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# The Photo-Fries Rearrangement of Hydroxyphenyl Cinnamates[*1]

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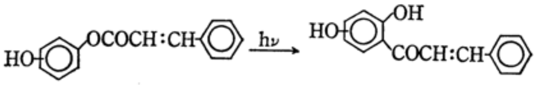
Our recent investigation of the photochemical Fries rearrangement of phenyl cinnamate[1] has prompted the present authors to attempt the preparation of the corresponding hydroxychalcones (4, 5, and 6) by the photo-irradiation of *o*-, *m*- and *p*-hydroxyphenyl cinnamates (1, 2, and 3).



| Hydroxyphenyl cinnamates | | Dihydroxychalcones | |
|---|---|---|---|
| (1) | *o*-OH | (4) | 2′,3′-di-OH |
| (2) | *m*-OH | (5) | 2′,4′-di-OH |
| (3) | *p*-OH | (6) | 2′,5′-di-OH |

As we have described in a previous communication,[1] if these photo-Fries rearrangements are successful there may arise the possibility of a light-catalyzed synthesis of the corresponding polyhydroxychalcones from various polyhydroxyphenyl monocinnamates.

*o*-Hydroxyphenyl cinnamate (1), mp 137—138°C, *m*-hydroxyphenyl cinnamate (2), mp 112—113°C, and *p*-hydroxyphenyl cinnamate (3), mp 166—167°C, were isolated from the reaction mixture obtained by the acylation of catechol, resorcinol, and hydroquinone with cinnamoyl chloride in pyridine. The structures of these compounds were confirmed by the elemental analyses and by a study of their IR spectra.

The yields of these monocinnamates were generally low because there was some difficulty in separating them from the mixture of mono- and di-cinnamates.

The irradiation was carried out in a benzene solution under a nitrogen atmosphere at room temperature using a high-pressure 100 W mercury arc. After irradiation, the benzene was evaporated *in vacuo*, and the residue was chromatographed on a column of silica gel; the resulting chalcones were recrystallized from methanol or benzene.

2′,3′-Dihydroxychalcone (4)[2] was obtained from (1) in a 20% yield; this structure was identified by the elemental analysis, by a study of the IR spectrum, and, furthermore, by its conversion into 8-hydroxyflavanone (7).[2] Similarly, 2′,4′-dihydroxychalcone (5)[3] and 2′,5′-dihydroxychalcone (6)[4] were obtained in 5 and 16% yields respectively; these structures were identified by a comparison of the melting points and UV and IR spectra with those of authentic samples. The formation of 3,′4′-dihydroxychalcone and 2′,6′-dihydroxychalcone from (1) and (2) respectively was expected in these photochemical reactions, but no such chalcones could be isolated from the above irradiation products.

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## Experimental

All the melting points are uncorrected.

***o*-Hydroxyphenyl Cinnamate (1).** Into a solution of 8.8 g of catechol in 60 m*l* of pyridine, 13.6 g of cinnamoyl chloride was slowly stirred over a period of about 1 hr at 45°C. The reaction mixture was then poured into cold water and extracted with ether. After the removal of the ether-insoluble crystals, the ether layer was washed with a dilute aqueous sodium hydrogencarbonate solution, dilute hydrochloric acid, and then water. The ether solution was evaporated *in vacuo*, and the residual crystals were dissolved in warm ethanol. After the removal of the ethanol-insoluble crystals by filtration, the filtrate was evaporated *in vacuo*; the resulting white crystals were then recrystallized from benzene. Yield, 4.76 g (24.8%), mp 140—141°C. IR (KBr): 3380 ($\nu_{OH}$) and 1708 cm$^{-1}$ ($\nu_{CO}$). UV: $\lambda_{max}^{EtOH}$ 283 m$\mu$ (log $\varepsilon$=4.49).

Found: C, 75.15; H, 5.32%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

Catechol dicinnamate was obtained from the ether-insoluble part. Yield, 6.3 g (29.6%), mp 126—127°C (from ethanol). IR (KBr): 1730 and 1720 cm$^{-1}$ ($\nu_{CO}$).

Found: C, 77.99; H, 5.03%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.92%.

***m*-Hydroxyphenyl Cinnamate (2).** This compound was prepared in a 3.7% yield by the same method as in the case of (1). Mp 112—113°C (from benzene). IR (KBr): 3350 ($\nu_{OH}$) and 1692 cm$^{-1}$ ($\nu_{CO}$). UV: $\lambda_{max}^{EtOH}$ 284 m$\mu$ (log $\varepsilon$=4.42).

Found: C, 75.21; H, 5.21%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

Resorcinol dicinnamate, yield, 22.8%, mp 118—119°C (from ethanol). IR (KBr): 1728 cm$^{-1}$ ($\nu_{CO}$).

Found: C, 77.86; H, 5.11%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.92%.

***p*-Hydroxyphenyl Cinnamate (3).** To a stirred solution of 8.8 g of hydroquinone in 60 m*l* of pyridine, there was slowly added 13.6 g of cinnamoyl chloride over a period of about 1 hr at 45°C. The reaction mixture was then poured into cold water and extracted with ether, and the ether layer was washed with a dilute aqueous sodium hydrogencarbonate solution, dilute hydrochloric acid, and then water. The ether solution was evaporated *in vacuo*, and the residual white crystals were dissolved in warm methanol. After the removal of the methanol-insoluble crystals by filtration, the filtrate was evaporated *in vacuo*; the resulting white crystals were recrystallized from ethanol. Yield, 4.0 g (20.8%), mp 167—168°C. IR (KBr): 3389 ($\nu_{OH}$) and 1695 cm$^{-1}$ ($\nu_{CO}$). UV: $\lambda_{max}^{EtOH}$ 283 m$\mu$ (log $\varepsilon$=4.49).

Found: C, 75.04; H, 5.28%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

Hydroquinone dicinnamate was obtained from the above methanol-insoluble part. Yield, 3.3 g (11.0%), mp 186—188°C (from benzene). IR (KBr): 1735 cm$^{-1}$ ($\nu_{CO}$).

Found: C, 78.12; H, 5.19%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.92%.

**Irradiation of *o*-Hydroxyphenyl Cinnamate (1).** A solution of 500 mg of (1) in 300 m*l* of dry benzene was irradiated under a nitrogen atmosphere at room temperature by a high-pressure 100 W mercury arc for 30 hr. After irradiation, benzene was evaporated *in vacuo* and the resulting crude mixture was chromatographed on a 570×30 mm column of silica gel. 2′,3′-Dihydroxychalcone (4) was obtained as orange crystals from the first elution with ligroin-benzene-ethyl acetate (2 : 2 : 1). Yield, 100 mg (20%), mp 149—150°C (from methanol) (lit. mp 151°C²⁾). IR (KBr): 3460 ($\nu_{OH}$) and 1632 cm$^{-1}$ ($\nu_{CO}$). UV: $\lambda_{max}^{EtOH}$ 232 (log $\varepsilon$=4.32), 322 m$\mu$ (4.63).

Found: C, 75.22; H, 5.27%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

This chalcone (4) was converted into 8-hydroxyflavanone, mp 191—192°C (lit. mp 192°C²⁾), by refluxing it with methanolic hydrochloric acid for 10 hr.

**Irradiation of *m*-Hydroxyphenyl Cinnamate (2).** A solution of 1.0 g of (2) in 300 m*l* of benzene was irradiated for 30 hr as has been described above. Elution with benzene-ethyl acetate (2 : 1) gave 400 mg of white crystals, which were identified as the unchanged starting materials by a comparison of the IR spectrum with that of (2). The second fraction gave 50 mg of yellow crystals, which were identified as 2′,4′-dihydroxychalcone (5) by a comparison of the IR spectrum with that of an authentic sample. Mp 146—147°C (from benzene) (lit. 150—151°C³⁾). The third fraction gave 110 mg of resorcinol, while the fourth fraction, which was eluted with methanol, gave 120 mg of brown, viscous polymeric products.

**Irradiation of *p*-Hydroxyphenyl Cinnamate (3).** A solution of 1.0 g of (3) in 500 m*l* of benzene was irradiated for 30 hr and then worked up as has been described above. Elution with chloroform-ethyl acetate (10 : 1) gave 160 mg of orange crystals, which were identified as 2′,5′-dihydroxychalcone (6) by a comparison of the IR spectrum with that of an authentic sample. Mp 172—173°C (from methanol) (lit. mp 173—173.5°C⁴⁾). IR (KBr): 3280 ($\nu_{OH}$) and 1637 cm$^{-1}$ ($\nu_{CO}$). UV: $\lambda_{max}^{EtOH}$ 229 (log $\varepsilon$=4.12), 316 (4.37) and 408 m$\mu$ (3.69).

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