Synthesis and Spectral Data of Ethyl 3-Aryl-4,5-diphenyl-5-oxopentanoates

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The Michael reaction of substituted ethyl cinnamates with α-phenylacetophenone in the presence of sodium ethoxide at room temperature gave a mixture of *erythro*- and *threo*-ethyl 3-aryl 4,5-diphenyl-5-oxopentanoates. The reaction products were identified by their elemental analysis, nuclear magnetic resonance, infrared, and mass spectral data.

Introduction

The condensation of α-phenylacetophenone with ethyl phenylpropiolate (*1–3*) or ethyl arylpropiolates (*4*) have been reported to give 4,5,6-triaryl-2-pyrones. The reaction of α-phenylacetophenone with ethyl cinnamate and the synthetic potentialities of sodium ethoxide catalyzed addition of the carbanions to the carbon–carbon double bond of ethyl cinnamate leading to compounds with two vicinal chiral centers have been

Table I. Results for Ethyl 3-Aryl-4,5-diphenyl-5-oxopentanoates

compd	formula	mp, °C	yield, %	reaction time, days	mass (*m/e*, %)	NMR(CDCl$_3$) δ (protons)
IIIa	$C_{26}H_{26}O_3$	166–8	33	6	386 (9.5) 191 (27) 149 (62) 105 (100) 77 (65)	0.95 (t, 3H) 2.55 (dd, 2 H) 3.78 (q, 2 H) 4.08 (m, 1 H) 5.37 (d, 1 H; *J* = 12 Hz) 7.50 (m, 14 H) 2.14 (s, ArCH$_3$)
IVa	$C_{26}H_{26}O_3$	154–6	37	6	386 (11) 191 (23) 149 (65) 105 (100) 77 (75)	0.98 (t, 3 H) 2.44 (dd, 2 H) 3.80 (q, 2 H) 4.22 (m, 1 H) 4.38 (d, 1 H) 7.52 (m, 14 H) 2.16 (s, ArCH$_3$)
IIIb	$C_{25}H_{23}O_3Cl$	167–8	38	1	408 (3) 406 (10) 211 (29) 105 (100) 77 (73)	1.03 (t, 3 H) 2.43 (dd, 2 H) 3.87 (q, 2 H) 4.10 (m, 1 H) 4.98 (d, 1 H; *J* = 11.2 Hz) 7.46 (m, 14 H)
IVb	$C_{25}H_{23}O_3Cl$	162	10	1	408 (4) 406 (11) 211 (32) 169 (27) 105 (100) 77 (65)	1.05 (t, 3 H) 2.50 (dd, 2 H) 3.81 (q, 2 H) 4.05 (m, 1 H) 5.01 (d, 1 H) 7.48 (m, 14 H)
IIIc	$C_{25}H_{23}O_3Br$	254–6	32	2	452 (9) 450 (10) 255 (35) 213 (27) 105 (100) 77 (52)	1.03 (t, 3 H) 2.44 (dd, 2 H) 3.88 (q, 2 H) 4.10 (m, 1 H) 4.98 (d, 1 H; *J* = 10.6 Hz) 7.51 (m, 14 H)
IVc	$C_{25}H_{23}O_3Br$	162–3	14	2	452 (8) 450 (9) 255 (32) 213 (25) 196 (80) 105 (100) 77 (50)	1.05 (t, 3 H) 2.47 (dd, 2 H) 3.75 (q, 2 H) 4.15 (m, 1 H) 4.95 (d, 1 H) 7.63 (m, 14 H)
IIId	$C_{25}H_{22}O_3Cl_2$	114–116	15		442 (8) 440 (13) 245 (27) 203 (35) 196 (83) 105 (100) 77 (67)	0.99 (t, 3 H) 2.45 (dd, 2 H) 3.77 (q, 2 H) 4.15 (m, 1 H) 4.97 (d, 1 H; *J* = 11.3 Hz) 7.53 (m, 13 H)
IVd	$C_{25}H_{22}O_3Cl_2$	53–54	21	3	442 (7) 440 (12) 245 (25) 203 (37) 196 (80) 105 (100) 77 (63)	1.04 (t, 3 H) 2.45 (dd, 2 H) 3.82 (q, 2 H) 4.05 (m, 1 H) 4.99 (d, 1 H) 7.49 (m, 13 H)

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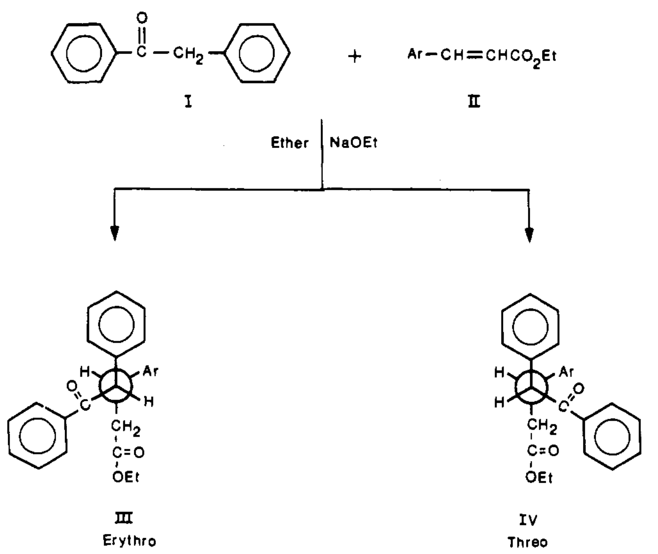
Scheme I



	Ar
a	4-CH$_3$·C$_6$H$_4$–
b	4-Cl·C$_6$H$_4$–
c	4-Br·C$_6$H$_4$–
d	2,4-dichlorophenyl

studied extensively in the literature (*5*). In some cases, both diastereomers have been isolated (*6*).

In the course of our study on the condensation reaction of α,β-unsaturated esters with active methylene compounds, we now report the condensation of α-phenylacetophenone with substituted ethyl cinnamates. These condensations yielded a mixture of erythro and threo isomers of ethyl 3-aryl-4,5-diphenyl-5-oxopentanoates, as shown in Scheme I. Similar to 1,2,3,5-tetraphenylpentane-1,5-dione (*7*), the erythro configurations (IIIa–d) were assigned to the high melting point esters and the threo configurations (IVa–d) to the low melting esters.

Experimental Section

Unless otherwise stated, IR spectra were measured with a Pye-Unicam SP 300 spectrophotometer for solutions in CHCl$_3$, ^{1}H NMR spectra were measured with a Brucker WP 80-SY spectrometer for solutions in deuterated chloroform containing tetramethylsilane as internal standard, and MS spectra were measured with a 7070-E VG analytical organic mass spectrometer. Compounds were analyzed at the M-H-W Laboratories, Phoenix, AZ. Melting points were determined with an electrothermal melting point apparatus and are uncorrected. Elemental analysis in agreement with theoretical values were obtained and submitted for review.

General Procedures. In each condensation, equimolar amounts of α-phenylacetophenone and substituted ethyl cinnamates were added successively to a suspension of sodium ethoxide in dry ether (150 mL). The mixture was kept at room temperature for 1–6 days and then poured into water (200 mL) and extracted with ether. The ethereal extract yielded a crude solid which after crystallization from ethanol afforded ethyl 3-aryl-4,5-diphenyl-5-oxopentanoates, the low melting point fraction (threo). The alkaline aqueous layer was acidified with dilute hydrochloric acid and extracted with ether and the ethereal extract was shaken with dilute sodium hydrogen carbonate solution. Evaporation of the ether yielded the second diastereomer of the high melting point (erythro) of ethyl 3-aryl-4,5-diphenyl-5-oxopentanoates. The infrared spectra of these esters showed a ketonic carbonyl stretching frequency in the range of 1670–1695 cm^{-1} in addition to an ester carbonyl stretching frequency in the range 1710–1735 cm^{-1}. The results are shown in Table I.

Registry No. I, 451-40-1; IIa, 20511-20-0; IIb, 6048-06-2; IIc, 15795-20-7; IId, 1504-68-3; IIIa, 102697-19-8; IIIb, 102697-21-2; IIIc, 102697-23-4; IIId, 102697-25-6; IVa, 102697-20-1; IVb, 102697-22-3; IVc, 102697-24-5; IVd, 102697-26-7.

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Reaction of 2′-Hydroxychalcone Dibromides with Me$_2$SO

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2′-Hydroxychalcone dibromides on treatment with Me$_2$SO gave 2′-hydroxychalcone, 2′-hydroxy-3′- or 2′-hydroxy-5′-bromochalcone, flavone, monobrominated flavone, 6,8-dibromoflavone, 3-bromoflavone, and 3-, 6-, or 8-dibromoflavone.

Several workers have used Me$_2$SO for the oxidation and also for oxidative halogenation (*1*, *2*). In the present communication, the action of Me$_2$SO on 2′-hydroxychalcone dibromides (**1**) is reported.

2′-Hydroxychalcone dibromides (**1a**) on heating with Me$_2$SO for 3 h gave **3b**, **2a**, **9b**, **8b**, **9c**, and **6a**; at room temperature the reaction products were **3b**, **2a**, and **6a**, **1d** with warm Me$_2$SO afforded **3e**, **9e**, **8e**, but, at room temperature, **3e** and

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