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A NOVEL TYPE OF ADDUCTS IN THE PHOTOCHEMICAL REACTIONS OF o-CHLORANIL WITH ALDEHYDES

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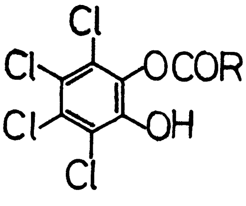
Photochemical reactions between o-chloranil and aldehydes were extensively studied. In the reactions with iso-butyraldehyde and 2-ethylbutyraldehyde, photo-adducts of a novel type proved to be produced. The structure of these photo-adducts determined by IR, PMR, and mass spectra, and by elemental analysis was compatible with 3,3-dialkyl-5,6,7,8-tetrachloro-2,3-dihydro-1,4-benzodioxin-2-ol (II).

In the photochemical reactions of o-quinones with formyl compounds such as aldehydes and glyoxals, the corresponding monoesters of quinols have been reported as the reaction products.1) Thus, phenanthraquinone gives 9-acyloxy-10-hydroxyphenanthrenes on irradiation with aldehydes2) and glyoxals3) in solution. However, only a few examples have been known for the similar reactions of 1,2-benzoquinones with formyl compounds.4) We have extensively studied the photochemical reactions of o-chloranil with a variety of aldehydes, including both aliphatic and aromatic ones. This communication describes a novel type of photo-adducts produced in a few of these reactions.

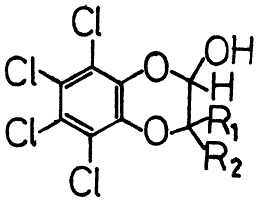
Benzene solutions of o-chloranil and aldehydes were irradiated in usual glass tubes through water layer 5 cm thick using 300-W high-pressure mercury arc lamp, until the red color of the solutions had almost faded to pale yellow. The products, isolated from the reaction mixtures by the usual procedure, were the monoesters of tetrachlorocatechol (I), with two exceptions described below. These monoesters (yield : 20-65%) showed characteristic IR bands; ν_{OH} : 3240-3380 cm^{-1}, $\nu_{C=O}$: 1705-1762 cm^{-1}. The physical constants of the monoesters are summarized in Table 1.

Table 1. Physical Constants of the Monoesters of Tetrachlorocatechol (I)

R :	melting point (°C)	IR (cm^{-1}, KBr disk)
C_2H_5	105.5-106.0	ν_{OH} : 3300, $\nu_{C=O}$: 1747
$n\text{-}C_3H_7$	96.0-97.5	ν_{OH} : 3310, $\nu_{C=O}$: 1738
$CH_2=CH$	128 - 130	ν_{OH} : 3300, $\nu_{C=O}$: 1730
$CH_3CH=CH$	174 - 175	ν_{OH} : 3240, $\nu_{C=O}$: 1732
C_6H_5	174.0-174.5[5)]	ν_{OH} : 3260, $\nu_{C=O}$: 1723
$p\text{-}ClC_6H_4$	216.0-216.5	ν_{OH} : 3290, $\nu_{C=O}$: 1723
$m\text{-}NO_2C_6H_4$	204.0-206.0	ν_{OH} : 3380, $\nu_{C=O}$: 1762
1-Naphthyl	207.0-208.5	ν_{OH} : 3270, $\nu_{C=O}$: 1705



(I) ,



(II)

IIa, $R_1 = R_2 = CH_3$
b, $R_1 = R_2 = C_2H_5$

In the reactions of o-chloranil with iso-butyraldehyde and 2-ethylbutyraldehyde, however, photo-adducts of a novel type (II) proved to be produced instead of the usual monoester type adducts. These aldehydes are characterized by chain branching at the position α to their carbonyl groups. The structure of these photo-adducts was unambiguously confirmed by the following examinations, which is illustrated by the case of IIa (white needles, mp 176.5-177.0°C, yield : 35%);

Elemental analysis : Found : C, 37.75; H, 2.44; Cl, 44.35%.

Calcd for $C_{10}H_8O_3Cl_4$: C, 37.77; H, 2.53; Cl, 44.60%.

Mass spectrum : m/e = 318 (M^+), 246 ($[\text{o-chloranil rest}]^+$).

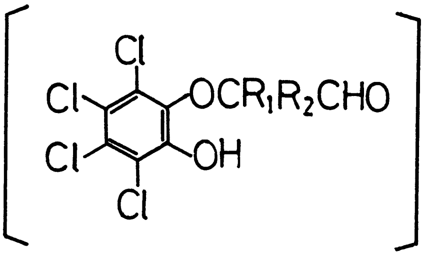
These results indicate one to one combination of o-chloranil and the aldehyde in the molecule of the photo-adduct.

The IR spectrum (KBr disk) of IIa exhibited the presence of hydroxyl group (3190 cm^{-1}), but none of carbonyl group.

The PMR spectrum (solvent : $CDCl_3$) showed four characteristic groups of lines in the regions of δ 1.35 (3H, singlet due to one methyl group), 1.46 (3H, singlet due to the other methyl group), 3.33 (lH, doublet due to hydroxyl group), and 5.25 (lH, doublet). The proton in the hydroxyl group coupled with the other proton attached to the same carbon atom (J = 6.0 Hz). This was confirmed by the fact that on addition of deuterium oxide into the sample the signal at δ 3.33 disappeared completely and the doublet signal at δ 5.25 changed to singlet.

The structure of the photo-adduct between o-chloranil and 2-ethylbutyraldehyde (white needles, mp 142.0-143.5°C, yield : 27%) was similarly determined as IIb by its IR, PMR, and mass spectra, and by elemental analysis.

The formation of the resulting photo-adducts of a novel type (II) might be rationalized by considering a mechanistic pathway involving the initial abstraction of the tertiary hydrogen α to the carbonyl group in preference to the formyl hydrogen, followed by the formation of a conventional 1,4-adduct[6] (III), which then changed intramolecularly to its hemiacetal, the final product.



(III)

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5) The melting point was in accord with that reported earlier; ref. 4.

6) 1,4-Addition is known to occur on irradiation of o-chloranil in dioxane; M. B. Rubin, J. Org. Chem., 28, 1949 (1963). The occurance of 1,4-addition has also been observed in the photochemical reactions of o-chloranil with some alkylbenzenes.

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