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OXIDATIVE FORMATION AND PHOTOCHEMICAL ISOMERIZATION OF SPIRO-EPOXY-2,4-CYCLOHEXADIENONES

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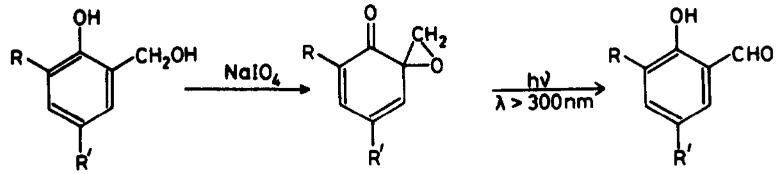
The oxidation of salicylalcohol (I; R=R′=H) by sodium periodate was recently reported to give a dehydrodimer by spontaneous Diels-Alder reaction of the intermediary spiro-epoxy-2,4-cyclohexadienone II (R=R′=H). Analogous dehydrodimers were obtained from 3,5-dimethyl- and 3-hydroxymethyl-5-methyl-salicylalcohol.[1]

We have found that monomer spiro-epoxy-2,4-cyclohexadienones II can be prepared and isolated in excellent yields when the periodate oxidation is applied to ortho-hydroxymethylphenols having at least one bulky substituent which, due to steric hindrance,[2] prevents Diels-Alder dimerization of II. For instance, when a solution of sodium periodate (0.11 mol) in water (125 ml) is added to stirred solution of 2,4-di-tert.-butyl-6-hydroxymethylphenol (Ia; 0.1 mol) in methanol (500 ml), sodium iodate rapidly starts precipitating. Filtration after five hours gives a yellow filtrate from which the spiro-epoxy-2,4-cyclohexadienone IIa precipitates in about 95 % yield after partial removal of solvent by vacuum evaporation.

Spiro-epoxy-2,4-cyclohexadienones IIb - IIg were prepared from the correspondingly substituted salicylalcohols Ib - I g (see Table 1) in a similar manner as described for IIa, though they were isolated, in most cases, by extraction with methylene chloride.



I II III

Table 1. Formation of Spiro-epoxy-2,4-cyclohexadienones II[4]

II	R	R′	Yield %	m.p. °C	λ_{max} nm (ε)	ν'C=O; C=C
a	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	95	79-81	327 (3900)	1670: 1645
b	C_6H_{11}	CH_3	95	oil	334 (4050)	1075; 1655
c	$HOCH_2$	$t\text{-}C_4H_9$	100	oil	329 (3750)	1665; 1645
d	$HOCH_2$	C_6H_5	70	121-22	342 (2700)	1650; 1630
e	CH_3	$t\text{-}C_4H_9$	85	78-80	328 (3450)	1670; 1645
f	H	$t\text{-}C_4H_9$	77	68-71	323 (3450)	1675; 1640
g	H	I	80	103-05	327 (2600)	1665 (broad)

Compounds IIa - IIg are pale yellow in color, their structures being supported by elemental analyses, by their reduction with sodium borohydride to give the corresponding salicylalcohols Ia - Ig, and by their spectroscopic data (see Table 1). In the NMR spectrum the methylene protons of the oxiran group in compounds IIa - IIg show characteristic spin-spin coupling (J_{AB} about 8 cps). The absorption in the IR spectrum between 1675 and 1630 cm^{-1} is indicative of the cyclohexadienone structure. In their UV spectrum, compounds IIa - IIg exhibit an absorption maximum around 330 nm as expected for the 2,4-cyclohexadienone chromophore.[3]

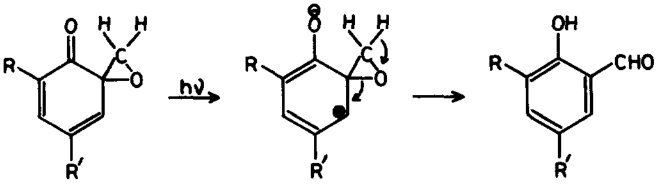
Thermally, compounds IIa - IIg are rather stable, undergoing isomerization to salicylaldehydes sluggishly and in low yields at about 120°C. However, upon irradiation (immersion well apparatus; high-pressure mercury lamp PHILIPS HPK 125 W) at room temperature in solution through Pyrex under nitrogen, spiro-epoxy-2,4-cyclohexadienones IIa - IIg smoothly aromatize to give the substituted salicylaldehydes IIIa - IIIg in good to excellent yields.

Table 2. Photochemical Preparation of Substituted Salicylaldehydes III[4]

III	R	R′	Yield %	m.p.
a	t-C_4H_9	t-C_4H_9	90	58-61° (Lit.[5] 61.5-63°)
b	C_6H_{11}	CH_3	94	129-130° (Lit.[6] 128.5°)
c	$HOCH_2$	t-C_4H_9	88	86-87°
d	$HOCH_2$	C_6H_5	75	122-123°
e	CH_3	t-C_4H_9	70	42-44°
f	H	t-C_4H_9	73	Phenylhydrazone 184° (Lit.[7] 184°)
g	H	I	60	101° (Lit.[8] 102°)

For example, irradiation of IIa (7.02 g; 20 mmol) in ethanol (200 ml) for 90 minutes gave an almost colorless solution from which 3,5-di-tert.-butylsalicylaldehyde (IIIa) was isolated in 90-95 % yield after vacuum evaporation of solvent. The substituted salicylaldehydes IIIb - IIIg (see Table 2) were prepared in the same fashion by irradiation of spiro-epoxy-2,4-cyclohexadienones IIb - IIg.

Photochemical reactions of 2,4-cyclohexadienones reported previously generally resulted in skeletal rearrangements, or led to ring-opened products.[9] The isomerization of spiro-epoxy-2,4-cyclohexadienones may be rationalized by a dipolar intermediate[10] undergoing aromatization as indicated in structure IV.



IV

We have found no evidence for the conceivable aromatization of II to give substituted 1,2-methylenedioxybenzenes. UV-spectroscopic monitoring of

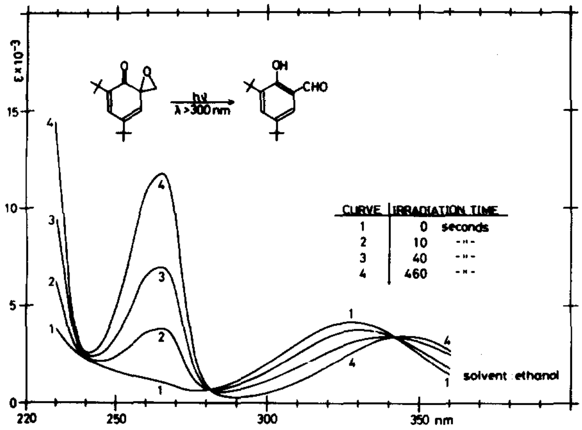


Fig. 1. Photochemical Isomerization of Ia (5×10^{-5} molar solution; 1 cm cell)

the photochemical isomerization reveals, in all cases, the exhibition of isosbestic points (see Fig. 1), indicating that the conversion of II into III is quite clean and that the salicylaldehydes are photochemically stable.

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References

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