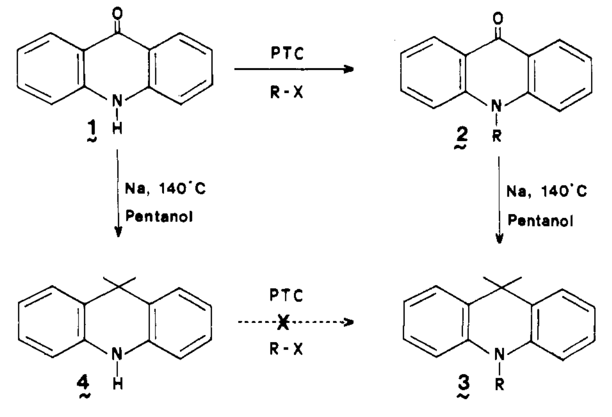
Scheme I



Indeed, they lead back to the 9-oxo homologues within a few weeks even if they are bottled in brown flasks, safe from air. This has been proved by TLC.

Experimental Section

***Alkylation of 9(10H)-Acridinones 2*: *General Procedures*.** A stirred mixture of 9(10*H*)-acridinones **2** (10 mmol), alkylating agents (15 mmol), triethylbenzylammonium chloride (0.3 mmol), aqueous 50% sodium hydroxide (10 mL), and butanone (20 mL) is refluxed for about 2 h at 80 °C. The reaction mixture is poured into hot water and left overnight at room temperature. The precipitated solid is collected, washed with water, and dried before recrystallization from ethanol or ethanol-water mixture.

***Alkylation of 2e*.** A stirred mixture of 9(10*H*)-acridinones **2** (15 mmol), alkylating agents (37.5 mmol), triethylbenzylammonium chloride (7.5 mmol), aqueous 50% potassium hydroxide (75 mL), and toluene (150 mL) is refluxed for 5 days. The toluene layer is separated, washed three times with water (50 mL each time), dried with sodium sulfate, and evaporated in vacuo. The residual oil is recrystallized from light petroleum and provides a microcrystalline yellow powder.

***Preparation of 9,10-Dihydroacridines 3*: *General Procedure*.** 9(10*H*)-Acridinone (10 mmol) is refluxed with pentanol (150 mL) and treated with sodium (7.5 g) added in small amounts until the sodium has dissolved and the greenish fluorescence has vanished. After cooling and cautiously diluting with water (150 mL), pentanol was distilled off in a current of steam. The residue of 9,10-dihydroacridine was filtered off, washed with water, dried, and recrystallized from ethanol.

***Thin-Layer Chromatography*.** Thin-layer chromatography was carried out on silica gel plates (20 × 20 cm). Experiments were performed in Desaga tanks, with the following system: chloroform; ethanol; dioxane (93-5-2 v/v). Plates were examined under an ultraviolet lamp (366 nm) yielding fluorescent spots (R_f values of **2** are about 0.60; R_f values of **3** are about 0.78).

Registry No. **2**, 578-95-0; **2a**, 719-54-0; **2b**, 60536-17-6; **2c**, 60536-22-3; **2d**, 13396-07-1; **2e**, 117121-15-0; **3a**, 4217-54-3; **3b**, 18448-45-8; **3c**, 102008-08-2; **3d**, 78305-11-0; **3e**, 94436-61-0; **4**, 92-81-9.

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Synthesis and Properties of Substituted Dicinnamylidene Cycloketones

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Different substituted dicinnamylidene cycloketones were synthesized via base-catalyzed condensations of substituted cinnamaldehydes and different cycloketones. The reaction products were identified on the basis of their infrared, proton and carbon-13 nuclear magnetic resonance, and ultraviolet spectral data as well as elemental analysis. Some of the synthesized compounds show fluorescence properties in solution.

Introduction

In the course of our study on the condensation of α,β-unsaturated Michael acceptors with compounds having active

Table I. Results for Substituted Dicinnamylidene Cycloketones (IIIa-k)

compd	mol formula	reaction time, min	crystn solvent	mp, °C	yield,[a] %
IIIa	$C_{23}H_{20}O$	20	C_2H_5OH	209-210	84
IIIb	$C_{25}H_{24}O_3$	30	CH_3COOH	204-205	77
IIIc	$C_{24}H_{22}O$	50	C_2H_5OH	185-186	85
IIId	$C_{24}H_{20}N_2O_5$	20	CH_3COOH	220-221	91
IIIe	$C_{26}H_{26}O_3$	60	C_2H_5OH	203-205	78
IIIf	$C_{25}H_{24}O$	30	C_2H_5OH	164-166	84
IIIg	$C_{25}H_{22}N_2O_5$	20	CH_3COOH	215-216	85
IIIh	$C_{27}H_{28}O_3$	20	C_2H_5OH	141-142	73
IIIi	$C_{25}H_{24}O$	60	C_2H_5OH	212-214	65
IIIj	$C_{27}H_{28}O_3$	50	C_2H_5OH	110-112	68
IIIk	$C_{28}H_{30}O_3$	20	C_2H_5OH	193-194	75

[a] These reported yield values are for crude products.

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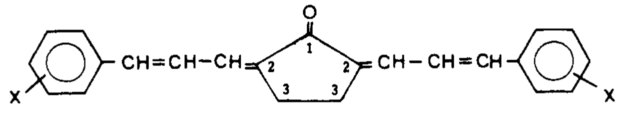
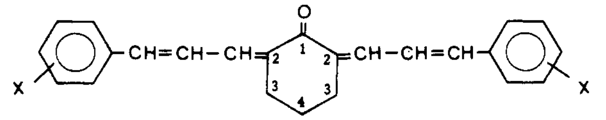
Table II. Infrared, Ultraviolet, and Proton Nuclear Magnetic Resonance Spectral Data of Compounds IIIa-k

	electronic spectra				IR spectra		NMR (CDCl$_3$)		
compd	(EtOH) λ_{max}, nm	ϵ	(CHCl$_3$) λ_{max}, nm	ϵ	cm^{-1}	ν	δ	assignt	no. H
IIIa	407	65 733	404	44 800	3045	C–H	2.91 (s)	-CH$_2$-	4
					2950		6.95–7.35 (m)	Ar–H -CH=	16
					1655	C=O			
					1630	C=C			
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1490				
IIIb	426	76 775	427	55 410	3010	C–H	2.89 (s)	-CH$_2$-	4
					2970		3.90 (s)	-OCH$_3$	6
					1645	C=O	7.05–7.62 (m)	Ar–H -CH=	14
					1620	C=C			
					1605	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1490				
IIIc	388	62 030	387	53 030	3020	C–H	1.89 (m)	-CH$_2$-	2
					2950		2.75 (dd)	-CH$_2$-	4
					1650	C=O	6.80–7.30 (m)	Ar–H -CH=	16
					1630	C=C			
					1605	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1495				
IIId	376	64 450	377	37 960	3040	C–H	1.60 (m)	-CH$_2$-	2
					2980		2.75 (dd)	-CH$_2$-	4
					1655	C=O	7.00–7.45 (m)	Ar–H CH=C	14
					1625	C=C			
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1505				
IIIe	409	70 430	406	64 850	3005	C–H	1.91 (m)	-CH$_2$-	2
					2995		2.79 (dd)	-CH$_2$-	4
					1645	C=O	3.89 (s)	-OCH$_3$	6
					1630	C=C	6.95–7.29 (m)	Ar–H -CH=	14
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1490				
IIIf	388	70 625	380	44 020	3050	C–H	1.20 (d)	CH$_3$-	3
					2980		2.33–2.71 (m)	-CH$_2$- -CH-	5
					1655	C=O			
					1630	C=C	7.05–7.32 (m)	Ar–H -CH=	16
					1610	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1590				
IIIg	378	61 475	379	67 560	3045	C–H	1.15 (d)	CH$_3$-	3
					2950		2.20–2.30 (m)	-CH$_2$- -CH-	5
					1645	C=O			
					1625	C=C	7.10–7.45 (m)	Ar–H -CH=	14
					1605	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1505				
IIIh	406	53 515	404	44 900	3050	C–H	1.18 (d)	CH$_3$-	3
					2950		2.30–2.89 (m)	-CH$_2$- -CH-	5
					1650	C=O			
					1625	C=C	3.86 (s)	OCH$_3$	3
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$	7.05–7.37 (m)	Ar–H -CH=	14
					1590				
IIIi	356	61 670	352	62 075	3060	C–H	1.75 (m)	-CH$_2$-	4
					2950		2.92 (m)	-CH$_2$-	4
					1650	C=O	6.80–7.25 (m)	Ar–H -CH=	16
					1630	C=C			
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1590				
IIIj	351	58 950	349	49 850	3050	C–H	1.76 (m)	-CH$_2$-	4
					2930		2.95 (m)	-CH$_2$-	4
					1660	C=O	3.85 (s)	OCH$_3$	6
					1635	C=C	6.95–7.25 (m)	Ar–H -CH=	14
					1600	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1510				
IIIk	354	53 610	349	41 600	3010	C–H	1.66 (m)	-CH$_2$-	6
					2920		2.80 (m)	-CH$_2$-	4
					1665	C=O	3.85 (s)	OCH$_3$	6
					1630	C=C	7.10–7.50 (m)	Ar–H -CH=	14
					1605	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$			
					1510				

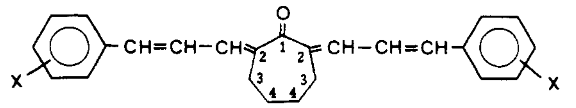
Table III. Carbon-13 Chemical Shift Values for Compounds III



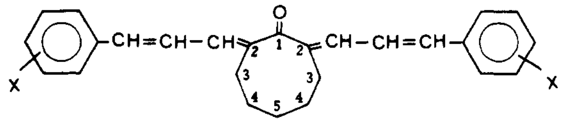
compd	C-1	C-2	C-3
IIIa	194.6	128.4	24.1
IIIb	194.7	128.9	24.1



compd	C-1	C-2	C-3	C-4
IIIc	188.0	127.2	26.7	22.2
IIId	179.4	128.3	26.8	22.1
IIIe	188.6	126.9	26.7	22.3
IIIf	188.5	128.7	34.9	28.5
IIIg	188.2	127.5	34.9	28.4
IIIh	188.6	128.1	34.6	28.5



compd	C-1	C-2	C-3	C-4
IIIi	197.9	127.2	27.8	27.1
IIIj	203.7	127.9	31.2	27.7



compd	C-1	C-2	C-3	C-4	C-5
IIIk	204.8	126.2	55.6	39.2	30.4

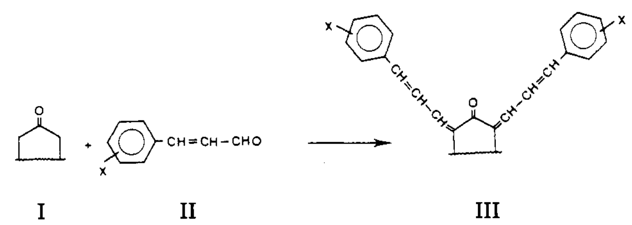
methylene groups (*1*), we reported the condensation of α-phenyl-*p*-morpholinoacetophenone with ethyl arylpropiolates and the condensation of ethyl arylpropiolates with cycloketones (*2*). Since the benzyl cyanides are good Michael donors and useful reagents for carbon–carbon bond formations, we also reported the reaction between different ethyl cinnamates and benzyl cyanides (*3*) as well as the reaction between different substituted chalcones with a variety of substituted phenylacetonitriles (*4*, *5*). Al-Jobour and Shandala (*6*) have reported the condensation of phenylpropiolic esters with α- and β-tetralones in the presence of sodium ethoxide to yield 5,6-dihydro-7,8-benzoflavones and ethyl β-(2-tetralon-1-yl)cinnamates, as a result of Claisen and Michael reactions, respectively.

A literature search (*7*–*9*) revealed that little, if any, information was available concerning the condensation of substituted cinnamaldehydes with different cycloketones and the fluorescence properties of the reaction products (*10*, *11*).

Experimental Section

Infrared spectra (Table II) were recorded as KBr disk using a Pye-Unicam SP 300 instrument. Proton and carbon-13 spectra (Table III) were run on a Bruker WP 80-SY instrument using deuteriated chloroform containing tetramethylsilane as internal standard. Ultraviolet spectra were recorded in ethanol and chloroform solutions using a Varian DMS 100 spectrophotometer. Compounds were analyzed at M-H-W Laboratories, Phoenix, AZ. Melting points (Table I) were determined on an Electrothermal melting point apparatus and were uncorrected. Elemental analyses in agreement with theoretical values were obtained and submitted for review. Table IV shows the fluorescence data of some products III.

Scheme I



III	I	X
a	cyclopentanone	H
b	cyclopentanone	2-methoxy
c	cyclohexanone	H
d	cyclohexanone	2-nitro
e	cyclohexanone	2-methoxy
f	4-methylcyclohexanone	H
g	4-methylcyclohexanone	2-nitro
h	4-methylcyclohexanone	2-methoxy
i	cycloheptanone	H
j	cycloheptanone	2-methoxy
k	cyclooctanone	2-methoxy

Table IV. Fluorescence Data for Compounds III in Acetonitrile Solutions[a]

compd	excitation[b]	emission[b]
IIIa	468	546
IIIb	490	536
IIIe	468	532
IIIf	468	510
IIIg	500	548

[a] Measurements were recorded on a Perkin-Elmer MPF-44B spectrophotofluorometer using acetonitrile as solvent. [b] Wavelengths are in nm.

In each reaction, a (1:2) molar ratio of cyclic ketones and substituted cinnamaldehydes were added successively to a mixture of sodium in absolute ethanol (200 mL). The mixture was stirred at room temperature for 20–60 min. A heavy solid was formed, separated by suction filtration, washed with a small amount of petroleum ether (40–60 °C) and then recrystallized from the appropriate solvent. Partial evaporation of the mother liquor yielded a further amount of the desired products as shown in Scheme I.

Registry No. II (X = H), 104-55-2; II (X = 2-methoxy), 1504-74-1; II (X = 2-nitro), 1466-88-2; IIIa, 21856-78-0; IIIb, 117069-05-3; IIIc, 18977-40-7; IIId, 117069-06-4; IIIe, 117069-07-5; IIIf, 25672-06-4; IIIg, 117069-08-6; IIIh, 117069-09-7; IIIi, 21856-79-1; IIIj, 117069-10-0; IIIk, 117069-11-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 4-methylcyclohexanone, 589-92-4; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8.

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