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PHOTOCHEMICAL, THERMAL, AND CoTPP-CATALYZED DECOMPOSITION OF 2-PYRAZINONE 3,6-ENDOPEROXIDES. NOVEL SYNTHESIS OF THE UNSYMMETRICAL IMIDES

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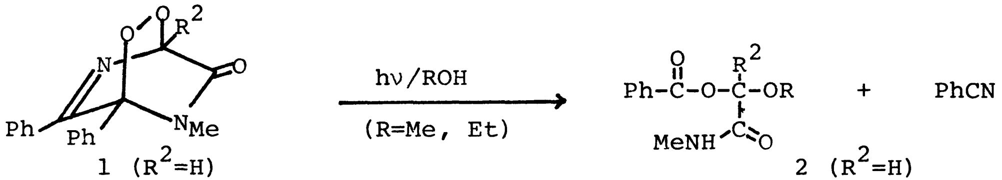
Photochemical, thermal, and CoTPP-catalyzed decomposition of 2-pyrazinone 3,6-endoperoxides, which were readily obtained by the reaction of 2-pyrazinones with singlet oxygen, gave the unsymmetrical imides in moderate to high yields.

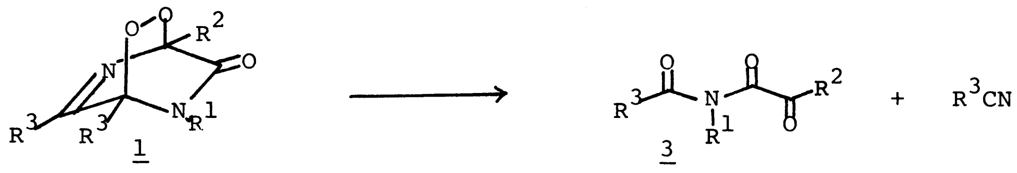
We previously reported that the irradiation of 2-pyrazinone 3,6-endoperoxides (1) in alcohol afforded the amide derivatives (2).[1] The unsymmetrical imide (3) was assumed to be an intermediate for the formation of 2.



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{\underset{MeNH\nearrow C\searrow O}{|}}{\overset{\overset{R^2}{|}}{C}}{-}OR}$$

1 (R^2=H)   2 (R^2=H)

We describe here the photochemical, thermal, and CoTPP-catalyzed decomposition of the 2-pyrazinone 3,6-endoperoxides (1) and the novel synthesis of unsymmetrical imides (3). When the 2-pyrazinone 3,6-endoperoxide (1a)[2] was irradiated in dichloromethane in a Pyrex tube with a high pressure mercury lamp under argon, the unsymmetrical imide, N-benzoyl-N-pyruvaloylmethylamine (3a) [bp 105-108 °C/2 Torr; IR(film) 1680, 1310, 790, 710, and 690 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 2.38 (s, 3H), 3.26 (s, 3H), 7.23-7.88 (m, 5H); ^{13}C-NMR($CDCl_3$) δ 25.8(q), 32.9(q), 128.8(d), 128.9(d), 133.0 (d), 133.8(s), 171.3(s), 173.5(s), 194.4(s)][3] was obtained in 33% yield along with benzonitrile. The unsymmetrical imide (3a) thus obtained reacted with methanol at 45 °C to yield the amide derivative (2a: R=Me, R^2=Me) (26%). Similarly, irradiation of 2-pyrazinone 3,6-endoperoxides (1b-g) gave the unsymmetrical imides (3b-g) in 21-60% yields. The formation of 3 could be readily explained in terms of electrocyclic ring opening of 1 with a loss of the corresponding nitriles. Furthermore, the unsymmetrical imides (3) were also obtained by the thermal reaction of 1. The pyrazinone 3,6-endoperoxides (1) were heated to reflux in toluene to give the unsymmetrical imides (3) in moderate yields accompanied with the corresponding nitriles (15-60%). An interesting reaction was observed in the 2-pyrazinone 3,6-endoperoxide (1e). The endoperoxide (1e) was refluxed in toluene to give the unsymmetrical imide (3e) (20%) and the parent 2-pyrazinone (4) (69%) with a liberation of singlet oxygen.[4] The endoperoxides (3), when heated to their respective melting points, also gave the unsymmetrical imides (3) in high yields. Recently, catalytic rearrangement of bicyclic 1,4-endoperoxides was found with cobalt meso-tetraphenylporphine (CoTPP) by Foote et al.[6] This sequence represents a synthetically useful route from 1,3-dienes to diepoxides under mild conditions. We applied this method for the synthesis of unsymmetrical imides (3) by the decomposition of 1. Treatment of 1 with 5 mol% CoTPP in dichloromethane at room temperature gave the unsymmetrical imides (3) in high yields along with the corresponding nitriles (65-80%).



1	R^1	R^2	R^3
a	Me	Me	Ph
b	Me	Et	Ph
c	Me	Pr^n	Ph
d	Me	Pr^i	Ph
e	Me	Ph	Ph
f	Me	Me	Me
g	Et	Et	Ph

Table 1. Yield of Unsymmetrical Imides (3) (%)

	Photolysis	Thermolysis A a)	Thermolysis B b)	CoTPP-catalyzed
3a	33	70	>95	93
3b	47	50	>95	71
3c	60			
3d	21	46	>95	94
3e	44	20(69)c)	>95	92
3f	52			
3g	40			

a) Refluxed in toluene. b) Heat in a melt at higher temperature than mp. c) Yield in parenthesis is for 1-methyl-3,5,6-triphenyl-2-pyrazinone (4).

Many papers concerning the preparation of the symmetrical imides have been reported,7) however, those of the unsymmetrical imides are few.8) The reactions described here would be the convenient method for the synthesis of unsymmetrical imides (3), since the starting endoperoxides (1) are readily prepared from the 2-pyrazinone with singlet oxygen and indefinitely stable when stored in the solid at room temperature.

References

1) T. Nishio, N. Nakajima, M. Kondo, Y. Omote, and M. Kaftory, J. Chem. Soc., Perkin Trans. 1, 1984, 391. In these photochemical reactions, the unsymmetrical imide, N-benzoyl-N-oxaloylmethylamine (3: R^1=Me, R^2=H, R^3=Ph), could not be isolated even when the irradiation was carried out in aprotic solvents such as dichloromethane, chloroform, and benzene.
2) The 2-pyrazinone 3,6-endoperoxides (1) were readily prepared from the corresponding 2-pyrazinones with singlet oxygen.
3) All new compounds gave satisfactory spectral and microanalytical data.
4) Singlet oxygen thus liberated was trapped with 1,3-diphenylisobenzofuran (5)5): A solution of the endoperoxide (1e) and 5 in toluene was refluxed to give the imide (3e) (trace), 1,2-dibenzoylbenzene (52%), and the 2-pyrazinone (4) (47%).
5) H.H. Wasserman, J.R. Sheffer, and J.L. Cooper, J. Am. Chem. Soc., 94, 4991(1972).
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7) O.H. Wheeler and O. Rasado, "The Chemistry of Amides," ed by J. Zabicky, Interscience Publishers, London (1970), p.335.
8) J. Vecemans and G. Hoornaert, Tetrahedron, 36, 943 (1980).

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