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https://doi.org/10.15017/6586

出版情報：九州大学機能物質科学研究所報告. 4 (2), pp.197-200, 1991-03-30. 九州大学機能物質科学研究所
バージョン：
権利関係：

Rep. Inst. Adv. Mat.
Study, Vol. 4 No. 2
pp. 197~200 (1990)

Photoaddition Reaction of 5,5-Dimethylcyclohexane-1,3-dione with Quadricyclane.

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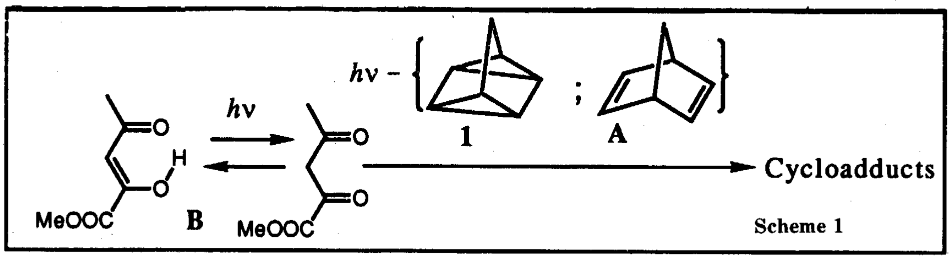
Abstract: The photoproducts identified from dimedone and quadricyclane were not cycloadducts, but the substituted nortricyclane derivatives, being contrasting to those from methyl 2,4-dioxopentanoate and quadricyclane.

Although the photochemical behavior of norbornadiene (**A**) and quadricyclane (**1**) is regarded to be important in both theoretical and practical view points; there are a number of studies on the photochemical interconversion of **1** and **A**, but so far vary few on the photaddition reaction of **1** or **A** as a cycloaddend.[1-4] Recently, we have carried out a photochemical reaction of **A** and **1** with an enolized β-diketone, methyl 2,4-dioxopentanoate (**B**), which revealed different product distributions due to different mechanisms involved.[5]



Scheme 1

Among the photoproducts obtained from **1** and **B**, there were products derived from the ketonic tautomer of **B** and **1**. Therefore, it is worth investigating a photoreaction of **1** with other β-diketones having more ketonic contribution in the excited state. This in mind, we have investigated the photoaddition reaction of 5,5-dimethylcyclocexane-1,3-dione (**2**), dimedone, with **1** as described herein.

The UV-light irradiation of **2** with excess **1** in ethyl acetate gave a complex mixture, from which **3** to **6** were separated by means of the column chromatography and HPLC.

The ^{1}H NMR of the major product, **3** [a colorless oil, 13%, ^{1}H NMR δ=0.91 (3H, s), 1.12 (3H, m), 1.20 (3H, s), 1.25 (2H, m), 1,28 (1H, t, J=5.5 Hz), 1.78 (1H, dm, J=16.0 Hz), 2.78 (dm, J=16.0 Hz), and 9.24 (1H, s, OOH). ^{13}C NMR δ=11.2, 11.5, 11.8, 26.0, 30.1, 30.7, 31.2, 32.3, 34.6, 50.9, 52.1, 99.2, 203.7, and 204.0. MS m/z, 248 (5), 247 (13), 205 (10), 153 (13), 143 (14), 121 (23), 93 (100), and

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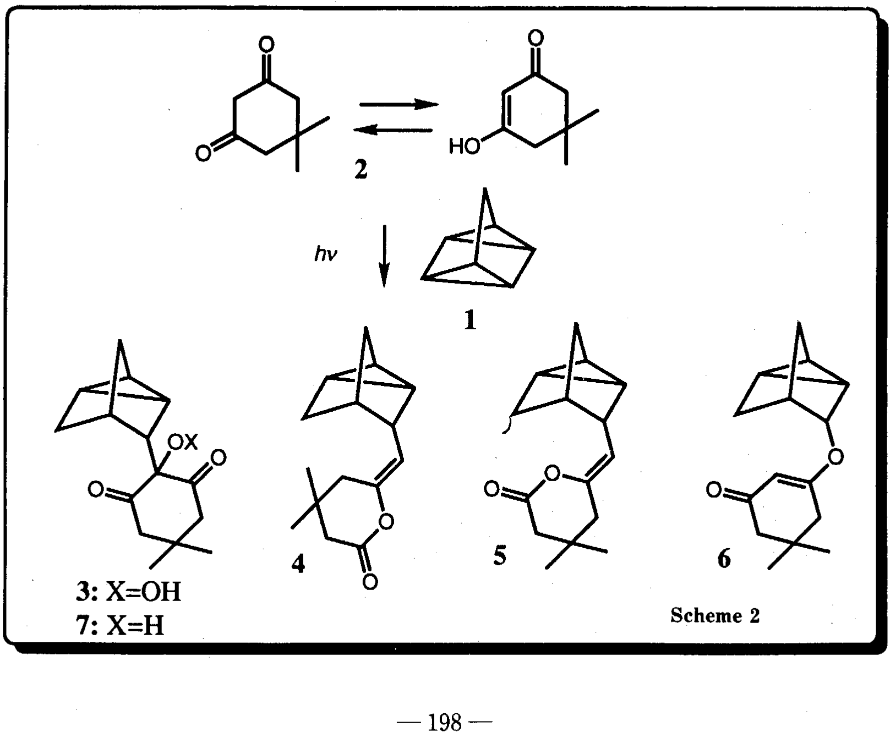
Received December 4, 1990

33 (57)], revealed two methyl singlets, as $\delta=0.91$ and 1.20, and a sharp singlet at $\delta=9.23$, which disappeared on addition of deuterium oxide showing to be a hydroperoxy group, but no olefinic proton signals. Its ^{13}C NMR spectrum showed three sp^3-carbon signals being ascribable to the carbons of cyclopropane ring, $\delta=11.2$, 11.5, and 11.8, in addition to two carbonyl carbon signals, $\delta=203.7$ and 204.0. The sodium sulfite reduction of **3** gav a hydroxy diketone (**7** [colorless crystals, mp 161-162°C. ^{1}H NMR $\delta=0.89$ (3H, s), 0.91 (1H, t, $J=5.0$ Hz), 1.07 (1H, dm, $J=10.3$ Hz), 1.14 (1H, t, $J=5.0$ Hz), 1.23 (3H, s), 1.27 (3H, m), 1.5-1.9 (1H, br m), 1.79 (1H, br s), 1.95 (1H, dm, $J=10.3$ Hz), 2.02 (1H, br s), 2.49 (2H, dm, $J=14.0$ Hz), 2.88 (1H, d, $J=14.0$ Hz), and 3.04 (1H, dm, $J=14.0$ Hz). MS *m/z*, 249 (9), 248 (530, 182 (18), 165 (26), 121 (30), 99 (14), 93 (100), 83 (47), 77 (24), and 41 (14). IR ν: 3500, 2950, 1740, 1460, 1420, 1350, 1300, 1180, 1140, 1080 cm^{-1}]). Therefore, **3** must be a nortricyclane, 2-(2-nortricyclyl)-2-hydroperoxycyclohexane-1,3-dione. The oxygenation might be taken place during the chromatographic work-up; no precursor diketone (**C**) could be detected and might be extremely unstable under those conditions.

The next two products, **4** [colorless crystals, mp 99-100°C, 7%. ^{1}H NMR $\delta=1.02$ (3H, s), 1.03 (3H, s), 1.0-1.5 (7H, m), 1.79 (1H, br s), 2.22 (2H, s), 2.41 (2H, s), 2.68 (1H, dm, $J=8.8$ Hz), and 4.47 (1H, dd, $J=8.8$, 1.0 Hz). ^{13}C NMR $\delta=9.6$, 11.2, 15.7, 27.7, 27.8, 29.3, 29.8, 33.9, 34.9, 39.7, 41.3, 44.5, 111.2, 146.0, and 168.4. MS *m/z*, 223 (17), 232 (100), 217 (8), 204 (17), 190 (10), 148 (26), 134 (10), 93 (7), 92 (8), and 83 (63). IR ν: 3050, 2950, 2870, 1765, 1745, 1710, 1370, 1240, 1160, 1110, and 1045, cm^{-1}] and **5** [colorless oil, 1%. ^{1}H NMR $\delta=0.8$-1.3 (6H, m), 1.09 (6H, s), 1.41 (1H, dm, $J=10.0$ Hz), 1.72 (1H, br s), 1.77 (1H, dm, $J=7.6$ Hz), 1,96 (1H, br s), 1.99 (1H, br s), 2.40 (2H, s), and 4.88 (1H, br s). ^{13}C NMR $\delta=9.6$, 11.5, 14.6, 28.3, 29.1, 31.0, 32.8, 32.9, 33.9, 42.2, 45.5, 111.4, 150.6, and 169.4. MS *m/z*, 233 (14), 232 (80), 217 (22), 190 (52), 149 (28), 109 (47), 93 (100), 91 (58), 83 (89), and 77 (45). IR ν: 2950, 1770, 1690, 1450, 1360, 1240, 1210, 1160, 1115, and 990 cm^{-1}], showed very similar $\nu_{C=O}$ in their IR spectra. The ^{1}H NMR spectrum of **4** showed an overlapped two methyl



2

1

3: X=OH
7: X=H

4

5

6

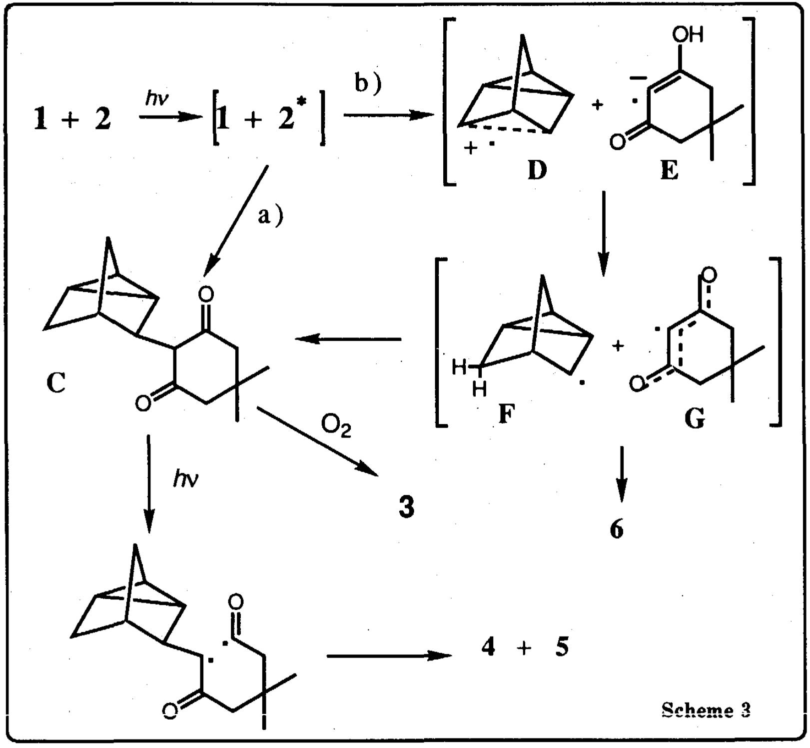
Scheme 2

singlet siglal, two sets of singlet methylene signals, and a proton signal at $\delta=4.47$, and that of **5** also revealed these features, but its olefinic proton signal appeared at $\delta=4.88$. Thus, these compounds must be an E/Z-isomeric pair of enol lactones, and **4** with a high-field signal should be Z-, and **5** with a low-field signal, E-isomer.

The remaining product, **6** [a colorless oil, 1%. ^{1}H NMR $\delta=1.07$ (3H, s), 1.2-1.4 (5H, m), 1.46 (1H, dm, $J=10.6$ Hz), 1.79 (dm, $J=9.9$ Hz), 2.14 (1H, br s), 2.22 (2H, s), 2.26 (2H, br s), 4.19 (1H, br s), and 5.47 (1H, br s). ^{13}C NMR $\delta=11.5$, 13.1, 28.3, 28.4, 30.2, 30.4, 32.5, 33.0, 43.2, 50.7, 83.4, 102.4, 175.9, and 199.6. MS m/z, 233 (6), 232 (30), 167 (42), 93 (100), 91 (29), and 77 (25). IR v: 2950, 1660, 1610, 1380, 1340, 1310, 1210, 1160, and 1140 cm^{-1}], was nortricyclyl enol ether of dimedone.

A different behavior in the photoaddition reactions with different β-diketones was interesting; with our hands, only norbornyl derivatives could be identified from **1** and **B**, but, in a sharp contrast, only the nortricyclyl derivatives were characterized from **1**and **2**. Although these features are subject of detailed studies in future, it is interesting that the different substrates caused different types of product formation. In other words, no cycloadduct could have been isolated from **1** and **2**.

For a probable mechanism, the following scheme should be provided.



Scheme 3

Namely, since oxygen was carefully removed from the reaction system, the hydroperoxide **3** shold be formed during the work up in a dark process. The immediate precursor (**C**) of **3** is also appropriate as a common precursor of enol-δ-lactones (**4** and **5**).[6] In a formal sense, **C** could be formed via either a) a photochemical ene reaction or b) a recombination of the two radical species derived from the addends, **1** and **2**. Between these equally probable pathways, the electron transfer process is favored by the similar occurrence of the process in the reaction of **1** and **B**, where a chelated hydrogen of the radical anion species was reluctant to transfer to the counter-radical cation to result in a recombined diradical and to further cycloadducts. In the present case, a hydride shift from the radical anion **E** to radical cation **D** could be facile to form neutral radicals (**F** and **G**), which gave **6** and **C**. Further, **C** caused a cleavage of β-diketone part to a diradical, whose recombination gave *E*/*Z*-pair of enol-δ-lactones, **4** and **5**. Such enol lactone formation via α-cleavage was a characteristic feature of non-enolizable β-diketones.[6] Certainly, the enol contents of monoalkyl derivatives of dimedone are known to be negligible.[7] A responsibility of **C** in the formation of **4** and **5** will be a subject of forthcoming paper.[8]

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8) Conversion of **C** into **4** or **5** is speculative. We admit that the non-enolizable 1,3-diketone can not be excited so efficiently through a Pyrex-glass filtered high-pressure mercury lamp in ethyl acetate. This will be verfied when photoirradiation of the indenpendently prepared **C** is carried out.