levulinic acid.

Diimide reduction of endoperoxide (2) in CH_2Cl_2 at ca. -50°C and subsequent silica gel chromatography at ca. -20°C afforded ozonide (3) in 69% yield, 96% pure by iodometry. Spectral data: ^{1}H NMR ($CDCl_3$)δ(ppm) 1.70-2.60 (12H, m, CH_2) and 2.00 (6H, s, CH_3); ^{13}C NMR ($CDCl_3$)δ(ppm) 22.3 (t, ring CH_2), 29.6 (q, CH_3), 36.7 (t, CH_2-C=O), 53.3 (t, bridgehead CH_2), 111.5 (s, bridgehead) and 296.8 (s, C=O); IR (CCl_4)ν(cm^{-1}) 3000 and 2960 (aliphatic CH), 1725 (C=O), 1425 (CH_2), 1360 (CH_3), 1170 (C-O). Catalytic reduction of ozonide(7) gave quantitatively the 2,5,8,11-tetraoxododecane (8), mp 90-92°C (lit.[4] mp 95-96°C).

On heating a $CDCl_3$ solution of ozonide (3) at 80°C for 2 h, ^{13}C NMR monitoring showed that the carbon resonances of (3) diminished and new resonances appeared at 110.3, 111.6 and 207.2 ppm, along with the characteristic resonances of the tetraone (8) at 29.8 (CH_3), 35.9, 36.1 and 36.9 (CH_2C=O) and 207.1 and 207.8 (C=O) ppm. On extensive heating, the new resonances also disappeared, while those of the tetraone (8) increased. The thermolysis mixture was chromatographed on silica gel at ca. -20°C, eluting with CH_2Cl_2. The rearranged ozonide (7) was isolated in 32% yield (99% by iodometry). Spectral data: ^{1}H NMR ($CDCl_3$) δ(ppm) 1.60 (3H, s, bridgehead CH_3), 1.90-2.40 (4H, m, ring CH_2), 2.10 (5H, s, CH_3C=O and bridgehead CH_2) and 2.50-2.70 (6H, broad s, -CH_2C=O); IR (CCl_4)ν(cm^{-1}) 3020, 2970 and 2920 (aliphatic CH); 1730 (C=O) and 1370 (CH_3). The ^{13}C resonances at 110.3 and 111.6 ppm are adscribed to the distinct bridgehead carbons. On catalytic hydrogenation (7) gave quantitatively tetraone (8).

The clear-cut results of our investigation are that the furan endoperoxide (2) leads to the "anomalous ozonide" product (4) via intramolecular Baeyer-Villiger rearrangement but no intramolecular trapping product (6), while the bicyclic ozonide (3) gives the intramolecular trapping product (7) but no intramolecular Baeyer-Villiger product. It is unlikely that the thermal transformations (2) → (4) and (3) → (7) are concerted rearrangements[5] since with simpler model compounds we demonstrated that external carbonyl trapping agents led preferentially to oxygen transfer products, i.e. intermediates were intercepted in these reactions.[2] Also the ozonolysis of α,β-unsaturated carbonyl substrates provides evidence for carbonyl oxides as intermediates.[8] Therefore, we suggest that both in the (2) → (4) and (3) → (7) transformations carbonyl oxides are involved, respectively (C-2) and (C-3). However, while carbonyl oxide (C-2) prefers to undergo intramolecular Baeyer-Villiger rearrangement into enol ester (**4**), presumably via dioxirane (D-2), carbonyl oxide (C-3) prefers to become intramolecularly trapped in the form of ozonide (**7**). The destabilizing nature of the enone moiety in carbonyl oxide (C-2) apparently promotes the cyclization into its dioxirane (D-2), which then subsequently rearranges into (**4**). That alkenyl migration is prefered over alkyl migration is well documented in Baeyer-Villiger rearrangements.[7] We conclude that the energy barrier between the carbonyl oxide and dioxirane valence isomers is sufficiently low to allow ready interconversion.[9]

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