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TRAPPING OF INTERMEDIATES WITH MOLECULAR OXYGEN IN CYANO ENONE-OLEFIN PHOTOCYCLOADDITION[1]

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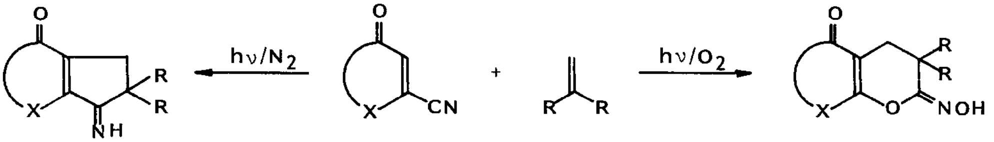
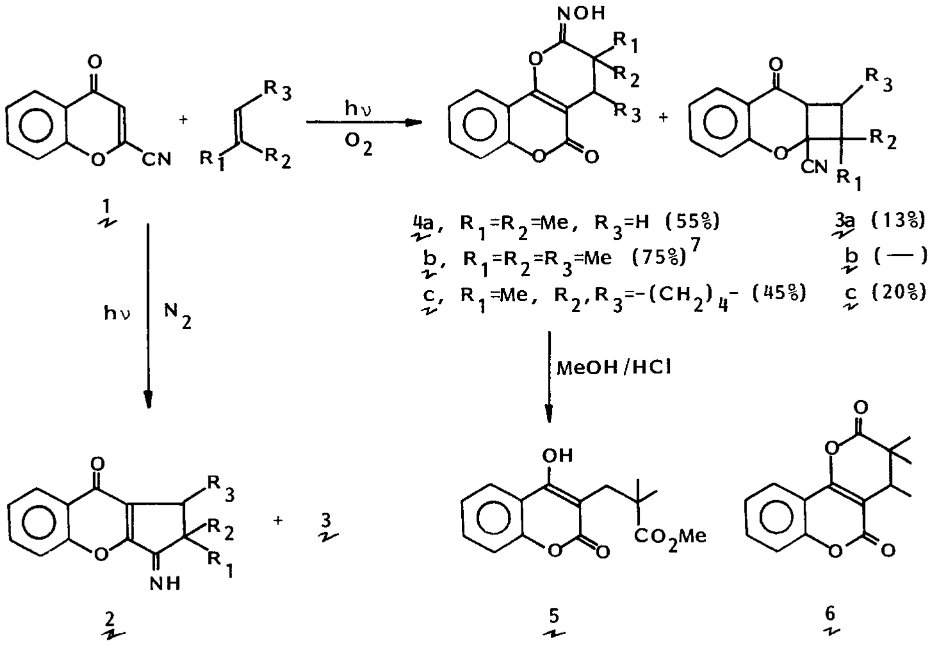
Summary: Oxygen trapping reactions of 1,3-biradical intermediates formed in the photoaddition of 2-cyanochromone or 6-cyano-1,3-dimethyluracil to olefins have been described.

Trapping reactions of biradicals or biradicaloid species with chemical agents have long been of interest to photochemists.[2] Trapping of the intermediates in photochemical reactions with molecular oxygen often leads to synthetically useful peroxide formation.[2,3] One of our interests in this area is to develop the oxygen trapping reaction as a synthetically useful photooxidation and as a method for probing the nature of the transient species being trapped. In our previous work we reported an anomalous photoaddition of cyano-substituted enone systems to olefins resulting in the formation [3 + 2] cycloadducts by interception of the intermediate 1,4-biradicals by the cyano groups.[4] We report herein a novel oxygen trapping reaction of 1,3-biradical intermediates in the photoadditions leading directly to oxygenated adducts via nitrile oxide intermediates as exemplified in Eq. 1.

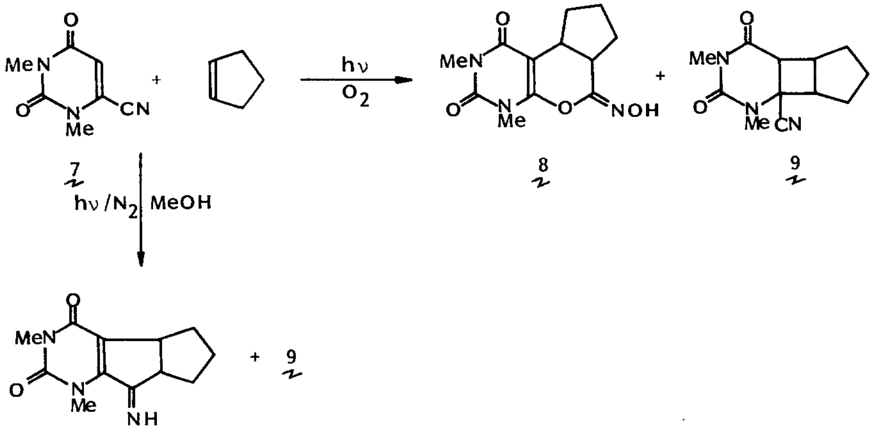


(1)

We previously noted that irradiation of 2-cyanochromone (1) in methanol in the presence of isobutene under a nitrogen atmosphere gives [3 + 2] cycloadduct 2a (81%) and [2 + 2] cycloadduct 3a (12%).[4d] However, the same irradiation (Pyrex-filtered light) under oxygen bubbling produced a different product 4a (55%) with the yield of cyclobutane 3a (13%) being unchanged. The structure of 4a was assigned on the basis of spectral data[5] and confirmed by converting it to 4-hydroxycoumarin 5 (90%) by acid treatment (MeOH-HCl).[6] Similar oxygen trapping reactions have been observed when 1 was irradiated in acetonitrile under oxygen bubbling in the presence of other 1,1-disubstituted olefins that give sterically hindered tertiary radicals, such as 2-methyl-2-butene or 1-methylcyclohexene (Eq. 2).[4] In contrast, irradiation of 1 with less substituted simple olefins or with electron-deficient olefins, where [2 + 2] cycloaddition is prevailing under nitrogen conditions, never produced the oxygenated adducts but gave only [2+2] cycloadducts under the aerobic conditions. These results clearly indicate that molecular



(2)

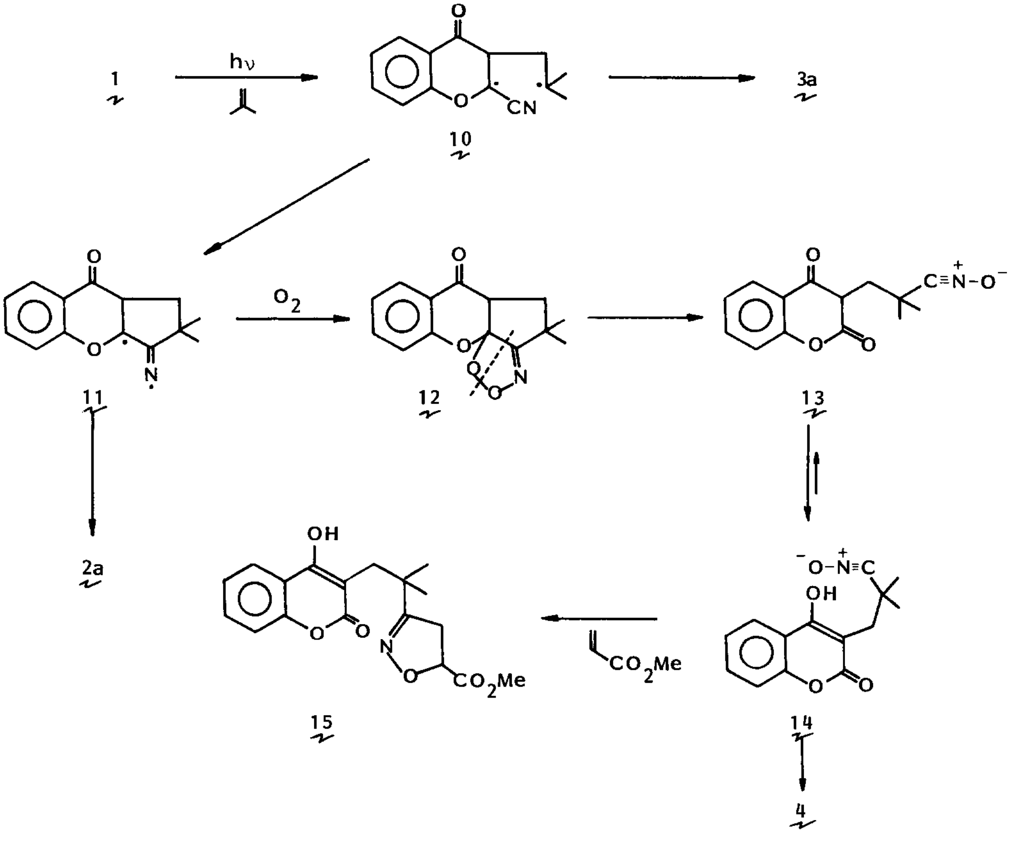


(3)

oxygen preferentially intercepts an intermediate leading to [3 + 2] cycloadducts. In support of this, a similar oxygen trapping reaction have been observed in the photoaddition of 6-cyano-1,3-dimethyluracil (7) to olefins where [3 + 2] cycloaddition was already demonstrated to occur preferentially in alcoholic solvents.[4] For example, irradiation of 7 and cyclopentene in acetonitrile under oxygen bubbling afforded 8[5] (45%) together with 9 (25%), as indicated in Eq. 3.

A reasonable mechanism accounting for the formation of these oxidation products is shown in Scheme 1. The five-membered iminyl biradical 11, a precursor of the [3 + 2] cycloadduct 2,[4] might be intercepted by ground-state triplet oxgyen giving rise to cyclic peroxide 12.[8] Subsequent ring cleavage of 12 would then furnish nitrile oxide 13 which after enolization to more stable 4-hydroxycoumarin isomer 14 undergoes internal addition to give 4. In fact, the intervention of nitrile oxide 14 was confirmed by following trapping experiment. Irradiation

Scheme 1



of 1 and isobutene in acetonitrile under oxygen conditions in the presence of excess methyl acrylate afforded isooxazoline 15[5] (12%) in addition to 3a (35%) and 4a (13%).

The finding that the yield of [2 + 2] cycloadduct 2 was not changed significantly by the presence of oxygen strongly suggests that 1,4-biradical 10 undergoes extremely rapid ring closure to 3, whereas 1,3-biradical 11 has a longer lifetime enough to allow reaction with molecular oxygen. The present work has demonstrated a novel type of oxidative photoaddition of cyano heterocycles to olefins and provides a useful route to 3-substituted 4-hydroxycoumarins.[9]

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5. All new compounds gave satisfactory elemental analyses and spectral data. Selected spectral data follow. 4a: mp 213-215 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 6 H), 2.66 (s, 2 H), 7.26-7.70 (m, 3 H), 7.80 (br, 1 H,OH), 7.90-8.04 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.6, 33.1, 33.2, 101.7, 113.8, 116.6, 122.5, 124.3, 132.1, 152.6, 153.9, 155.1, 162.0; mass spectrum m/e (relative intensity) 259 (M^+, 98), 244 (53), 199 (47), 176 (100). 4c: mp 230-235 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 1.20-2.25 (m, 8 H), 3.20 (t, 1 H, J = 6.0 Hz), 7.20-7.80 (m, 4 H), 8.10 (br, 1 H). 5: mp 97-99 °C, ^{13}C NMR ($CDCl_3$) δ 25.5, 32.8, 44.3, 53.0, 101.7, 115.8, 116.1, 123.5, 123.6, 131.5, 152.4, 162.2, 164.6, 183.6. 6: mp 163-165 °C, ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 3 H), 1.28 (d, 3 H, J = 7.1 Hz), 1.40 (s, 3 H), 3.30 (q, 1 H, J = 7.1 Hz), 7.20-7.98 (m, 4 H). 8: mp 193-194 °C; ^{1}H NMR ($CDCl_3$) δ 1.78-2.70 (m, 8 H), 3.30 (s, 3 H), 3.35 (s, 3 H), 9.00 (br, 1 H, OH). 15: viscous oil, ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 1.34 (s, 3 H), 2.98 (s, 2 H), 3.24-3.58 (m, 2 H), 3.78 (s, 3 H), 5.07 (dd, 1 H, J = 8.0, 8.0 Hz), 7.14-7.60 (m, 3 H), 7.86-7.98 (m, 1 H), 8.20 (br, 1 H, OH).
6. The ^{13}C NMR spectrum can readily discriminate the coumarin structure 4 from an alternative chromone structure. Carbonyl carbons of coumarins usually appear at $160 \sim 170$ ppm, whereas those of chromones are at $170 \sim 180$ ppm.
7. This compound could not be isolated in a pure form and was directly converted to 6 by treatment with aqueous acetone-HCl.
8. Attempts to isolate 12 at low-temperature irradiation have been unsuccessful so far.
9. For a review, see M. Darbarwer and V. Sundaramurthy, *Synthesis*, 337 (1982).

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