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PHOTOCHEMICAL DIMERIZATION OF 2-ACYL-1,4-QUINONES

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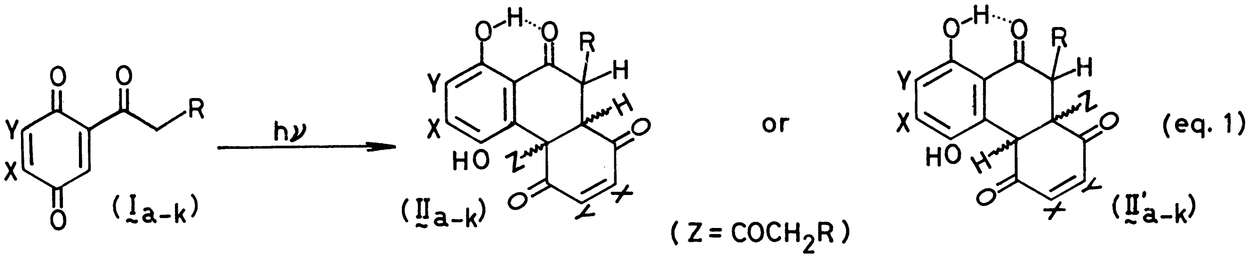
Upon irradiation 2-acyl-1,4-quinones (I) underwent a regiospecific condensation to give their dimers, polycyclic compounds (II). An alternative structure (II'), though it is compatible with the NMR spectra of the dimers, was excluded on the basis of converting one of the dimers to a 9,10-phenanthrenequinone derivative (IV). No condensation of I with dienophiles occurred.

Irradiation of a degassed solution (0.05-0.2 M) of 2-acyl-1,4-benzoquinone or naphthoquinone (I)[1,2] in a Pyrex vessel by means of 300-W high pressure mercury lamp gave a dimer (eq. 1). The yields[3] of the dimers obtained from I$_{a-k}$, irradiation times, and solvents[4] are tabulated below. The solutions of I$_{a-k}$ gave no signs to afford such dimers after standing for a fairly long time without light at room temperature.

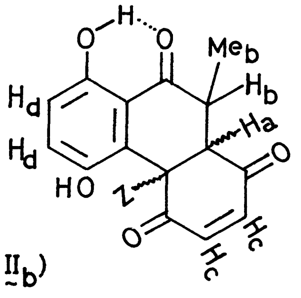


(Z = COCH$_2$R)

	a	b	c	d	e	f	g	h	i	j	k
R	H	Me	Et	n-Pr	n-Bu	H	Me	Me	H	Me	Et
X	H	H	H	H	H	Me	Me	Br	(CH=CH)$_2$		
Y	H	H	H	H	H	H	H	H			
yield (%)	60	40	80	15	44	40	20	10	0	30	25
irradiation time (hr)	100	15	15	10	13	70	15	15	20	10	10
solvent#	c	c	c	a	a	c	c	c	b	b	b

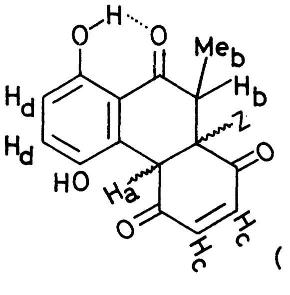
a, benzene-cyclohexane; b, benzene; c, carbon tetrachloride

Structural elucidation is exemplified by the dimer of $\underset{\sim}{I}_b$. The ^{1}H-NMR-spectrum of the dimer was compatible with the structure $\underset{\sim}{II}_b$; δ([$^2H_6$]-acetone) 0.96(t, 3H, J=7.0 Hz, Me_a), 1.45(d, 3H, J=7.0 Hz, Me_b), 2.0-3.0(m, 3H, H_b and $-CH_2-$), 4.08(d, 1H, J=3.5 Hz, H_a), 6.62(ABq, 2H, J=10.0 Hz, $2H_c$), 7.01(ABq, 2H, J=9.0 Hz, $2H_d$), 9.43(s, 1H, OH), and 12.44(s,1H, chelated OH). The above assignment was further substantiated by the ^{1}H-NMR-spectrum of the corresponding dimer of 2-(2'-[$^2H_2$]-propanoyl)-1,4-benzoquinone, i.e. 2'-deuterated $\underset{\sim}{I}_b$; singlets were observed at δ = 0.96, 1.46, and 4.09. Zinc dust distillation of the dimer of $\underset{\sim}{I}_c$ gave phenanthrene which was identified as 9,10-phenanthenequinone.



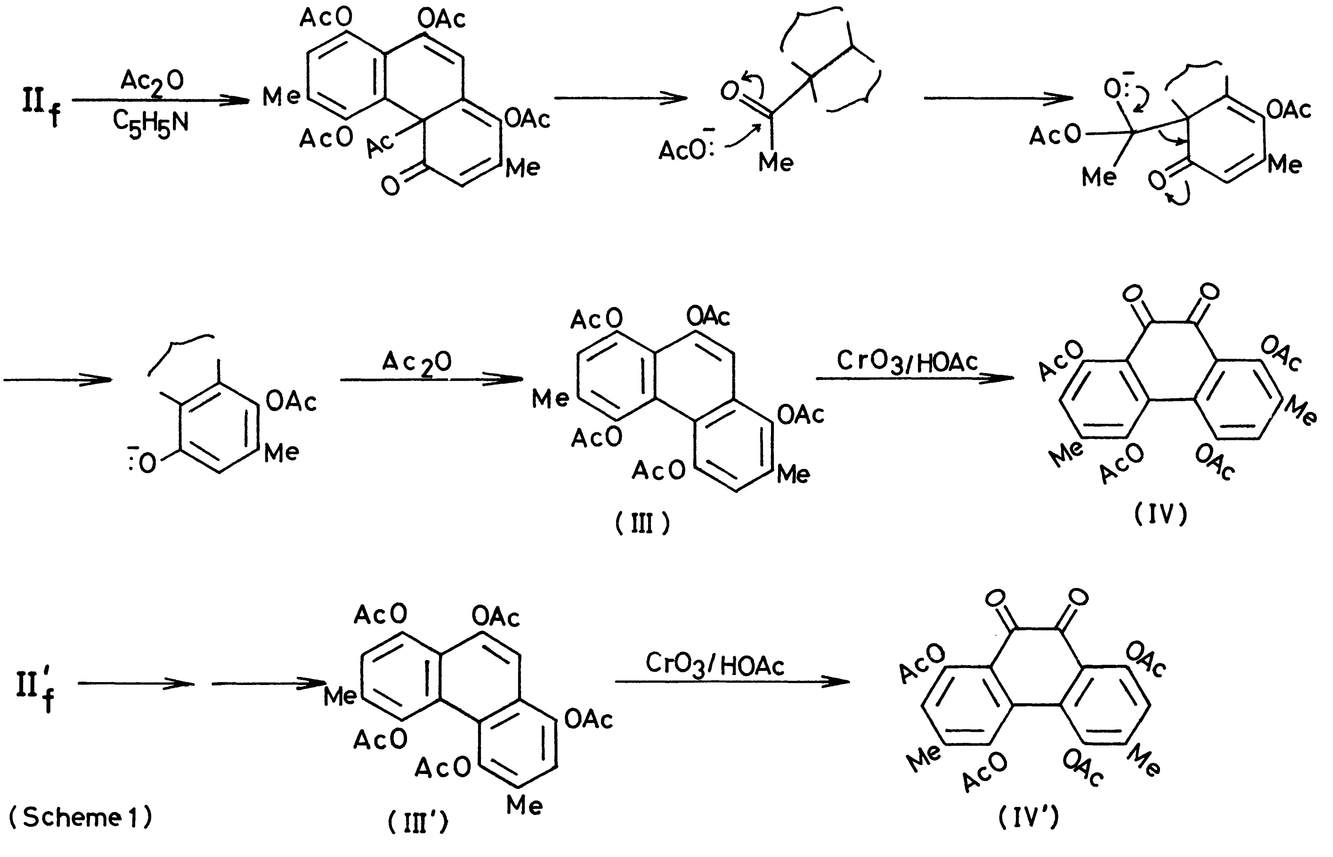
($\underset{\sim}{II}_b$)

(Z = $COCH_2Me_a$)



($\underset{\sim}{II}'_b$)

An alternative structure $\underset{\sim}{II}'_b$, less compatible with its ^{1}H-NMR-spectrum because of a fairly large coupling constant (J=3.5 Hz) between H_a and H_b, was discarded on the basis of the following series of reactions. Treating the dimer of $\underset{\sim}{I}_f$, whose structure



(III)

(IV)

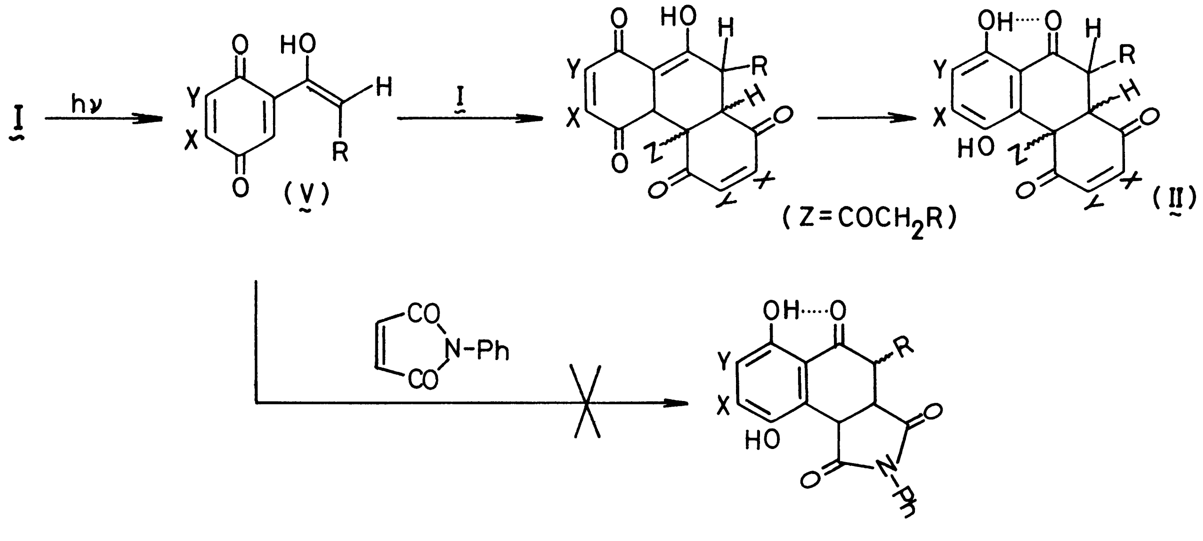
(III')

(IV')

(Scheme 1)

is either $\mathbf{II}_f$ or $\mathbf{II}'_f$, with acetic anhydride containing a small amount of pyridine, we obtained a pentaacetoxy derivative. Plausible paths of the reactions are shown in Scheme 1. The ^{13}C-NMR spectrum of the pentaacetoxy derivative suggested either structure **III** or $\mathbf{III}'$. Subsequent oxidation of the pentaacetoxy derivative with CrO_3 gave a 9,10-phenanthrenequinone derivative. By this procedure **III** will be oxidised to **IV**, and $\mathbf{III}'$ to $\mathbf{IV}'$. The NMR spectra of $\mathbf{IV}'$ should be more simple than those of **IV** because the former has a symmetry axis. Actually, the obtained phenanthrenequinone derivative gave a ^{13}C-NMR spectrum consistent with the structure **IV**, showing two signals of methyl carbons attached to a nucleus carbon (δ [$CDCl_3$] 16.11 and 17.74), two of nucleus carbons bound to a hydrogen (126.79 and 132.97), and twelve of other nucleus carbons (120.60, 122.39, 125.32, 128.58, 129.39, 135.25, 142.25, 144.69, 146.80 148.43, 180.33, and 181.31).[5] The ^{1}H-NMR spectra of the phenanthrenequinone derivative also supported the structure **IV**.[6]

A plausible reaction mechanism via the regiospecific cycloaddtiion of a photochemically formed enol (**V**) is formularized in eq. 2. In appearance, such a cycloaddition reaction is a photo-induced Diels-Alder rection.[7] However, the use of other dienophiles to our reaction seems to be unfavorable, because even in the presence of two times moles of maleic anhydride, N-phenylmaleimide, or dimethyl acetylenedicarboxylate, $\mathbf{I}_a$ and $\mathbf{I}_f$ afforded $\mathbf{II}_a$ and $\mathbf{II}_f$, respectively, as the main product.[8] From the sterical view-point, such a mode of cycloadditions as the present reaction is less favorable, but in all cases examined the products showed the similar mode of cycloaddition. The investigation of the reaction mechanism is still in progress.



(eq. 2)

References and Notes

1) I was prepared by oxidation of the corresponding 2-acylhydroquinone with silver oxide or DDQ.

2) All new compounds gave satisfactory data in elemental analysis and on mass spectroscopy.

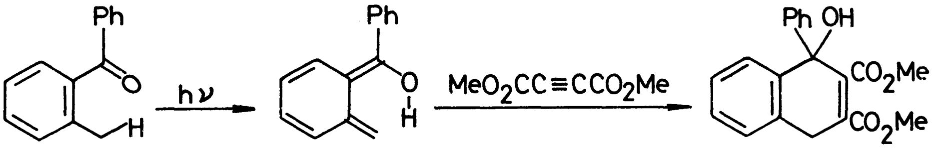
3) The dimers were thermally unstable and purified by precipitation from chloroform or acetone solutions by adding petloleum ether. They also decomposed with moisture and their yields somewhat depended on the manipulation of the resulting products.

4) Variation of solvents affected little on the yields of a dimer.

5) In accordance with the ^{1}H-NMR spectra^6 which showed three singlets due to four acetoxy groups, four acetoxy methyl carbons and four carboxy carbons gave three signals (δ [$CDCl_3$] 20.34, 20.67, and 21.32, and 168.13 168.27, and 170.08) respectively.

6) δ [$CDCl_3$] 2.16(s,3H), 2.27(slightly splitted d, 6H), 2.30(s, 3H), 2.42(s, 6H), 7.08(s, 1H), and 7.48(s, 1H); δ ([$^2H_5$]-pyridine) 2.15(s, 6H), 2.22(s, 3H), 2.32 (s,3H), 2.39(s, 6H), and 7.69(s, 1H) (a signal which might arise at about δ =7.2 was masked with the signals of residual pyridine); deuterium labeling of acetoxy groups revealed that the signals of the methyl groups bound to nucleus arose at δ =2.27 in $CDCl_3$ and at δ =2.15 and 2.22 in [$^2H_5$]-pyridine.

7) A similar reaction was found in the Diels-Alder reaction of the dienol photochemically formed from 2-methylbenzophenone (N. C. Yang and C. Rivas, J. Amer. Chem. Soc., 83, 2213 (1961). For analogous examples of photoenolization see, A. Schonberg, "Preparative Organic Photochemistry", Springer-Verlag, New York (1968), p. 24.



8) No other products could be isolated from the reaction mixtures.

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