Tetrahedron Letters No. 37, pp 3443 - 3446.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/0908-3443$02.00/0

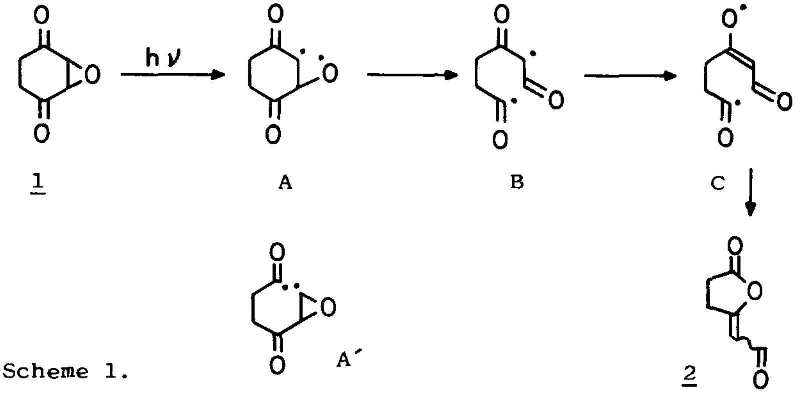
A NEW SYNTHESIS OF γ-ALKYLIDENE-γ-BUTYROLACTONES

A DRAMATIC SOLVENT EFFECT IN THE PHOTOCHEMICAL REARRANGEMENT OF 2,3-EPOXY-1,4-CYCLOHEXANEDIONES

Tohru Kitamura, Takeshi Imagawa, and Mituyosi Kawanisi
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Kyoto 606, Japan

We would like to report the photo-induced rearrangements of 2-epoxy-1,4-cyclohexanediones to the γ-alkylidene-γ-butyrolactones <u>2</u> or the triketones <u>3</u>; the reaction courses are determined dramatically by the solvent used. The reaction giving <u>2</u> promises to be an entry to a synthetic method of the γ-alkylidene-γ-butyrolactones, a structural unit in a variety of 3-alkylidene-phthalides occurring in plants.$^{1)}$

One of the most efficient photochemical reactions is the rearrangement of α,β-epoxy ketones into β-diketones.$^{2)}$ Since this reaction is known to be initiated formally by initial homolysis of the oxirane ring to give a biradical and by subsequent β-alkyl migration with odd electron, we have envisioned that photolysis of the epoxycyclohexanedione <u>1</u> would produce the biradical A, which would undergo subsequent ring opening to B and further rearrange to C, in view

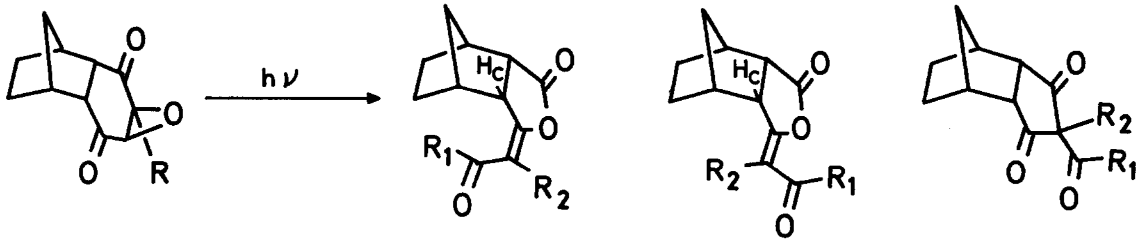


Scheme 1.

of the relative stability of acyl and alkoxy radicals. Cyclization of this biradical would result in the formation of the γ-alkylidene-γ-butyrolactones 2 (Scheme 1).

Irradiation of the epoxy diketone 1a[3] in CH_2Cl_2, using a 100-W high pressure Hg lamp (pyrex), gave only the tricarbonyl compound 3a (42%; mp 131-134°), a product in a similar line to the photochemical rearrangement of the epoxy ketones.[4]

On the other hand, irradiation of 1a in acetone and subsequent short-path distillation gave a 3 : 1 mixture of the lactones 2aE and 2aZ in 38% yield, which were separable by preparative GLC. However irradiation of 1 in a variety of solvents such as hexane, benzene, AcOEt, and CH_3CN led only to 3a.[5]



1 2E 2Z 3

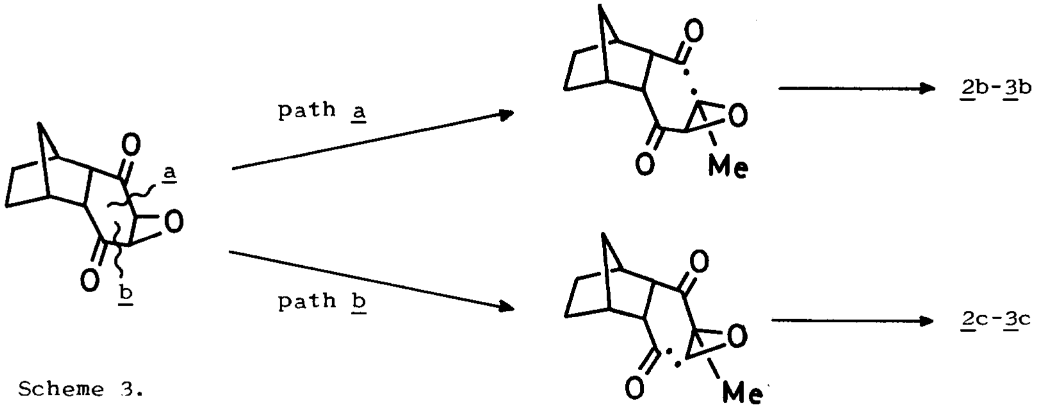
a: R = H
b: R = Me

a: $R_1 = R_2 = H$
b: $R_1 = Me$, $R_2 = H$
c: $R_1 = H$, $R_2 = Me$

Scheme 2.

An unsymmetrically substituted epoxy diketone 1b[3] gave on irradiation in AcOEt the triketone 3b (43%; mp 52-53°) as a sole product.

Irradiation of 1b in acetone and preparative TLC separation[6] afforded the ketonic lactones 2bE (20%) and 2bZ (19%) and an unseparable mixture of the aldehydic lactones 2cE, 2cZ, and triketone 3b. NMR analysis of the crude reaction mixture showed that the ratio of 2bE, 2bZ, 2cE, 2cZ, and 3b was 1 : 1.3 : 0.4 : 0.2 : 1.9.[7] Another possible product 3c was not found. The explanation for the ratio of (2bE + 2bZ + 3b)/(2cE + 2cZ + 3c) = 7/1 is more feasible by the intermediate A' as the path a is a major one between two possible modes of bond fission, owing to the stability of the resulting biradical.



Scheme 3.

The configurations of the above isomers (2E and 2Z) were easily assigned on the basis of their characteristic NMR chemical shifts. In particular, i) H_c in the E isomers are strongly deshielded by carbonyl group to appear at lower field than that for the Z isomers and ii) R_2 (=H) in the E isomers and R_1 (=H or Me) in the Z isomers are considerably deshielded by virtue of its cis relationship to the lactone oxygen.[8)]

Table. NMR chemical shifts of 2

		R_1	R_2	H_c
2aE	(R_1=R_2=H)	9.78	5.93	3.92
2aZ		10.02	5.28	3.58
2bE	(R_1=Me, R_2=H)	2.20	6.10	3.88
2bZ		2.42	5.23	3.13

The formation of 2 can be apparently accounted for as the coupling of acyl radical and O radical (C-O coupling) of the biradical C, and that of 3 can result from the coupling of acyl radical and C radical (C-C coupling) of the biradical B (Scheme 1).

Although a precice explanation of the role of solvents in determining the course of rearrangements cannot be made, this pronounced solvent effect implies the different nature of the intermediates for both products. At present we speculate that the product 3 is generated by the concerted migration from excited 1 as suggested for the rearrangement of the epoxy ketones[2)] and the product 2 by the stepwise radical mechanism. We are continuing to study this point.

References and Notes

1) H. Mitsuhashi and T. Muramatsu, Tetrahedron, 20, 1971 (1964); Y. R. Naves, Helv. Chim. Acta, 26, 1281 (1943); H. J. Gold and C. W. Wilson III, J. Org. Chem., 28, 985 (1963); H. Mitsuhashi, U. Nagai, T. Muramatsu, and H. Tashiro, Chem. Pharm. Bull., 8, 243 (1960).

2) G. W. Griffin and A. Padwa, "Photochemistry of Heterocyclic Compounds", O. Buchardt, ed., Wiley-Interscience, New York, 1976, p. 41.

3) D. F. O'Brien and J. W. Gates, Jr., J. Org. Chem., 30, 2593 (1965).

4) Irradiation of 3a in acetone under the similar conditions did not show any change.

5) Irradiation of 1a in diethyl ether gave a mixture of two products, both of which were the 1 : 1 adducts between 1a and diethyl ether. In view of the importance of the mechanistic implication, the structural elucidation of the adducts having 1-ethoxyethyl moiety were actively attempted, but the partial structure originated from 1a could not be clarified.

6) Silica gel layers for preparative use were prepared using phosphate buffer solution.

7) Olefin protons of 2bE (δ 6.10) and 2bZ (δ 5.23), aldehyde protons of 2cE (δ 9,48) and 2cZ (δ 10.15) and methyl protons of 3b (δ 2.50) were integrated.

8) C. F. Ingham, R. A. Massy-Westropp, G. D. Reynolds, and W. D. Thorpe, Aust. J. Chem., 28, 2499 (1975).

(Received in Japan 29 May 1978; received in UK for publication 11 July 1978)