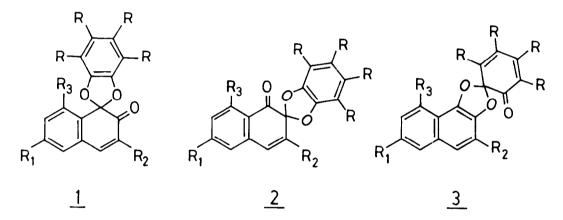
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## NOVEL PHOTOISOMERIZATION OF SPIRODIENONES

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<u>Abstract</u>: Spironaphthalenones of the type  $(\underline{1})$  have been demonstrated to undergo isomerization to (2) upon UV irradiation.

2,4-Cyclohexadienones have been established to undergo 1,6-bond cleavage upon photolysis<sup>1,2</sup>. On the other hand, 6,6-spiroepoxy-2,4-cyclohexadienone is reported to result in aromatization via  $\beta$  C-0 bond cleavage upon excitation<sup>3</sup>. Here, we report a novel photoarrangement of spironaphthalenones [ (<u>1</u>) and (<u>2</u>)] involving  $\beta$  C-0 bond cleavage; rearrangement of such type is not common.



The spironaphthalenones (<u>lb-li</u>) and (<u>2b-2i</u>) were prepared<sup>4</sup> by the oxidation of the corresponding substituted  $\beta$ -naphthols with <u>o</u>-chloranil in benzene. Compounds (<u>la</u>) and (<u>2a</u>) were prepared<sup>5</sup> by the oxidation of 1-(2'-hydroxy-phenoxy)-2-naphthol with <u>o</u>-chloranil in benzene.

Photolysis of benzene solution (0.002-0.004M) of  $(\underline{1})$  and  $(\underline{2})$  were carried out in pyrex tubes under deareated conditions using 450 W medium pressure mercury lamp. Results are presented in the table. Inspection of the table reveals that  $(\underline{1a-lg})$  readily photoisomerize to  $(\underline{2a-2g})$  in near quantitative yield. On the other hand, spironaphthalenones  $(\underline{1h})$  and  $(\underline{1i})$  photoisomerize to  $(\underline{2h})$  and  $(\underline{2i})$ respectively in reduced yields. Similar irradiation of  $(\underline{2a+2g})$  did not bring about any change whereas  $(\underline{2h})$  and  $(\underline{2i})$  rearranged to  $(\underline{1h})$  and  $(\underline{1i})$  respectively. The photosiomerization is believed to originate from the lowest excited singlet state, as triplet quenchers such as naphthalene ( $E_T=61$  Kcal/mole) and cyclohexadiene (52 Kcal/mole) failed to quench the photorearrangement in the case of  $(\underline{1b})$  and  $(\underline{1g})$ .

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Isomeric spirodienones	extent of isomerization ( $st$ )	
	$(\underline{1}) \longrightarrow (\underline{2})$	$(\underline{2}) \rightarrow (\underline{1})$
<u>La</u> ) and $(2a): R_1 = R_2 = R_3 = R = H$	100	0
<u>lb</u> ) and ( <u>2b</u> ): $R_1 = R_2 = R_3 = H$ ; R=Cl	100	0
Lc) and $(2c)$ : $R_1 = R_2 = H$ ; $R_3 = Me$ ; $R = Cl$	100	0
<u>ld</u> ) and ( <u>2d</u> ): $R_1 = R_2 = H; R_3 = pr^{i}; R = Cl$	90	0
Le) and (2e): $R_1 = R_2 = bu^t$ ; $R_3 = H$ ; $R = C1$	100	0
$\underline{t}$ ) and $(\underline{2t})$ : $R_1 = R_3 = H; R_2 = bu^t; R = C1$	90	0
Lg) and $(2g): R_1 = CN; R_2 = R_3 = H; R = C1$	95	0
(h) and (2h): $R_1 = OMe; R_2 = R_3 = H; R=Cl$	25	75
$(\underline{1})$ and $(\underline{21})$ : $R_1 = Br; R_2 = R_3 = H; R=Cl$	75	25

The photorearrangement could be visualized as occurring through the intermediacy of spirocyclohexadienone of the type  $(\underline{3})$  formed by initial  $\beta$  C-O cleavage. Further work, to have a deeper insight into its mechanism is under progress.

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