

INTERMOLECULAR PHOTOREACTION OF BENZENECARBOTHIOAMIDE WITH β -IONONE^{#,1}

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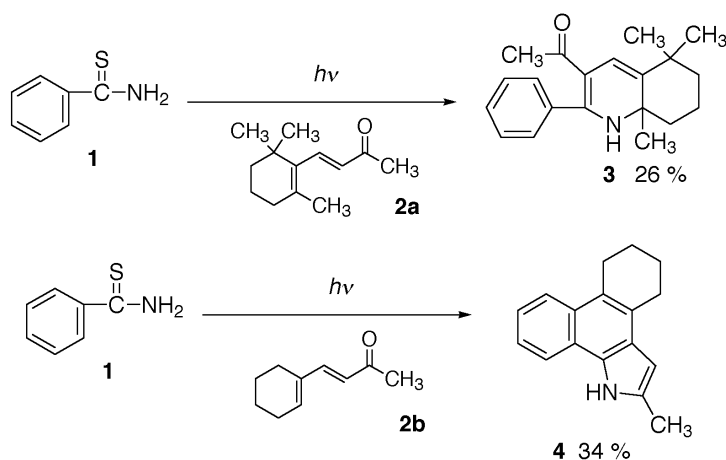
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Abstract - Irradiation of benzenecarbothioamide with β -ionone in benzene gives 1,5,6,7,8,8a-hexahydroquinoline derivative in moderate yield.

In a previous paper, we reported that arenecarbothioamides undergo the Paterno-Büchi type reaction with diene conjugated carbonyl compounds to give 2-arylpyridines, 2,6-diarylpiperidines, and benzofused pyridines.² As an extension of this photoreaction, irradiation of arenecarbothioamide with β -ionone, diene conjugated carbonyl compound, was performed. Although intramolecular photoreaction of β -ionone has been extensively studied,³ few reports have dealt with the intermolecular photoreaction of β -ionone.

In the photoreaction of benzenecarbothioamide (**1**) with β -ionone (**2a**) in benzene, 1,5,6,7,8,8a-hexahydroquinoline derivative (**3**) was obtained in 26 % yield as sole product.⁴ Furthermore, photoreaction of **1** with 4-cyclohex-1-enylbut-3-en-2-one (**2b**), β -ionone analog (no possessing



[#] This paper is dedicated to Emeritus Professor Yuichi Kanaoka, Hokkaido University, on the occasion of the 75th birthday.

three methyl substituents), was performed under similar conditions. An unexpected tetracyclic indole derivative (**4**) was obtained in 34 % yield.⁵

Structure of 1,5,6,7,8,8a-hexahydroquinoline derivative (**3**) was assigned on the basis of the spectral data and elemental analysis. MS spectrum of **3** showed the molecular ion peak at M^+ 295, which suggested a molecule generated by loss of hydrogen sulfide from the adduct of **1** and **2a**. In the IR spectrum of **3**, the absorptions of an NH and a carbonyl group appeared at 3240 and 1680 cm^{-1} , respectively. Further, $^1\text{H-NMR}$, $^1\text{H-}^1\text{H COSY}$, $^{13}\text{C-NMR}$, DEPT, and $^1\text{H-}^{13}\text{C COSY}$ experiments suggested the presence of the partial structures as illustrated in Figure 1. The entire structure of **3** was determined by the analysis of the HMBC (^1H detected heteronuclear multiple bond connectivity) correlation.

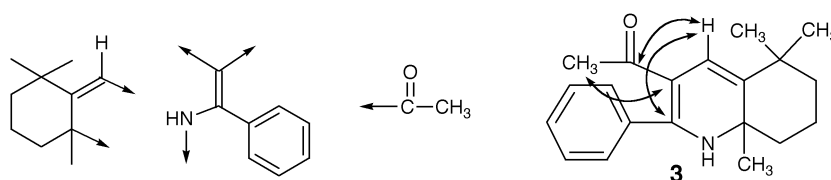
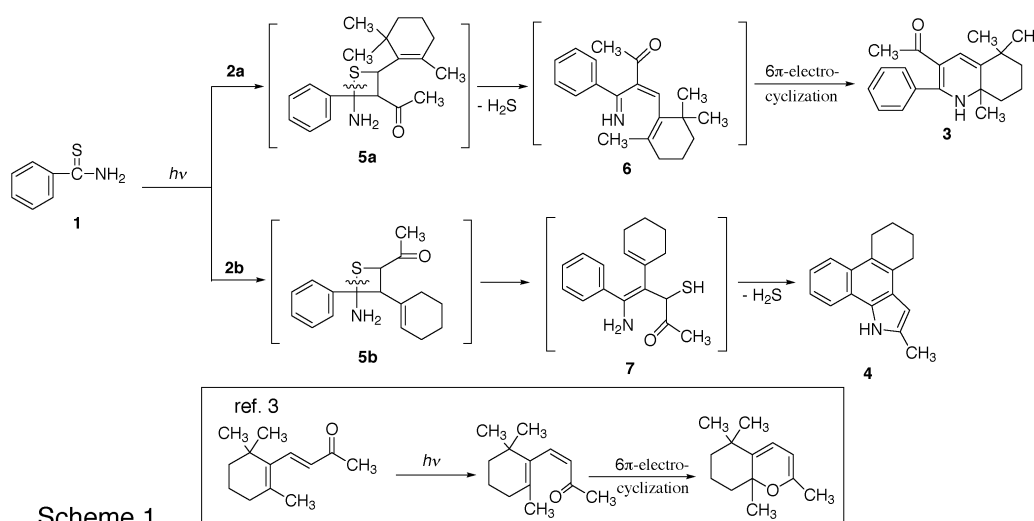


Figure 1. Estimated partial structures and HMBC correlation of **3**

As shown in Scheme 1, the reaction (**1** + **2a** → **3**) seems to proceed in several steps involving initial thietane (**5a**) formation between the thiocarbonyl and α,β -double bond of **2a**, leading to the key intermediate penta-2,4-dienylideneamine derivative (**6**), which subsequently cyclizes to the 1,5,6,7,8,8a-hexahydroquinoline derivative (**3**) by 6π -electrocyclization. Such a 6π -electrocyclization reaction was already observed in the intramolecular photocyclization of β -ionone (Scheme 1).³



Scheme 1

In the case of 4-cyclohex-1-enylbut-3-en-2-one (**2b**), the reaction seems to proceed *via* phenylbutadiene intermediate (**7**)⁶ which arises from the initially formed thietane (**5b**), leading to

tetracyclic indole derivative (**4**).

As for the formation of **3**, the C-S bond formation in the first step occurred at β -position of carbonyl group in **2a**, whereas for **4** the formation occurred at α -position in **2b** (no possessing three methyl substituents). Further, the fission of the resulting thietane ring was affected by the mode of thietane formation (head to head or head to tail orientation), leading to conjugated diene intermediates of two types (**6** and **7**). Thus, the difference of a reacting site in α,β -double bond seems to reflect the steric and/or electrical requirements of α,β -unsaturated carbonyl compounds. However, no clear evidence is available at this time to be capable of an explanation for the difference.

This result shows an example of the remarkable difference in the photochemical behavior between β -ionone (**2a**) and 4-cyclohex-1-enylbut-3-en-2-one (**2b**). In addition, this reaction seems to be first example of photochemical 6π -electrocyclization reaction of aliphatic diene conjugated imine such as penta-2,4-dienylideneamine derivative (**6**).⁷ A detailed study on further synthetic application and the reaction pathway of this reaction is in progress.

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4. Irradiation of thioamide (**1**) with β -ionone (**2a**).
A mixture of **1** (0.69 g, 5 mmol) and **2a** (2.88 g, 15 mmol) in benzene (200 mL) was irradiated for 20 h with a 1 kW high pressure mercury lamp through a Pyrex filter under N_2 . After removal of the solvent *in vacuo*, the residue was chromatographed over a silica gel column (hexane–ethyl acetate, 3 : 1; v/v). Photoproduct (**3**) was obtained in 26 % yield as sole product.
1-(5,5,8a-Trimethyl-2-phenyl-1,5,6,7,8,8a-hexahydroquinolin-3-yl)ethanone (**3**): colorless needles, mp 210-212 °C; IR (Nujol) 3240, 1680 cm^{-1} ; 1H -NMR ($CDCl_3$) δ 1.21 (s, 3H), 1.28 (s,

- 3H), 1.38 (s, 3H), 1.4-1.9 (6H, m), 1.67 (s, 3H), 4.29 (br s, 1H), 6.75 (s, 1H), 7.3-7.58 (m, 5H); ^{13}C -NMR (CDCl_3) δ 18.7 (t), 27.4 (q), 29.3 (q), 31.5 (q), 32.1 (q), 34.7 (s), 39.7 (t), 40.8 (t), 54.7(s), 111.7 (s), 117.2 (d), 128.6 (dx2), 129.4 (dx2), 130.1 (d), 136.0 (s), 137.4 (s). 152.3 (s), 194.5 (s); MS m/z 295 (M^+); *Anal.* Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.37; H, 8.64; N, 4.70.
5. 2-Methyl-4,5,6,7-tetrahydro-1*H*-dibenzo[*e,g*]indole (**4**): colorless oil; IR (Nujol) 3300 cm^{-1} ; ^1H -NMR (CDCl_3) δ 1.9-2.0 (m, 4H), 2.53 (s, 3H), 3.00 (t, 2H, $J=5.9\text{ Hz}$), 3.11 (t, 2H, $J=5.9\text{ Hz}$), 6.31 (s, 1H), 7.4-7.5 (m, 2H), 7.9-8.0 (m, 2H), 8.54 (br s, 1H); ^{13}C -NMR (CDCl_3) δ 13.8 (q), 22.7 (t), 23.6 (t), 25.8 (t), 27.3 (t), 100.1 (d), 119.2 (d), 120.5 (s), 122.9 (s), 123.1 (d), 124.0 (d), 124.1 (d), 125.1 (s), 128.3 (s). 1129.4 (s), 132.3 (s); MS m/z 235 (M^+); HRMS Calcd for $\text{C}_{17}\text{H}_{17}\text{N}$: 235.1361. Found: 235.1363.
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7. For study on the photocyclization of aromatic conjugated imine, see: A. Padwa, *Chem. Rev.*, 1977, **77**, 37 and references cited therein.