September, 1981] © 1981 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 54, 2855—2856 (1981) 2855

Cyclodehydrogenation of 3-Cinnamoyltropolones with 2,3-Dichloro-5,6-dicyanobenzoquinone

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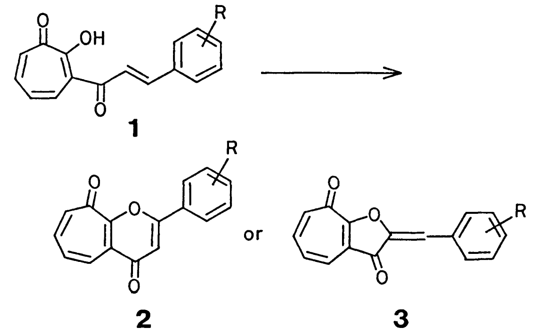
(Received April 15, 1981)

Synopsis. 3-Cinnamoyltropolone and 3-(3-methoxycinnamoyl)tropolone were oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone to give 2-phenyl- and 2-(3-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones, while 2′- and/or 4′-methoxy-substituted 3-cinnamoyltropolones gave 2-arylmethylene-2*H*-3,8-dihydrocyclohepta[*b*]furan-3,8-diones.

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is recently used for synthetic organic chemistry as a dehydrogenating or cyclodehydrogenating agent.[1a—c] In connection with our studies on cyclization reactions of 3-cinnamoyltropolones,[2—4] which have a 2′-hydroxychalcone-like structure, we have been interested in the use of DDQ for their cyclization reaction. Little is known about the DDQ cyclization of 2′-hydroxychalcones except for 2′-hydroxy-5′-prenyl-4,4′-diphenylchalcone, which gave the corresponding flavone.[5]

A mixture of 3-cinnamoyltropolones (**1a**—**i**) (1 mmol) and DDQ (2 mmol) in dry benzene was refluxed for 20 h. Thus, the reactions of 3-cinnamoyltropolone (**1a**) and 3-(3-methoxycinnamoyl)tropolone (**1c**) gave flavone-like compounds, 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones, while the other 3-cinnamoyltropolones (**1b**, **d**—**i**) which have the methoxyl group at 2′- and/or 4′-position gave selectively aurone-like compounds, 2-arylmethylene-2*H*-3,8-dihydrocyclohepta[*b*]furan-3,8-diones (**3b**, **d**—**i**). Each of the products was identified with comparison of its mp and IR and NMR spectra with those of the product from selenium dioxide oxidation[2] and alkaline hydrogen peroxide oxidation[3] of the corresponding 3-cinnamoyltropolones. The results are summarized in Table 1.

These results show that the DDQ is a useful cyclodehydrogenating reagent of 3-cinnamoyltropolones. This reaction might be extended to the oxidative cyclization of 2′-hydroxychalcones.



a R=H
c R=3-OCH$_3$

b R=2-OCH$_3$
d R=4-OCH$_3$
e R=2,3-(OCH$_3$)$_2$
f R=2,4-(OCH$_3$)$_2$
g R=3,4-(OCH$_3$)$_2$
h R=2,3,4-(OCH$_3$)$_3$
i R=3,4-(OCH$_2$O)

Scheme 1.

Experimental

Measurement. The melting points were determined with a Yanagimoto melting-point measuring apparatus and are uncorrected. The IR spectra were taken on a JASCO IRA-1 spectrophotometer. The NMR spectra were recorded with a Hitachi R-24 spectrometer (60 MHz).

*Oxidative Cyclization of 3-Cinnamoyltropolones (**1a**—**i**).* A mixture of 3-cinnamoyltropolone (**1a**—**i**) (1 mmol, 252—343 mg) and DDQ (2 mmol, 454 mg) in dry benzene (20 ml) was refluxed for 20 h. The reaction mixture was poured into a saturated sodium carbonate solution (100 ml) and extracted with chloroform. The extract was washed with water, dried over anhydrous sodium sulfate, and brought to dryness by evaporation of the solvent. The residue was recrystallized from benzene to afford 2-aryl-4,9-dihydro-

Table 1. Cyclodehydrogenation of 3-cinnamoyltropolones

	R	Product	Yield %	Mp °C	(Lit, mp)	Ref.
a	H	**2a**	46	200—202	(201—202)	2
b	2-OCH$_3$	**3b**	44	262—265	(261—262)	3
c	3-OCH$_3$	**2c**	43	212—213	(212—214)	2
d	4-OCH$_3$	**3d**	53	225—227	(227—228)	3
e	2,3-(OCH$_3$)$_2$	**3e**	38	225—226	(225—226)	3
f	2,4-(OCH$_3$)$_2$	**3f**	42	231—232	(231—233)	3
g	3,4-(OCH$_3$)$_2$	**3g**	39	282—284	(285—286)	3
h	2,3,4-(OCH$_3$)$_3$	**3h**	36	184—185	(183—184)	3
i	3,4-(OCH$_2$O)	**3i**	46	277—278	(279—280)	3

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cyclohepta[*b*]pyran-4,9-dione (**2a**, **c**) or 2-arylmethylene-2*H*-3,8-dihydrocyclohepta[*b*]furan-3,8-dione (**3b**, **d**—**i**).

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