CHEMISTRY LETTERS, pp. 653-656, 1982.

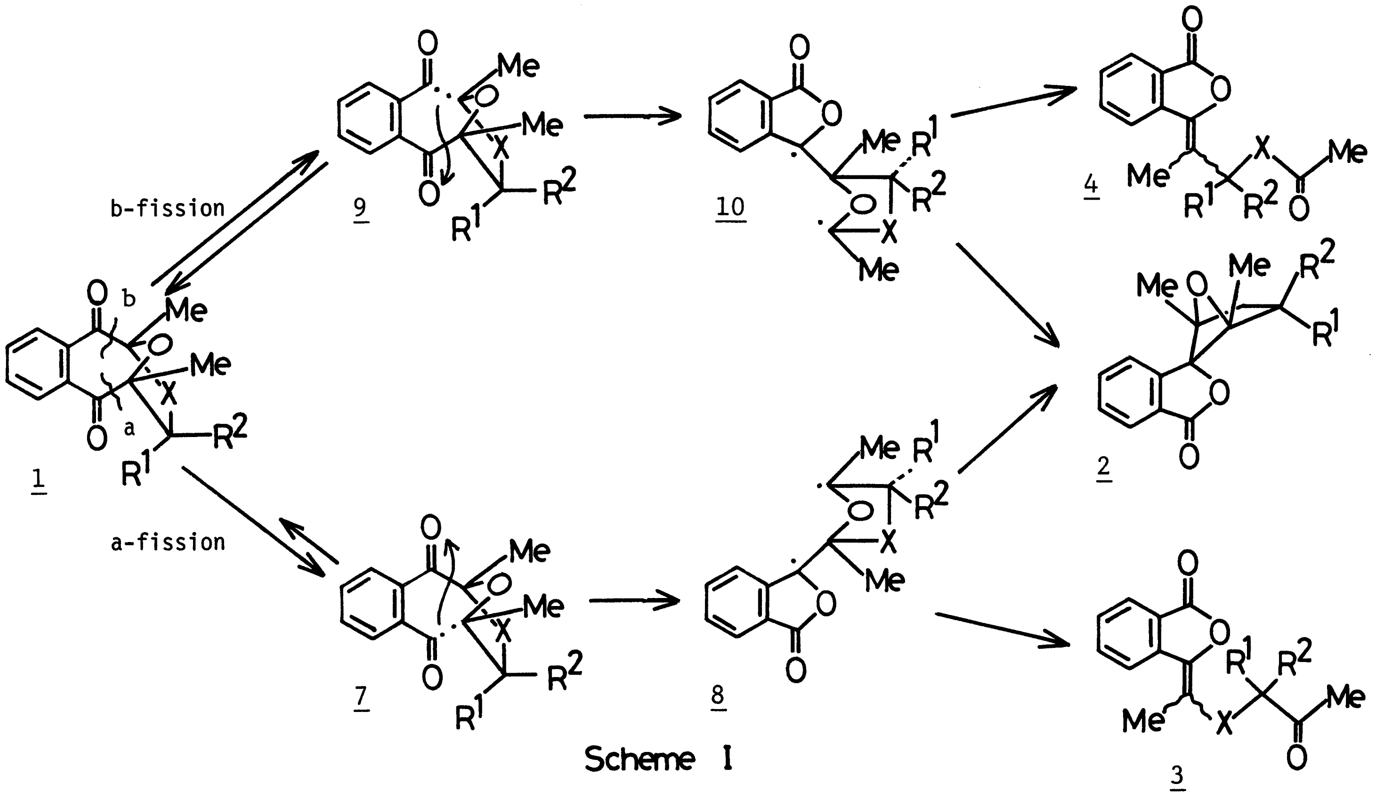
SELECTIVE α-CLEAVAGE IN PHOTOLYSIS OF 7-SUBSTITUTED-6,9-DIMETHYL-6,7,8,9-TETRAHYDRO-6α,9α-EPOXYBENZOCYCLOOCTENE-5,10-DIONE

Atsuhiro OSUKA*, Hitomi SUZUKI, and Kazuhiro MARUYAMA†
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790,
†Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

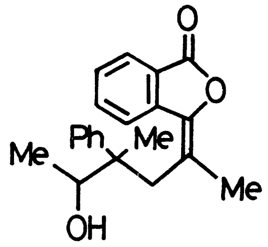
Photolysis of the title compounds in benzene gave spirophthalides and E- and Z-alkylidene phthalides via preferential α-cleavage at the more crowded side. On the basis of quantum yields and triplet lifetimes, this preference is indicated to arise from the different efficiencies of the radical recombination of possible biradicals.

Norrish Type I photoreactions of ketones have been studied in considerable detail.[1] The fact that substitution at α-position of ketones significantly enhances the reactivity of Norrish Type I cleavage is consistent with the notion of a homolytic fission,[2] while the effects of the β-substituents on the photochemical behavior are rather complicated.[2a,3] In the course of our studies on the photochemical reactions of epoxynaphthoquinones, we found that bicyclic diketones 1 underwent the photochemical rearrangement resulting in the simultaneous formation of spirophthalides 2 and alkylidene phthalides 3.[4] Now we will describe that in unsymmetrically substituted diketones 1a-f α-cleavage leading to rearrangement is directed toward the C-7 substituted side.

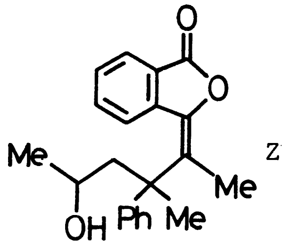
Irradiation of a benzene solution of 1a[5] (0.015 M) with Pyrex-filtered light furnished the spirophthalide 2a (46%) and the alkylidene phthalides E-3a (12%) and Z-3a (31%).[6] The latter products photochemically interconverted to each other. The structure of the alkylidene phthalide 3a came from the transformation of Z-3a into the corresponding alcohol Z-5a. The ^{1}H-NMR spectrum of Z-5a showed peaks at δ 1.18(d, J=7Hz, 3H), 1.34(s, 3H), 1.58(s, 3H), 3.02 and 3.34(ABq, J=15Hz, 2H), and 4.04(q, J=7Hz, 1H), only consistent with the structure of Z-5a not with Z-6a. Similar results were obtained with 1b-f and are collected in Table 1. The position of methoxycarbonyl group in 3c was determined on the basis of the fact that both E-3c and Z-3c were readily deprotonated with K_2CO_3 and alkylated with methyl iodide in dimethylformamide (DMF) to E-3d and Z-3d, respectively, which were in all respects identical with the alkylidene phthalides derived from the photolysis of 1d. The alkylidene phthalides E-3e and Z-3e were similarly alkylated (MeI, K_2CO_3/DMF) to give E-3f and Z-3f, respectively.



Scheme I



Z-5a



Z-6a

Results for 1g, 1h, and the oxygen analogs 1i-l were included in Table 1 for purposes of comparison.[7]

The photorearrangement is likely to begin with α-cleavage leading to a biradical 7, followed by lactonization to give a 1,4-biradical 8, which will cyclize to give 2 or isomerize to give 3. However, as the initial step, another biradical 10 could be formed as well as 7 and would collapse to the regioisomeric alkylidene phthalide 4. Thus, the predominant formation of 3 over 4 here requires the preference of a-fission over b-fission (designated in Scheme I) as the reaction course. On the other hand, photolysis of the oxygen analogs 1i-l led to the predominant formation of E-4i-l and Z-4i-l, which were presumably derived from b-fission.[7] Predominant b-fission in 1i-l may be simply accounted for by considering the bond strength to be cleaved. But it seems to be difficult to rationalize the results for 1a-f on the basis of simple energetic consideration of the bond to be cleaved.

The photoreaction of 1 was quenched by naphthalene or piperylene and sensitized by xanthone, indicating the triplet reaction. Quantum yields for the photorearrangement and triplet life times of 1 were determined at low conversions. It is very significant that eight diketones 1a-h have virtually the same triplet life times within experimental error, even though they rearrange in variant efficiencies. Since all eight diketones 1a-h cleave to biradicals of comparable stability, it would be expected that they would do so at comparable rates. On the other hand, the triplet life times of 1i-l are by a factor of 5-6

Table 1. Photochemical Rearrangement of Bicyclic Diketones 1

Diketones	X	R^1	R^2	Products (%)^a					Φ^b	$k_q\tau^c$	$1/\tau^d$
				2	E-3	Z-3	E-4	Z-4			
1a	CH_2	Me	Ph	46	12	31	-	-	0.69	510	9.8
1b	CH_2	Me	Me	41	13	13	-	-	0.57	600	8.3
1c	CH_2	H	CO_2Me	44	31	21	-	-	0.51	460	11.0
1d	CH_2	Me	CO_2Me	36	31	24	-	-	0.62	440	11.4
1e	CH_2	CN	H	41	19	20	-	-	0.47	580	8.6
1f	CH_2	CN	Me	25	22	36	-	-	0.57	550	9.1
1g	$CH\text{-}(CH_2)_3$		H	6	43^e	43^e	-	-	0.43	550	9.1
1h	$CH\text{-}(CH_2)_4$		H	-	42^e	40^e	-	-	0.18	700	7.1
1i	O	Me	Ph	-	-	-	27^f	38^f	0.021	85	59
1j	O	Me	Me	-	-	-	21^f	43^f	0.010	90	56
1k	O	Me	H	-	-	-	38^f	40^f	0.0086	105	48
1l	O	H	Me	-	-	-	38^f	42^f	0.0094	130	38

a, Isolated yields based on the consumed amounts of 1. b, Quantum yields for the disappearance of 1, ±10%. c, Least-squares slopes of linear Stern-Volmer plots with naphthalene as the triplet quencher, ±15%; M^{-1}. d, Assuming $k_q=5\times10^9\ M^{-1}s^{-1}$. e, In these cases, 3 and 4 are same. f, From reference 7.

shorter than those of the corresponding methylene analogs. The decrease in life time upon replacement of C-7 methylene with oxygen is entirely consistent with the primary photoprocess for 1 being α-cleavage to yield a biradical, since 1i-l can cleave to a better stabilized biradical.

However, the quantum yields seem to be primarily determined by the behavior of the biradical intermediates. Substituents at C-7 in 1 enhance the quantum yields, while replacement of C-7 methylene with oxygen drastically reduces the quantum yields. It is well recognized that radical recombination is one of the most common reactions derived from radical pairs from α-cleavage of alkyl aryl ketones.[8] Thus, the low quantum yields for 1i-l may reflect the efficient cage recombination of the biradical 9, while considerably high quantum yields for 1a-f may reflect the decreased propensity of the intermediate biradicals 7 to recouple. It is plausible in this rigid system that substituents at C-7 retard the radical recombination or render the biradical conformation favorable for the lactonization going to products sterically through something like buttressing effects, while oxygen at C-7 will exert negligible steric effects for radical reactions. Therefore we might conclude that the preference of a-fission over b-fission in 1a-f as the reaction course arises from the differences between the efficiencies of the recombination in the biradicals 7 and 9.

References

1, For general reviews see, a) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, 5, 92 (1972); b) N. J. Turro, "Modern Molecular Photochemistry", W. A. Benjamin/Commings, Menlo Park, California (1978), Chapter 13; c) P. J. Wagner, "Photorearragements *via* Biradicals of Simple Carbonyl Compounds", in "Rearrangements in Ground and Excited States", ed by P. de Mayo, Academic Press, New York (1980), p.p. 381-444.

2, a) R. Srinivasan and S. E. Cremer, *J. Am. Chem. Soc.*, 87, 1647 (1965); b) C. C. Badcock, M. J. Perone, G. O. Pritchard, and B. Rickborn, *ibid.*, 91, 543 (1969); c) H. G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *J. Org. Chem.*, 39, 691 (1974).

3, a) P. J. Wagner and R. W. Spoerke, *J. Am. Chem. Soc.*, 91, 4437 (1969); b) W. C. Agosta and W. L.Schreiber, *ibid.*, 93, 3947 (1971).

4, S. Arakawa, *J. Org. Chem.*, 42, 3800 (1977).

5, Bicyclic diketones 1a-h were obtained from the photo-induced cycloaddition of 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone to the corresponding olefins.

6, All new compounds gave satisfactory elemental analyses and spectral data. Selected spectral data follow; 2a: mp 137-138°C; IR (KBr) 1765(phthalide C=O), 1230, and 1140 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.90(s, 3H), 1.34(s, 3H), 1.90 (s, 3H), 2.60 and 2.84(ABq, J=12Hz, 2H), 7.3-7.5(m, 5H), and 7.5-8.1(m, 4H); ^{13}C-NMR ($CDCl_3$) δ 11.1(q), 14.6(q), 20.6(q), 48.2(t), 50.9(s), 89.6(s), 92.3(s), 99.3(s), and 168.7(ester), besides sp^2 carbons. E-3a: mp 118-119°C; IR (KBr) 1775(phthalide C=O) and 1700(ketone C=O) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.60(s, 6H), 1.98(s, 3H), 2.88 and 3.58(ABq, J=12Hz, 2H), 7.3(m, 5H), 7.4-7.7 (m, 3H), and 7.9(m, 1H); ^{13}C-NMR ($CDCl_3$) 18.2(q), 20.2(q), 25.6(q), 42.1(t), 56.3(s), 166.4(ester), and 209.5(ketone), besides sp^2 carbons. Z-3a: mp 194-195°C; IR (KBr) 1760(phthalide C=O) and 1705(ketone) cm^{-1}; ^1H-NMR($CDCl_3$) δ 1.60 (s, 3H), 1.64(s, 3H), 1.99(s, 3H), 2.90 and 3.76(ABq, J=14Hz, 2H), 7.2-7.4(m, 5H), and 7.4-8.0(m, 4H); ^{13}C-NMR ($CDCl_3$) δ 18.9(q), 19.3(q), 25.6 (q), 39.9(t), 56.2(s), 166.5(ester), and 209.8(ketone), besides sp^2 carbons.

7, a) K. Maruyama and A. Osuka, *Chem. Lett.*, 1979, 77. b) A. Osuka, *J. Org. Chem.*, in press.

8, F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, 37, 2102 (1972).

(Received February 24, 1982)