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# PHOTOISOMERIZATION OF PHTHALOYL SYSTEM TO ALKYLIDENE PHTHALIDES

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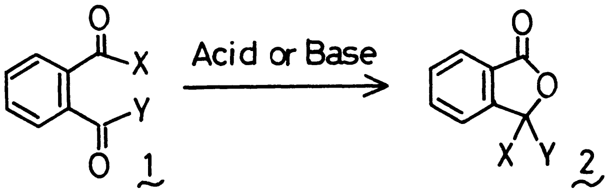
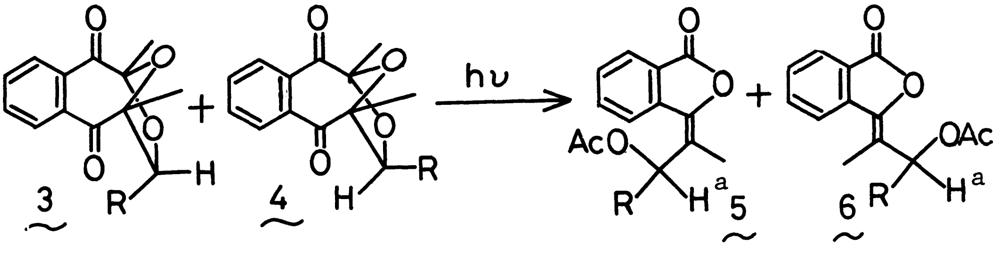
Irradiation of a benzene solution of bicyclic diketones 3 and/or 4 gave alkylidene phthalides 5 and 6 in good yields. Structural effects on the photoisomerization were discussed.

Acid- or base-catalyzed isomerization of phthaloyl system 1 to *as*-phthalyl system 2 has been long known1), but a photochemical counterpart has not been reported so far. In the course of our studies on the photochemical reactions of epoxynaphthoquinones, we found that bicyclic diketones 3a-h and 4a-h, upon irradiation, readily underwent photoisomerization, giving alkylidene phthalides 5a-h and 6a-h in good yields. The present work is concerned with investigation on the photoisomerization of a series of phthaloyl compounds 3a-h and 4a-h.



Irradiation of a benzene solution (0.02M) of 3a-h and/or 4a-h2) with a high-pressure Hg lamp for 30 hours gave a mixture of alkylidene phthalides 5a-h and 6a-h. These phthalides were separated by chromatography on silica gel and their structural assignments



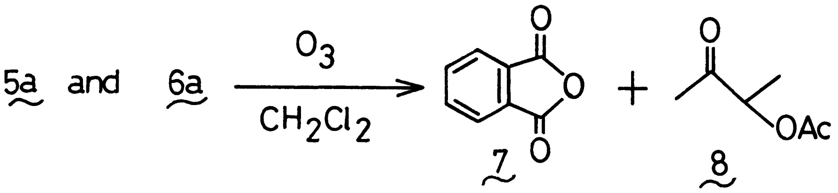
a, R=Me
b, R=Et
c, R=Pr
d, R=i-Pr
e, R=p-MeO-$C_6H_4$
f, R=p-Me-$C_6H_4$
g, R=Ph
h, R=p-Cl-$C_6H_4$

Table I. Photoisomerization of 3 and/or 4 to 5 and 6.

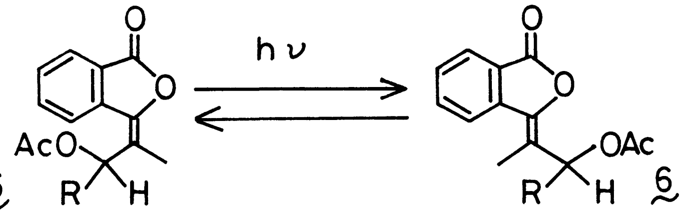
| Reactant | | | Total Yield (%)[a] | 5/6[b] | Products (mp, °C) | |
|---|---|---|---|---|---|---|
| 3a | + | 4a | 80 | 1.1 | 5a (84.5) | 6a (88) |
| 3b | + | 4b | 75 | 1.2 | 5b (88) | 6b (90) |
| 3c | + | 4c | 73 | 1.3 | 5c (105) | 6c (oil) |
| 3d | + | 4d | 66 | 1.0 | 5d (oil) | 6d (126) |
| 3e | + | 4e | 92 | 1.2 | 5e (119) | 6e (124) |
| 3f | + | 4f | 90 | 0.9 | 5f (127) | 6f (144) |
| 3g | + | 4g | 86 | 0.9 | 5g (135) | 6g (130) |
| 3h | + | 4h | 86 | 1.0 | 5h (153) | 6h (148) |

a), Isolated yields. b), Determined by HPLC.

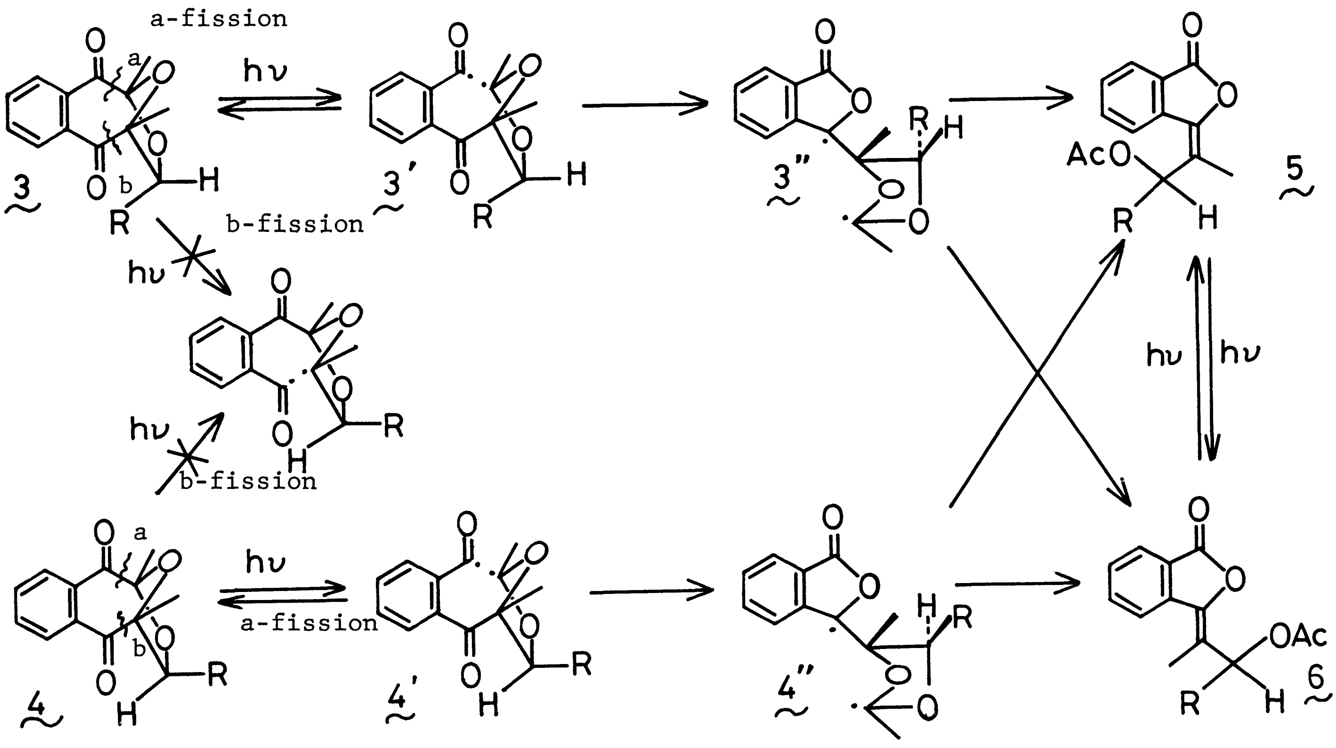
were made on the basis of their spectra ($^1$H NMR, IR, and mass) and elemental analyses.[3)] Further, the alkylidene phthalide structure of 5a and 6a was evidenced by the ozonolysis of 5a and 6a, which gave phthalic anhydride 7 and 3-acetoxy-2-butanone (8). The allylic methine protons of 5a-h (H$^a$; designated in eq. 1) were deshielded relative to those of 6a-h without exception, because of the proximity of H$^a$ to the benzene ring in 5a-h. The results are summarized in Table I.



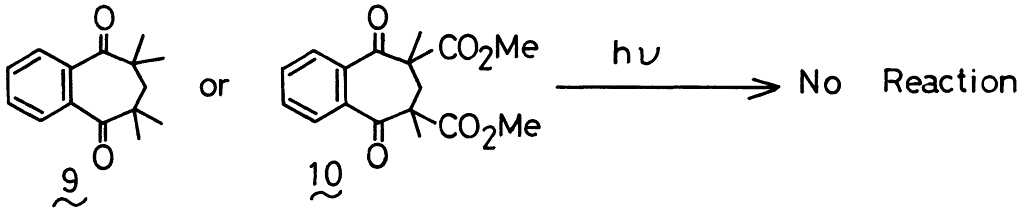
(E)-Alklidene phthalide 5a photoisomerized to (Z)-isomer 6a and *vice versa*. After 15 hours, a photoequilibrated mixture of 5a and 6a (5a/6a=1.2) was formed. Even at low conversion of 3a and 4a (5%), under which conditions photo-interconversion between 5a and 6a was negligible, this product ratio (5a/6a) remained unchanged. Thus, 5a and 6a should be formed in the nearly same ratio from the photolysis of either 3a or 4a.



A plausible mechanism for the photoisomerization of 3 and/or 4 to 5 and 6 is shown in Scheme I. The photoisomerization could begin with α-cleavage, followed by lactonization to give 1,4-diradicals 3'' and 4'' that cleaved to give 5 and 6. The α-cleavage of alkyl phenyl ketones is known as a highly reversible process and the



Scheme I



apparent inefficient quantum yields for the α-cleavage are explained in terms of the cage recombination of α-cleavaged radicals4). When the carbonyl group is present in enough proximity for the attack of the resulting acyl radical, some parts of 3a' and 4a' could undergo lactonization, leading to the formation of 3a'' and 4a'' respectively. The pronounced preference of a-fission over b-fission, which is evident from the product distribution5), is consistent with a stepwise radical rearrangement, since radical intermediate 3a' and 4a' may be fairly stabilized by the two ethereal oxygen atoms adjacent to the radical center.

For comparison, 2,2,4,4-tetramethylbenzosuberan-1,5-dione (9) and 2,4-dimethoxycarbonyl-2,4-dimethylbenzosuberan-1,5-dione (10)[6] were irradiated in benzene but no photoisomerization was observed even after 40 hours. Therefore, the radical stabilizing ability of the ethereal oxygen atoms situated β to carbonyl group or the strain arising from the bicyclic structure of 3 and 4 might be playing an important role in the facile photoisomerization of phthaloyl compounds to alkylidene phthalides.

References and Notes

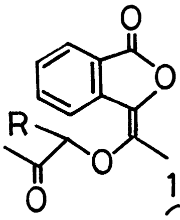
1) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold Publishing Corporation, New York, P. 796.

2) Bicyclo diketones 3a-h and 4a-h were obtained from the photo-induced cycloaddition of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone to aldehydes. K. Maruyama and A. Osuka, Chem., Lett., 77 (1979).

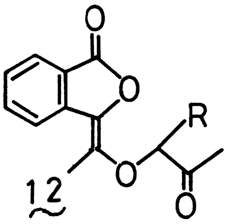
3) Spectral data of 5a and 6a; 5a: IR (KBr) 3000, 1775(phthalide C=O), 1740(ester C=O), and 1238 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.50(d, J=7Hz, 3H), 2.09(s, 6H), 6.27(q, J=7Hz, 1H), and 7.44-8.02(m, 4H); MS (m/e) 246($M^+$, 25), 205(15), 204(75), 186(70), and 161(100). 6a: IR (KBr) 3000, 1775(phthalide C=O), 1740(ester C=O), and 1242 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.44(d, J=7Hz, 3H), 2.07(s, 3H), 6.14(q, J=7Hz, 1H), a nd 7.40-8.00 (m,4H); MS (m/e) 246($M^+$, 25), 204(64), 187(50), 186(75), and 161(100).

4) F. D. Lewis and J. G. Magyer, J. Am. Chem. Soc., 95, 5973 (1974).

5) Once being b-fission occurred, enol ketones 11 and 12 would be formed. Neither 11 nor 12 was found in the reaction.



11



12

6) G. L. Buchanan and J. K. Sutherland, J, Chem. Soc., 2620 (1956).

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