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# INSERTION OF OXYGEN ATOM INTO FUSED CYCLOBUTANE RINGS VIA AN ALKOXYL RADICAL REARRANGEMENT[1)]

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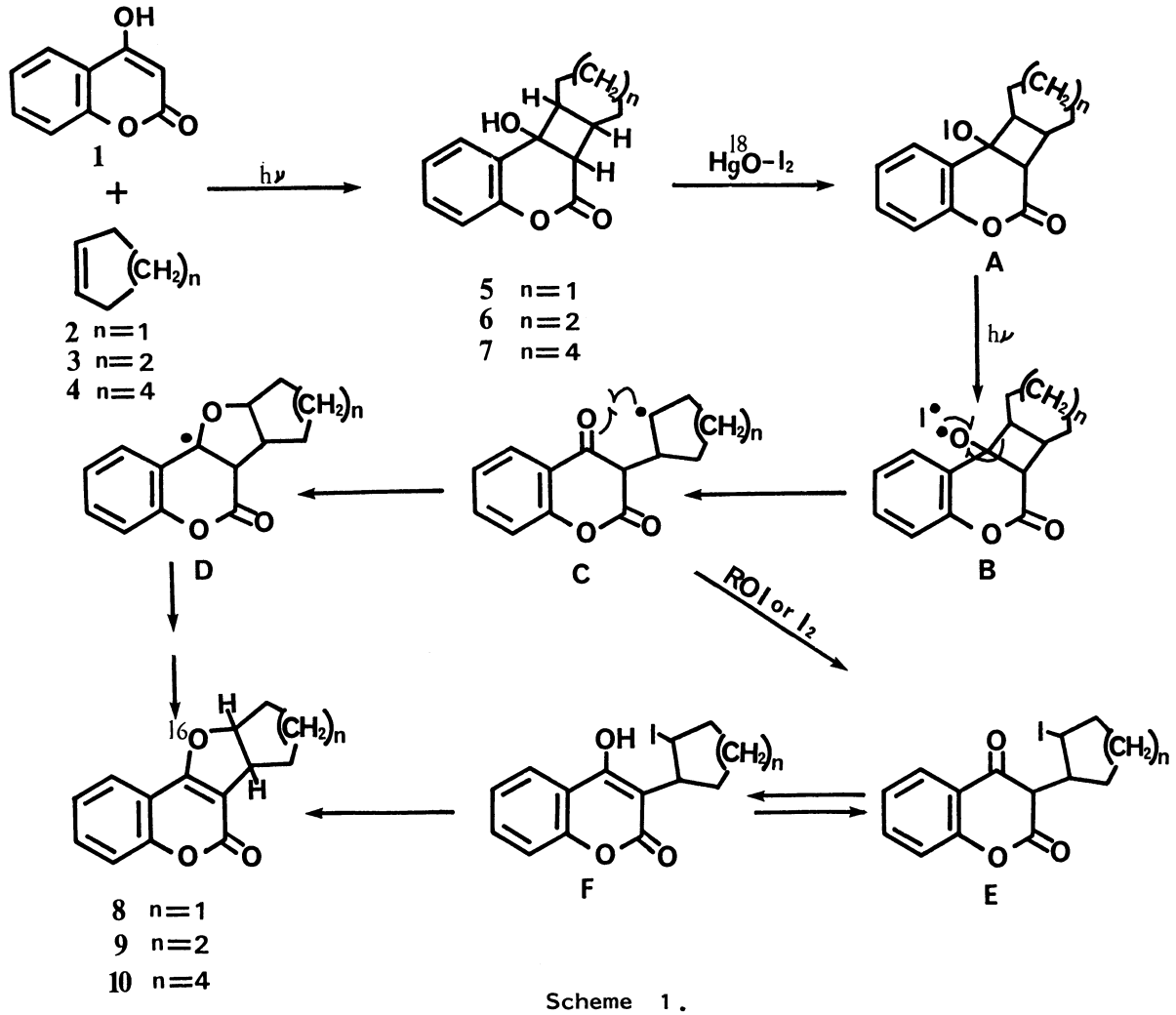
A new heteroatom insertion into cyclobutane rings via β-scission of alkoxyl radicals generated from photocycloadducts between 4-hydroxycoumarin and cycloalkenes is described.

The formation of heterocycles by heteroatom insertion into carbocycles is of great importance in organic synthesis and a variety of the method have been reported. In this communication we wish to report a novel oxygen atom insertion into a fused cyclobutane ring obtainable by the [$_{\pi}2$ + $_{\pi}2$] photocycloaddition of enolized carbonyl compounds to alkenes, to form fused dihydrofuran rings.

Fused cyclobutanols used in this study were the photochemical cycloadducts 5, 6, and 7 (Scheme 1) obtained from a photochemical cycloaddition of 4-hydroxycoumarin (1) with cyclopentene (2) or cyclohexene (3) or cyclooctene (4) by Reid and his colleagues.[2,3)] The stereochemistry of adduct 5 was established by an X-ray crystallographic analysis. The crystal data for 5 were as follows: $C_{14}H_{14}O_3$ triclinic, space group $P\bar{1}$, a=10.484(4), b=13.525(5), c=8.384(2)Å, α=90.05(3), β=103.07(2), γ=106.46(3)°, z=4, $D_c$=1.380 g $cm^{-3}$, μ($MoK_{\alpha}$)=0.900 $cm^{-1}$. 3199 Unique intensity data for 2θ<50° were collected on a Rigaku four-circle diffractometer with graphite-monochromated $MoK_{\alpha}$ radiation using the θ-2θ scanning technique.[4)] The structure was solved by means of the Monte Carlo direct method.[5)] The 16th random phase set for the 10 strongest reflections led to correct solution; an E-map based on 735 phases afforded all the non-hydrogen atoms. The structure thus obtained was refined by the block-diagonal least-squares method with anisotropic temperature factors. After all the hydrogen atoms had been located in a difference Fourier map, further least squares refinements were carried out




Scheme 1.

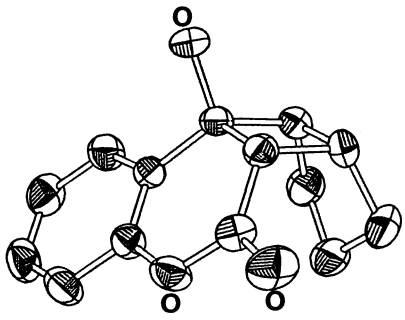


Fig. 1.
Perspective view of the molecule of 5.

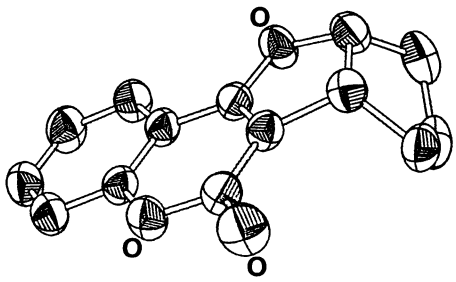


Fig. 2.
Perspective view of the molecule of 8.

including the hydrogen atoms; The final R value was 0.063. The molecular framework thus obtained is shown in Fig.1. Adduct 5 has thus a cis-syn-cis carbon framework. No evidence about the stereochemistry of adducts 6 and 7 have yet been made available.

Adduct 5 (300 mg) in benzene (60 ml) containing marcury(II) oxide (840 mg) and iodine (1.09 g)(each 3 equiv. mol) in a Pyrex vessel was irradiated with a 100-W Hg arc for 2 h under a nitrogen atmosphere to give a mixture of products from which a product 8 was obtained in a 39% yield by preparative TLC. The molecular formula of product (8) (m p 103-104 °C) was established as $C_{14}H_{12}O_3$ by means of elemental analysis and mass spectrometry (m/z 228, $M^+$, 76.7%).

The IR as well as UV spectra of 8 [6] have indicated that the coumarin nucleus was still intact and the full structure as cis-6b, 8, 9, 9a-tetrahydro-6H, 7H-cyclopenta[4,5]furo[3,2-C][1]benzopyran-6-one was again established by an X-ray crystallographic analysis.

The crystal data for 8 were as follows: $C_{14}H_{12}O_3$, monoclinic, space group $P2_1/c$, a=10.582(2), b=13.224(2), c=9.070(2)Å, β=99.55(2)°, z=4, $D_c$=1.361 g $cm^{-3}$, μ(CuKα)=7.42 $cm^{-1}$. 1811 Unique intensity data for 2θ<135° were collected on a Rigaku four-circle diffractometer with graphite-monochromated CuKα radiation.[4] The structure was elucidated by the Monte Carlo direct method,[5] using the 10 strongest reflections as the starting set. The 1st random phase set led to the correct solution; an E-map calculated with 374 phases revealed the locations of all the non-hydrogen atoms. The structure obtained was refined by the block-diagonal least-squares method with anisotropic temperature factors. After all the hydrogen atoms had been located in a difference Fourier map, several cycles of the full-matrix least-squares refinement were performed using anisotropic temperature factors for the non-hydrogen atom and isotropic ones for the hydrogen atoms: the final R value was 0.063. The molecular framework thus obtained is illustrated in Fig.2.

The analogous reaction of photocycloadduct 6 and 7 similarly gave 6b,7,8,9, 10,10a-hexahydro-6H-benzofuro[3,2-C][1]benzopyran-6-one (9),[7] mp 76-78 °C, and 6b, 7,8,9,10,11,12,12a-octahydro-6H-cycloocta[4,5]furo[3,2-C][1]benzopyran-6-one (10),[8] mp 137-139 °C, in 10% and 29% yields respectively.[9]

We further proved that the oxygen atom inserted to the ring exclusively originated from the hydroxyl groups of the starting cyclobutanols and not from the mercury(II) oxide by an $^{18}O$ labeling study. Thus, cyclobutanol (5) was

transformed into a dihydrofuran (8) with mercury(II) oxide $^{18}O$ (48.9 atom % O)[10] and iodine under the conditions described above. The mass spectrometric analysis showed no incorporation of $^{18}O$ into 8, providing evidence that the oxygen atom in the product 8 is derived from the hydroxyl group of 5.

The path leading to the products 8, 9, and 10 from the hypoiodites[11] is outlined in Scheme; photolysis of the hypoiodite (A), an initial intermediate, generates carbon radicals (C) via β-scission of the corresponding oxyl radical (B). The carbon-centered radical (C) traps the carbonyl oxygen within the species to form a dihydrofuranyl radical (D)[10] which gives the observed products via either dehydroiodination of another intermediate or the oxidation to a carbonium ion followed by the loss of a proton. Alternatively, the carbon-centered radical (C) abstracts an iodine atom from ROI or $I_2$ in a free radical chain process to generate an iodoenol (F) that would cyclize to give dihydrofuran 8, 9, or 10.

Further studies on a variety of cyclobutanol derivatives are in progress to explore the synthetic potential of this oxygen atom insertion to carbocycles and will be reported subsequently.[12]

References

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3) For a review of the 2+2 photocycloaddition between an α,β-unsaturated carbonyl compound and an alkene, see S. W. Baldwin, "Organic photo chemistry," ed by A. Padwa, M. Dekker Inc., New York, N.Y. (1981), Vol.5, Chap. 2, pp. 123-225.
4) The intensity measurements were performed at the High Brilliance X-Ray Diffraction Laboratory of Hokkaido University.
5) A. Furusaki, Acta Crystallogr., Sect. A, 35, 220 (1979).
6) $^1H$ NMR (100 MHz, $CDCl_3$) δ 1.36-2.31 (6H, m, 7,8 and 9-methylene groups), 3.96 (1H, diffused t, 6b-H), 5.54 (1H, 9a-H), and 7.17-7.67 (4H, m, aromatic H); IR (Nujol), 1713 and 1646 $cm^{-1}$ (br, -OCOC=C); UV (EtOH) 327 (ε4900), 313 (6800), 289 (6300), 227 (4500), and 207 (14200), MS 228 ($M^+$, 76.7%), 199 (100), and 121 (34.9).
7) $^1H$ NMR, δ 1.34-2.32 (8H, m, 7,8,9, and 10 methylene groups), 3.37 (1H, ddd, J=6, 7.6, and 8.1 Hz, 6b-H), 5.03 (1H, ddd, J=4.4, 4.2, and 8.1 Hz, 10a-H), and 7.20-7.73 (4H, m, aromatic protons); IR (Nujol), 1710 and 1635 $cm^{-1}$ (-OCOC=C-); MS 242 ($M^+$, 85%), 199 (100), and 121 (53).
8) $^1H$ NMR, δ 1.29-2.31 (7,8,9,10,11, and 12 methylene groups), 3.41 (1H, ddd, J=9.5, 9.3, and 9.3, (6b-H), 5.00 (1H, ddd, J=4.6, 4.6, and 9.3 Hz, 12a-H) and 7.17-7.69 (4H, m, aromatic protons); IR (Nujol) 1710 and 1640 $cm^{-1}$ (-OCOC=C-); MS 270 ($M^+$, 39%), 199 (100), and 121 (17).
9) The stereochemistry of these dihydrofuran derivatives is not proved although dihydrofuran ring of 9 is almost certainly cis-fused.
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