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Norrish Type II Photoreaction of 2,3-Dihydro-2,3-methano-1,4-naphthoquinones. A Novel Photorearrangement of α,β-Cyclopropyl Ketone to β,γ-Unsaturated Ketone

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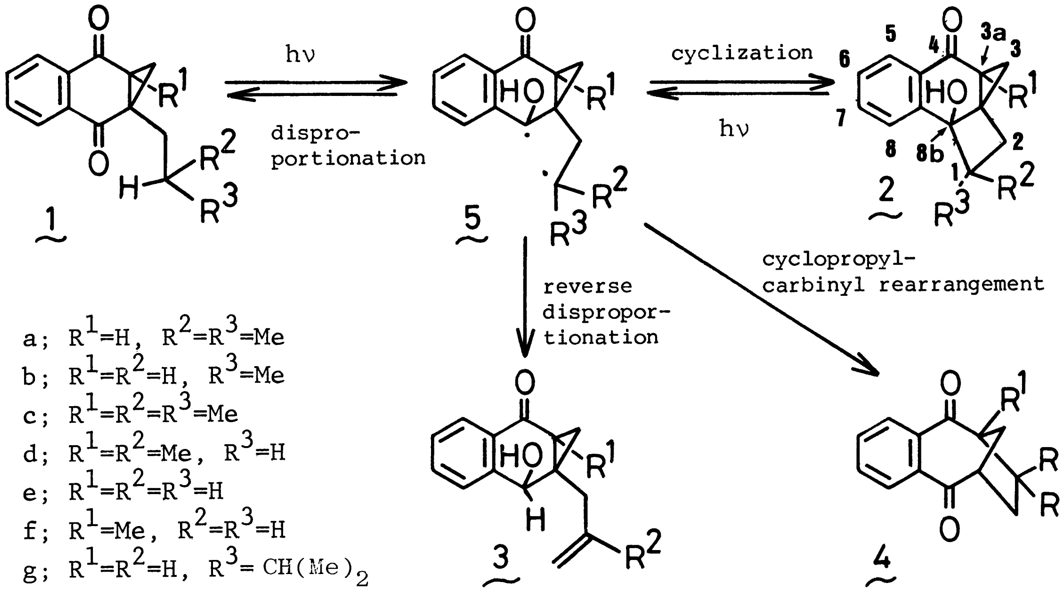
Irradiation of the title compounds gave cyclobutanols as the initial type II cyclization products, which were further photochemically rearranged to tricyclic β,γ-unsaturated ketones presumably via homolytic fission of cyclopropane ring followed by 1,2-alkyl migration.

Recently, we have reported that Norrish type II biradicals **5a-d** are formed on photoexcitation of the corresponding cyclobutanols **2a-d** as well as the normal type II pathway from methanonaphthoquinones **1a-d**.[1] The biradicals **5a-d** collapse to unsaturated keto alcohols **3a-d** by reverse disproportionation and/or to tricyclic diketones **4c** and **4d** by cyclopropylcarbinyl rearrangement (Scheme 1).[1] The photochemical generation of type II biradical from the corresponding cyclobutanol is quite rare. In continuation with these studies, we have now found a novel photorearrangement of cyclobutanols **2e** and **2f** to β,γ-unsaturated ketones **6** and **7**.

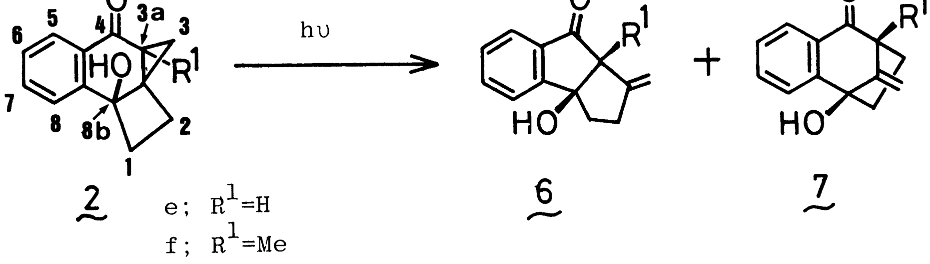
Irradiation of a solution of **1e** in benzene/tert-butanol (1:1) for 45 min followed by silica gel chromatography afforded cyclobutanol **2e** (60%, mp 107-108 °C) and two rearranged products, **6e** (17%, mp 78-79 °C) and **7e** (5%, mp 109-110 °C). Separate irradiation of **2e** for 3 h resulted in the formation of **6e** (51%) and **7e** (20%), indicating that the rearranged products **6e** and **7e** were the secondary photoproducts derived from **2e**. Structure assignments for these products were made on the basis of characteristic spectral data and elemental analyses. The IR spectrum of **6e** showed characteristic bands at 3400 cm^{-1} (hydroxy) and 1705 cm^{-1} (conjugated five-membered ketone); the ^1H-NMR ($CDCl_3$) spectrum indicated



a; R^1=H, R^2=R^3=Me
b; R^1=R^2=H, R^3=Me
c; R^1=R^2=R^3=Me
d; R^1=R^2=Me, R^3=H
e; R^1=R^2=R^3=H
f; R^1=Me, R^2=R^3=H
g; R^1=R^2=H, R^3= CH(Me)$_2$

Scheme 1.

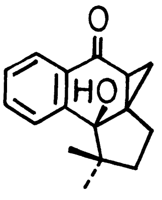
the presence of an allylic methine proton at δ 3.29 (dd, J=2 and 4 Hz, 1H) and exo-methylene protons at δ 4.95 (d, J=2 Hz, 1 H) and 5.15 (d, J=4 Hz, 1 H); ^{13}C-NMR (CDCl$_3$) revealed the presence of ketone carbonyl at δ 202.5, exo-methylene methylene carbon at δ 109.7 (t), hydroxybenzyl carbon at δ 86.1 (s), allylic methine carbon at δ 65.5 (d), and two methylene carbons at δ 39.2 (t) and 32.9 (t). The IR spectrum of **7e** showed characteristic bands at 3450 cm^{-1} (hydroxy) and 1685 cm^{-1} (conjugated ketone); the ^{1}H-NMR (CDCl$_3$) spectrum indicated the presence of an allylic methine proton at δ 3.63 (dd, J=1 and 7 Hz, 1H) and exo-methylene protons at δ 4.89 (d, J=1 Hz, 1H) and 5.00 (s, 1 H); ^{13}C-NMR (CDCl$_3$) revealed the presence of ketone carbonyl at δ 198.4, exo-methylene carbon at 101.5 (t), hydroxybenzyl carbon at δ 79.8 (s), allylic methine carbon at δ 56.0 (t), and two methylene carbons at δ 37.6 (t) and 22.6 (t). Similar irradiation of **2f** (mp 133.5-134 °C) gave **6f** (33%, mp 107-108 °C) and **7f** (40%, mp 114-116 °C).[2)] The tricyclic β,γ-unsaturated ketones **6f** and **7f** were again the secondary



photoproducts derived from **2f**.

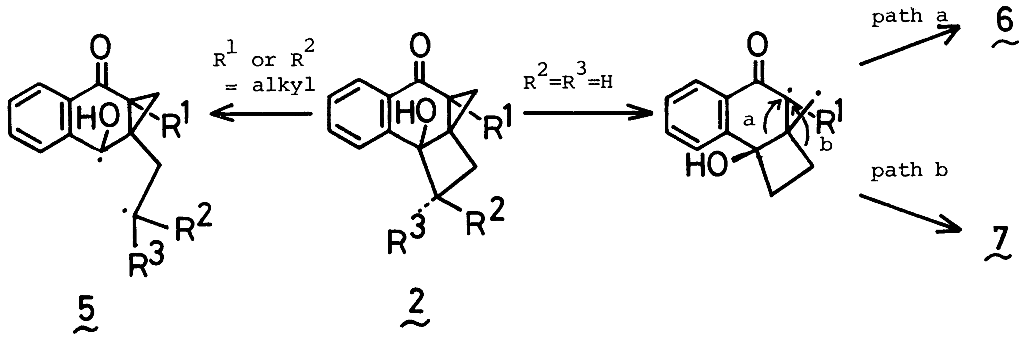
In contrast to the efficient cleavage of C(1)-C(8b) bond in photolysis of **2a-d**, photoexcitation of **2e** and **2f** gave only rearranged products **6e** and **7e** and **6f** and **7f**, respectively. If C(1)-C(8b) bond in **2e** or **2f** were cleaved, the starting diketone **1e** or **1f** should be formed in benzene via the disproportionation of type II biradical **5e** or **5f**. But we could not detect even traces of **1e** nor **1f** in the crude photolysate of **2e** and **2f** in benzene. Formation of **6** and **7** can be reasonably explained in terms of initial C(3)-C(3a) bond fission followed by migration of hydroxybenzyl group and methylene group, respectively. The photoisomerization of conjugated cyclopropyl ketones to enones has been extensively studied and now it is well understood to involve homolytic fission of cyclopropyl ring followed by 1,2-hydrogen shift.[3] However, to the best of our knowledge, no report seems to appear on the migration of alkyl group in the photochemical reaction of conjugated cyclopropyl ketones, although numerous examples of 1,2-alkyl migration have been reported in photochemistry of α,β-epoxy ketones.[4]

On the other hand, irradiation of a benzene solution of **1g** for up to 68% conversion afforded cyclobutanols **2g** (R^1=R^2=H, R^3=$CHMe_2$) (16%, mp 120-121 °C) and **2g'** (R^1=R^3=H, R^2=$CHMe_2$) (18%, mp 135-136 °C) and cyclopentanol[5] **8g** (52%, mp 131-132 °C). Irradiation of **2g** in benzene gave **1g** and **2g'**, indicating the preferential cleavage of the C(1)-C(8b) bond over the C(3)-C(3a) bond in **2g**. The cyclopentanol **8g** was quite stable under the irradiation conditions and did not afford any rearranged products nor the starting diketone **1g**. The photochemical stability of the cyclopentanol **8g** is noteworthy in the sense that the strained structure composed of fused four-membered ring and three-membered ring is necessary for the unprecedented photo-rearrangement of α,β-cyclopropyl ketones to β,γ-unsaturated ketone.



8g

In conclusion, the photochemistry of the cyclobutanol **2** can be summarized as follows; photorearrangements to β,γ-unsaturated ketones **6** and **7** predominantly occur in the cyclobutanols **2e** and **2f** having no substituent at 1-position, whereas C(1)-C(8b) bond cleavage to give type II biradical is much favored in 1-mono alkyl substituted or 1,1-dialkyl substituted cyclobutanols (Scheme 2). In either case, unique photoreactivities of **2** are apparently derived from their strained ring structure.



Scheme 2.

References

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5) The cyclopentanol **8g** was an intramolecular δ-hydrogen abstraction product, P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, J. Am. Chem. Soc., 94, 7500 (1972). **8g**; IR (KBr) 3420 (hydroxy) and 1660 (carbonyl); ^{1}H-NMR ($CDCl_3$) 0.54 (s, Me), 1.14(s, Me), 1.01 and 1.33 (dd, J=2 and 5 Hz, 2H), 1.7-2.4(m, 4H), and 7.2-8.0(m, 4H); ^{13}C-NMR ($CDCl_3$) δ 196.8 (s), 81.3 (s), 48.6 (s), 37.0(d), 36.1(t), 34.6(s), 30.4(t), 25.5(q), 21.2(q), and 16.2(t), in addition to 6 sp^2 carbons.

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