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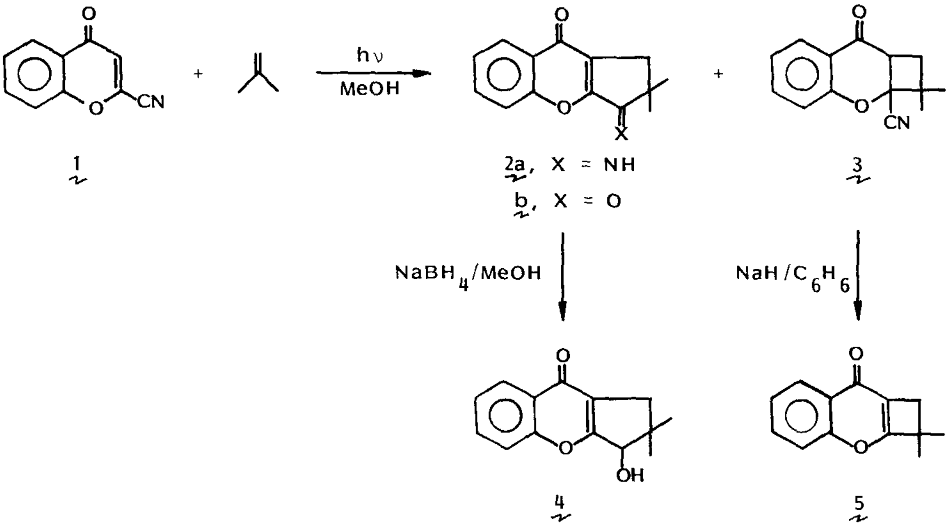
# PHOTOCHEMICAL [3 + 2] CYCLOADDITION OF 2-CYANOCHROMONE TO OLEFINS[1]

Isao Saito,* Koji Shimozono and Teruo Matsuura
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University,
Kyoto 606, Japan

*Summary: Irradiation of 2-cyanochromone in the presence of olefins gave rise to [3 + 2] cycloadducts together with the formation of normal [2 + 2] cycloadducts with the product ratio being temperature-dependent. The mechanism involving a vinyl nitrene intermediate was proposed.*

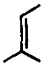
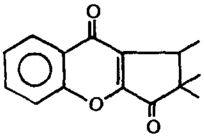
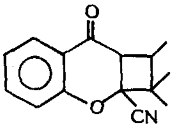
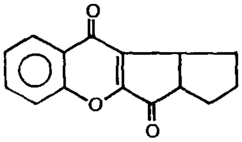
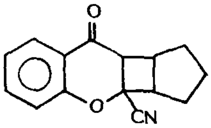
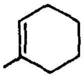
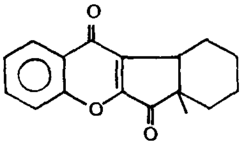
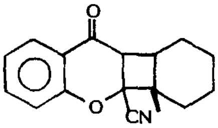
We have recently reported a novel type of temperature-dependent photoaddition of α,β-unsaturated nitriles to alkenes or alkynes resulting in 1,4-transfer of cyano group or the formation of [3 + 2] cycloadducts by interception of 1,4-biradical intermediates by the cyano groups.[2] These photochemical transformations provide an intriguing mechanistic probe on diverse mode of reactions of 1,4-biradical of the sort generally implicated in many photochemical cycloaddition reactions.[3] In order to explore the generality and the scope of this novel photoaddition, we have examined the photochemistry of 2-cyanochromone in the presence of olefins.[4] We report herein a temperature-dependent [3 + 2] photocyclization of 2-cyanochromone to olefins involving a vinyl nitrene intermediate.

Irradiation of 2-cyanochromone[5] (1, 1 mmol) in the presence of excess isobutene in methanol with Pyrex-filtered light under a nitrogen atomosphere followed by silica gel column chromatography produced the [3 + 2] cycloadduct 2b (81%) together with a minor amount of cyclobutane 3 (12%). The structures of 2b and 3 were assigned on the basis of their spectral data[6] and confirmed by converting them to 4 (85%) and 5 (55%), respectively, as indicated in Eq. 1. The ketone 2b formed from hydrolitically sensitive imine 2a[7] during workup. Irradiation of 1 with other olefins under similar conditions gave the corresponding [3 + 2] cycloadducts in competition with the formation of cyclobutanes (Table I). Acetophenone-sensitized irradiation of 1 with 1-methylcyclohexene produced 10 and 11 in approximately the same ratio as in the case of



(1)

Table I Products in the photoreaction of 1 with olefins[a]

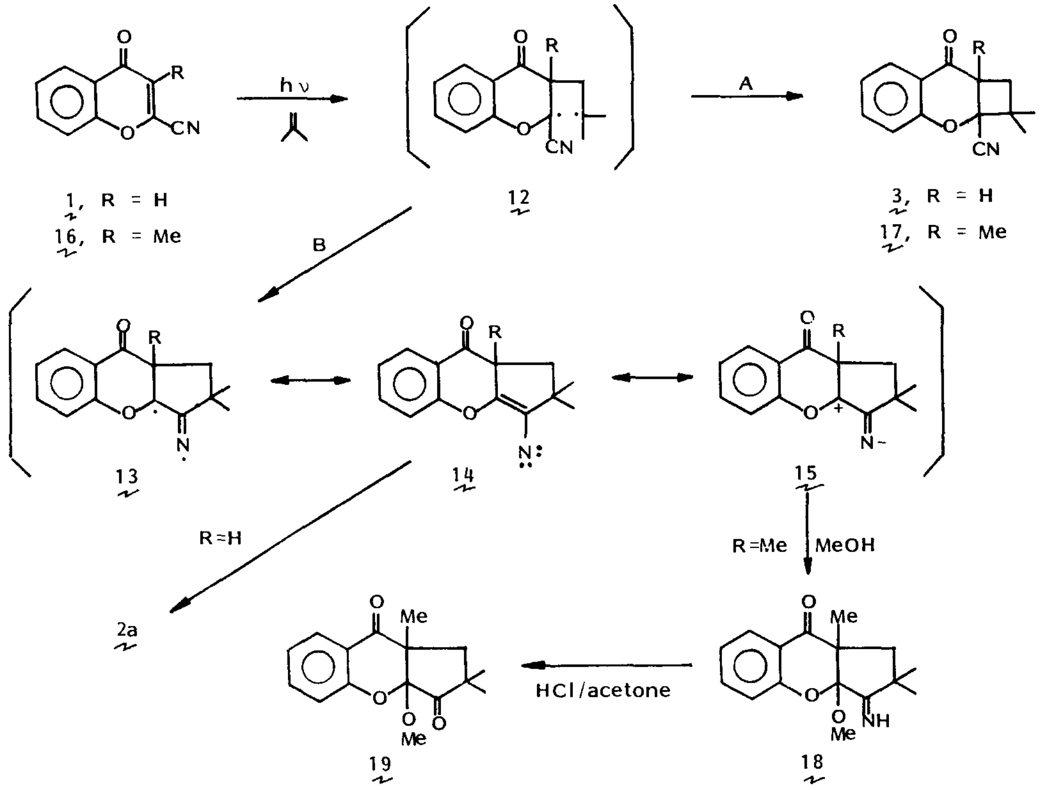
| Run | Olefin[b] | Solvent | Products (%)[c] | |
|---|---|---|---|---|
| 1 |  | $CH_3OH$ | <br>6 (33) | <br>7 (12) |
| 2 |  | $CH_3OH$ | <br>8 (20) | <br>9 (55) |
| 3 |  | $CH_3OH$ | <br>10 (52) | <br>11 (18) |
| 4 | | $CH_3CN$ | 10 (50) | 11 (15) |
| 5 | | $CH_3CN$-$t$-$C_4H_9SH$ (19:1) | 10 (55) | 11 (15) |
| 6 | | $CH_3OH$-EG[d] (3:1) | 10 (50) | 11 (10) |

[a] All irradiations were made with a 100 W high-pressure mercury lamp through Pyrex filter at ambient temperature; [1] = 10 mM. [b] 5 equiv to 1. [c] Isolated yield after silica gel column chromatography. [d] EG: ethylene glycol.

direct irradiation. Moreover, addition of piperylene considerably retarded the formation of 10 and 11.[8] These observations indicate that the lowest triplet state of 1 is responsible for the photoaddition with olefins. The most striking feature of this photoaddition is a dramatic temperature effect on the product ratio, paralleling that observed in the photoadditions of 6-cyanouracils[2a] and 3-cyanocyclohexenone[2d] to olefins. As shown in Table II, as the reaction temperature was raised, the yield of [3 + 2] cycloadduct 10 was increased at the expense of cyclobutane 11.

A reasonable mechanism accounting for these observations is shown in Scheme 1. This involves the formation of triplet 1,4-biradical 12 as a first step. Besides usual ring closure to cyclobutane 3 (path A) after spin inversion, 12 would undergo cyclization at the carbon of the cyano group to furnish five-membered-ring iminyl radical 13 (path B). The observed temperature effect is ascribable to the difference of the activation free energies associated with these two processes as proposed previously.[2] The iminyl radical 13 might undergo hydrogen reorganization leading to 2a either by hydrogen atom abstraction from hydrogen donors or by disproportionation. However, addition of *tert*-butyl mercaptan, a good hydrogen donor, to the reaction system never changed the product ratio (Run 5, Table I),[9] nor could we observe any disproportionation product.

Scheme 1



We therefore propose the vinyl nitrene intermediate **14** as the precursor of **2a**.[2d] Thus the iminyl radical **13**, when the unpaired spins become paired by spin inversion, can exist as a contributing resonance form **14**. Tautomerization of **14** would immediately give **2a**. This mechanism does not necessarily require hydrogen abstraction process.

The vinyl nitrene **14**, if formed, should be dipolar in nature, owing to the contribution of the resonance form **15**.[10] One would therefore expect the interception of the dipolar species with nucleophilic solvents, provided the tautomerization of the nitrene **14** to **2a** is prohibited by C-3 substitution.[11] In order to test this possibility, we have examined the photoreaction of 2-cyano-3-methylchromone (**16**) with isobutene. Irradiation of **16** (1 mmol) in the presence of isobutene in methanol at ambient temperature indeed produced the solvent-incorporated [3 + 2] cycloadduct **18**[6] (45%) together with cyclobutane **17**[6] (40%). Treatment of **18** with acetone containing HCl gave **19**[6] (55%). The formation of **18** strongly supports the intervention of the vinyl nitrene **14** in the photoaddition reaction.

Interestingly, this novel type of [3 + 2] photoaddition can occur in other cyano-substituted chromophores such as 2-cyanopyridine[2c] and 3-cyano-5,5-dimethyl-2-cyclohexenone.[2d] We are currently investigating other examples of this type of photoaddition.

Table II Temperature effect on the product ratio in the photoaddition of **1** to 1-methylcyclohexene[a]

| Temp (°C) | **10**/**11**[b] | Total yield (%)[c] |
|---|---|---|
| -78 | 0.05 | 67 |
| -20 | 0.65 | 70 |
| 0 | 1.75 | 68 |
| 18 | 3.4 | 70 |
| 64 | 7.0 | 55[d] |

[a] [**1**] = 10 mM; [1-methylcyclohexene] = 50 mM. [b] Determined by HPLC. [c] Isolated yield. [d] 2-Methoxychromone (10%) was obtained as by-product.

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2. (a) I. Saito, K. Shimozono and T. Matsuura, J. Am. Chem. Soc., **102**, 3948 (1980); (b) I. Saito, K. Shimozono, S. Miyazaki, T. Matsuura, T. Fukuyama and Y. Katsube, Tetrahedron Lett., **21**, 2317 (1980); (c) I. Saito, K. Kanehira, K. Shimozono and T. Matsuura, ibid., **21**, 2737 (1980); (d) I. Saito, K. Shimozono and T. Matsuura, J. Org. Chem. in press.
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6. All new compounds exhibited consistent spectral data ($^1$H and $^{13}$C NMR, UV, IR, MS) and elemental analyses.
7. The imine **2a** was isolated in >95% purity without chromatographic separation.
8. Linear Stern-Volmer plots were obtained for both compounds ($k_q\tau = 10 \pm 0.5\ M^{-1}$).
9. Formation of di-*tert*-butyl disulfide was never observed.
10. For a related system, see A. Hassner and F. W. Fowler, J. Am. Chem. Soc., **90**, 2869 (1968).
11. Formation of 1-azirine from nitrene **14** is precluded on steric grounds.

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