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AN ALKOXY RADICAL REARRANGEMENT OF PHOTOCYCLOADDUCT OF 4-HYDROXYCOUMARIN AND DIMETHYLBUT-2-ENE TO FUROCOUMARIN AND FUROBENZO-γ-pyrone. Coumarin— BENZO-γ-PYRONE TRANSFORMATION[1)]

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The alkoxy radical generated from a fused cyclobutanol obtained by the photocycloaddition of 4-hydroxycoumarin and dimethylbut-2-ene rearranges to a furocoumarin and a furo-benzo-γ-pyrone. The results afford further insight regarding the mechanism of the formation of the furocoumarins.

In our previous paper, we reported a new heteroatom insertion into cyclobutane rings to give furocoumarins, via β-scission of alkoxyl radicals generated from photocycloadducts of 4-hydroxycoumarin and cycloalkenes.

In this communication we wish to report a novel rearrangement of the alkoxy radical generated from fused cyclobutanol prepared by the photocycloaddition of 4-hydroxycoumarin and dimethylbut-2-ene to a furo-benzo-γ-pyrone, along with the formation of a furocoumarin previously reported.[2)] The rearrangement provides the first example of the transformation of a coumarin into a benzo-γ-pyrone.

Fused cyclobutanol 1 in this study was prepared according to the procedure reported by Reid and his colleagues.[3)] The stereochemistry of adduct 1 was established by an X-ray crystallographic analysis. The following were its crystal data: $C_{15}H_{18}O_3$, monoclinic, space group $P2_1/c$, $a = 14.508(7)$, $b = 6.644(6)$, $c = 14.099(8)$ Å, $\beta = 115.96(4)^\circ$, $z = 4$, $D_c = 1.252$ g cm^{-3}. The intensities of 1810 independent reflections with $2\theta < 50^\circ$ were obtained on a Rigaku four-circle diffractometer with graphite-monochromated Mo-Kα radiation using the ω-2θ scanning technique. The structure was solved by the Monte Carlo direct method[4] using 15 reflections as the starting set; an E-map derived from the 73rd random phase set afforded all the non-hydrogen atoms. After the structure had been refined by the block-diagonal least-squares method with anisotropic thermal paramaters, a difference Fourier synthesis was carried out; the resulting map revealed all the hydrogen atoms. Further full-matrix least-squares refinements were performed including one on hydrogen atoms with isotropic temperature factors. The final R value was 0.065. The molecular structure thus obtained has cis ring junction as shown in Fig. 1.

Adduct 1 (256 mg) in benzene (60 ml) containing mercury(II) oxide (648 mg) and iodine (759 mg) (each 3 mol equiv.) in a Pyrex vessel was irradiated with a 100-W Hg arc for 2 h under a nitrogen atmosphere. Two products 2 and 3 were

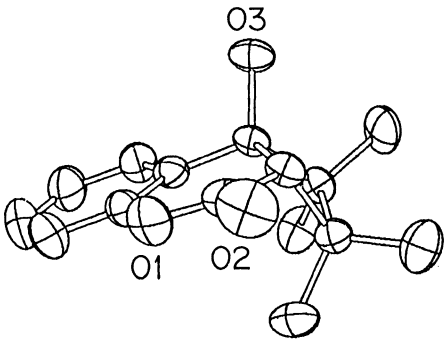
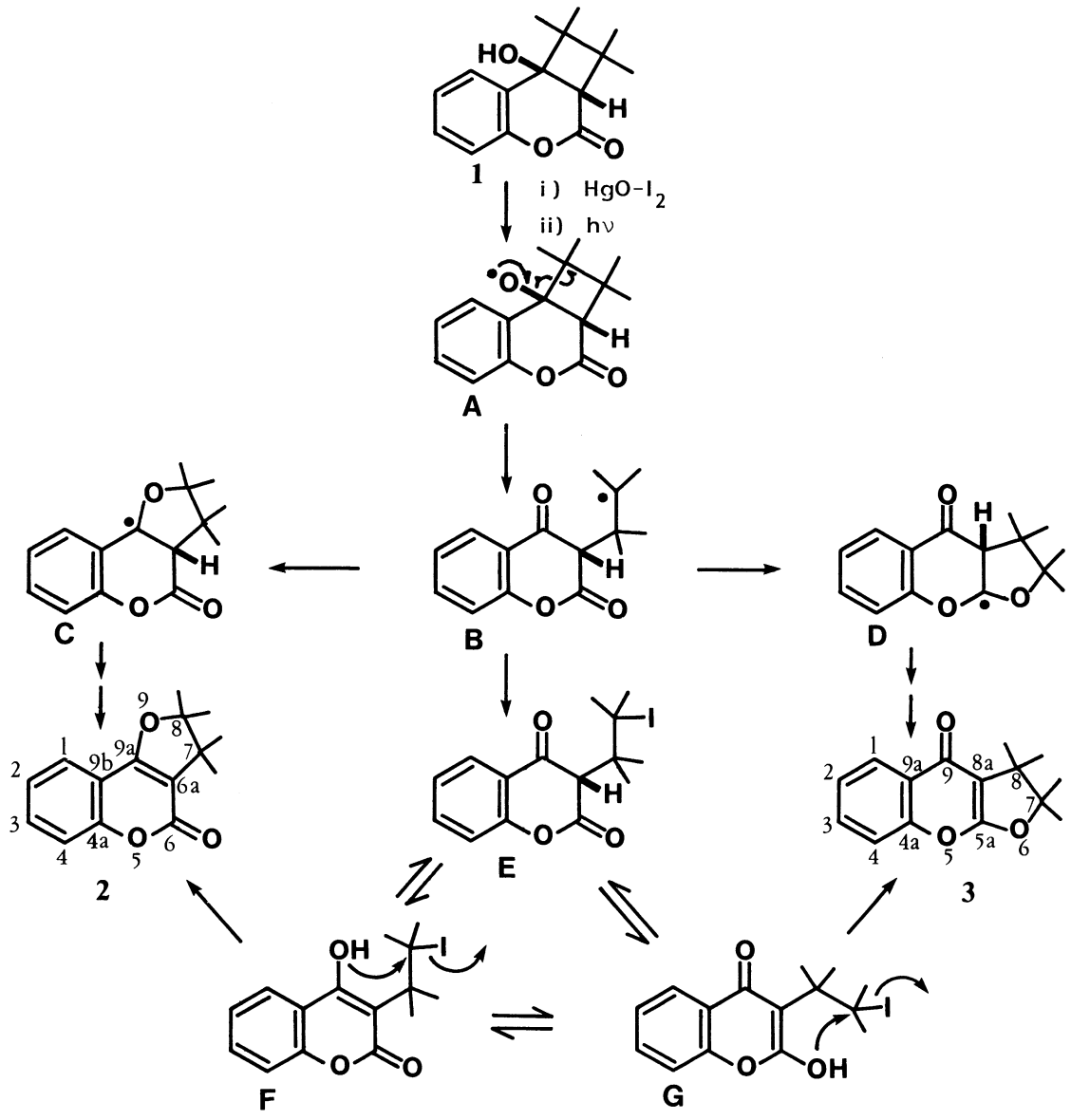


Fig. 1. X-Ray structure for cycloadduct 1.



Scheme 1.

obtained in 37 and 21% yields.[5] The molecular formulae of both 2 and 3 were established as $C_{15}H_{16}O_3$ by high resolution mass spectrometry. The two products were thus isomeric. The assignment of the structure of product 2 as a furocoumarin[2] arising from an oxygen insertion was straightforward since its coumarin nucleus was readily identified by the ^{13}C NMR spectrum[6] which gave a series of signals very similar to those of the furocoumarins previously reported.[2] The IR, ^1H NMR, and UV spectra[5] were also in accord with the assigned structure.

The isomeric product 3, on the other hand, was assigned the furobenzo-γ-pyrone structure 3 on the bases of its ^1H NMR, ^{13}C NMR, IR, and UV spectra.[7] Its ^{13}C NMR spectrum was especially indicative in assigning the structure. Of the pathways leading to products 2 and 3, that leading to 2 has already been discussed in the previous paper.[2] It has already been proved by an ^{18}O labeling study that the oxygen atom inserted to the ring exclusively originated from the hydroxyl groups of the starting cyclobutanol and not from the mercury(II) oxide.[2] The possible paths to 2 and 3 from the alkoxy radical A are outlined in the Scheme; both products are formed *via* a common intermediate radical B generated by the β-scission. As outlined, there are two principal paths each for the formation of 2 and 3. Although it has not been possible to decide a preference for these two mechanistic possibilities for the formation of the furocoumarin reported previously,[2] it now seems evident that products 2 and 3 are formed *via* a novel combination of carbonyl oxygen with the carbon-centred radical (B → C → 2 and B → D → 3) since the alternative pathways (B → E → F → 2 and B → E → G → 3) involve such species as tertiary iodide E and a benzo-γ-pyrone G formed by enolization. The involvement of the species G is very unlikely and it has been proved in an analogous system that the tertiary alkyl radical combines with the carbonyl oxygen intramolecularly rather than with iodine when the two reactions compete and the formation of tertiary alkyl iodide has not been observed.[8]

Several other examples of the intramolecular combinations of carbonyl oxygen with carbon-centred radical generated by β-scission of alkoxy radicals have recently been unveiled in our laboratory.[8]

References

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2) H. Suginome, C. F. Liu, and A. Furusaki, Chem Lett., 1984, 911.
3) D. J. Haywood, R. G. Hunt, C. J. Potter, and S. T. Reid, J. Chem. Soc., Perkin Trans. 1, 1977, 2458.
4) A. Furusaki, Acta Crystallogr., Sect. A, 35,229 (1979).
5) Based on the converted starting material.
6) ^1H NMR ($CDCl_3$, 100 MHz) δ 1.34 (6H, s, 7-dimethyl), 1.47 (6H, s, 8-dimethyl), δ 7.23-7.70 (4H, m, aromatic H); ^{13}C NMR ($CDCl_3$, ppm from TMS) δ 21.90 (7-dimethyl), 23.07 (8-dimethyl), 45.97 (C-7), 96.69 (C-8), 110.20 (C-6a), 113.25 (C-9b), 116.72, 122.70, 123.53, and 131.92 (the four aromatic carbons

with a hydrogen), 154.87 (C-4a), 160.2 (C-9a), and 163.98 (C-6); IR (Nujol) 1643 and 1714 cm^{-1} (OCOC=C). UV (EtOH) 328 (ε; 5700), 313 (8400), 289 (8000), 378 (5800), and 207 nm (24500); MS m/e 244 (M^+, 14%), and 229(M^+ $-CH_3$, 100%).

7) ^1H NMR ($CDCl_3$, 100 MHz) δ 1.42 (6H, s, 8-dimethyl), 1.48 (6H, s, 7-dimethyl), 7.28-7.67 (4H, m, aromatic H); ^{13}C NMR ($CDCl_3$, ppm from TMS), 22.27 (q, 8-dimethyl), 22.97 (q, 7-dimethyl), 45.53 (s, C-8), 96.15 (s, C-7), 102.77 (s, C-8a), 117.07, 124.98, 125.39, and 131.84 (each d, 4 aromatic carbons with a hydrogen), 124.51 (s, C-9a), 153.05 (s, C-4a), 167.11 (s, C-9), and 174.67 (s, C-5a), IR (neat) 1622 and 1563 cm^{-1} (OC=C-CO); UV (EtOH) 277 (ε; 2500) and 206 nm (16800); MS m/e 244 (M^+, 55%), and 229 (M^+-CH_3, 100%).

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