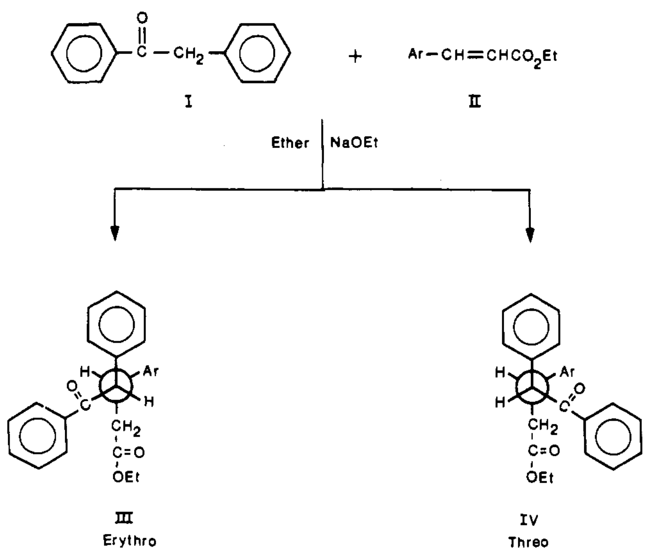
Scheme I



	Ar
a	4-$CH_3 \cdot C_6H_4$–
b	4-$Cl \cdot C_6H_4$–
c	4-$Br \cdot C_6H_4$–
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 $CHCl_3$, ^1H 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_2SO

N. Jagannadha Reddy,*[†] Sevak Ram Pawar, and Tarachand Sharma

School of Studies in Chemistry, Vikram University, Ujjain, India

John A. Donnelly

Chemistry Department, University College, Dublin 4, Ireland

2′-Hydroxychalcone dibromides on treatment with Me_2SO gave 2′-hydroxychalcone, 2′-hydroxy-3′- or 2′-hydroxy-5′-bromochalcone, flavone, monobrominated flavone, 6,6-dibromoflavone, 3-bromoflavone, and 3-, 6-, or 8-dibromoflavone.

Several workers have used Me_2SO for the oxidation and also for oxidative halogenation (*1*, *2*). In the present communication, the action of Me_2SO on 2′-hydroxychalcone dibromides (**1**) is reported.

2′-Hydroxychalcone dibromides (**1a**) on heating with Me_2SO 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_2SO afforded **3e**, **9e**, **8e**, but, at room temperature, **3e** and

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[†] Current address: KSP Road, Paloncha, Khammam Dt., AP 507 115, India.

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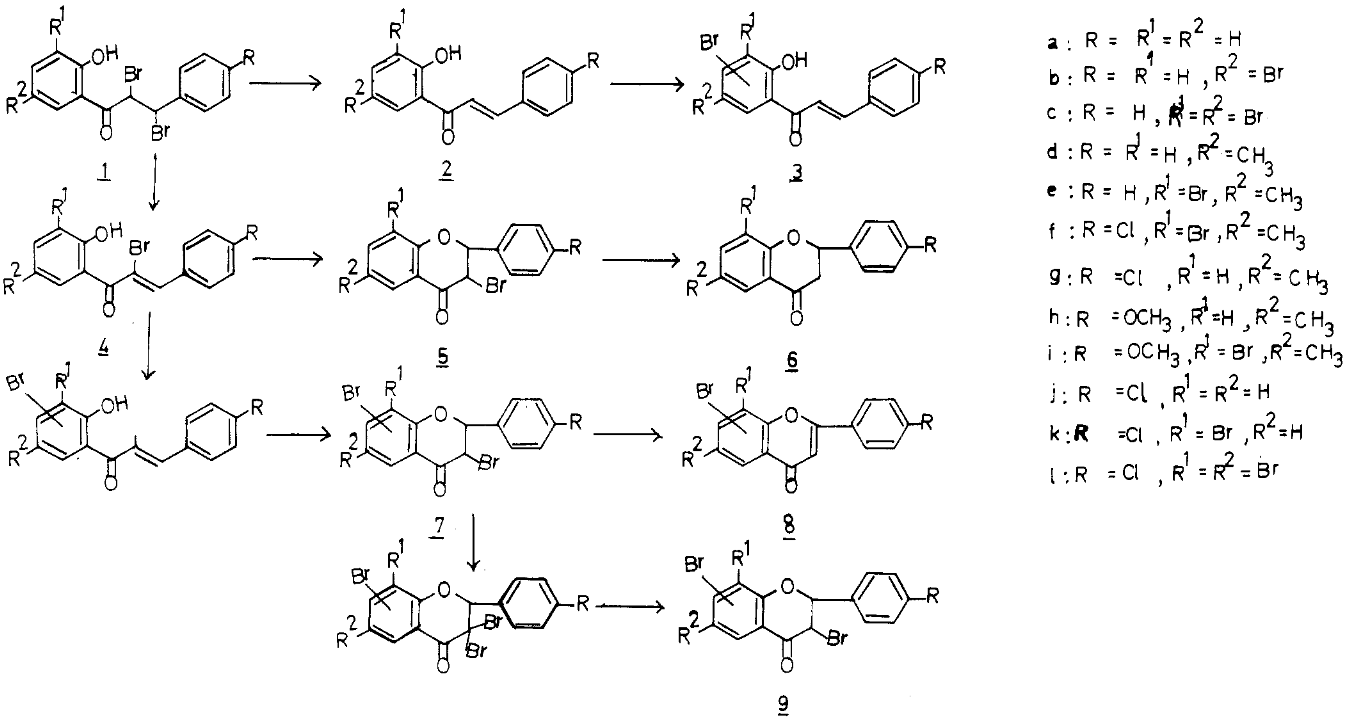
Table I. Reaction Products of Chalcone Dibromides with Me_2SO

compd	recrystn solvent	mp, °C (lit., °C)	nature	R	R^1	R^2	formula	NMR, δ
2a	EtOH	88–89 (89–90) (*4*)	yellow	H	H	H	$C_{15}H_{12}O_2$	7.6 (m, 11 H, aromatic and –CH═CH–), 13.2 (s, 1 H, –OH)
2g	EtOH	151–152 (151–153) (*5*)	yellow needles	Cl	H	CH_3	$C_{16}H_{13}ClO_2$	2.5 (s, 3 H, $-CH_3$), 7.54 (m, 9 H, aromatic and –CH═CH–), and 13.4 (s, 1 H, –OH)
2h	EtOH	99 (98–99) (*6*)	orange	OCH_3	H	CH_3	$C_{17}H_{16}O_3$	2.4 (s, 3 H, $-CH_3$), 3.85 (s, 3 H, $-OCH_3$), and 7.7 (m, 9 H, aromatic and –CH═CH–)
3b	EtOH	106 (106) (*7*)	yellow needles	H	H	Br	$C_{15}H_{11}BrO_2$	7.4 (m, 10 H, aromatic and –CH═CH–), 12.65 (s, 1 H, –OH)
3e	EtOH	108–109 (108) (*8*)	yellow needles	H	Br	CH_3	$C_{16}H_{13}BrO_2$	2.34 (s, 3 H, $-CH_3$), 7.7 (m, 9 H, aromatic and –CH═CH–), 13.4 (s, 1 H, –OH)
3f	EtOH	171–172	orange yellow needles	Cl	Br	CH_3	$C_{16}H_{12}BrClO_2$	9.3 (m, 9 H, aromatic and –CH═CH–), 15.8 (s, 1 H–OH), 2.1 (s, 3 H, $-CH_3$)
3i	EtOH	147–148	yellow	OCH_3	Br	CH_3	$C_{17}H_{15}BrO_3$	
3k	EtOH	189	yellow	Cl	Br	H	$C_{15}H_{10}BrClO_2$	9.3 (m, 9 H, aromatic and –CH═CH–), 15.8 (s, 1 H, –OH)
6a	benzene/petroleum ether	99 (99) (*9*)	white needles	H	H	H	$C_{15}H_{12}O_2$	6.6 (s, 1 H, H-3), 7.4 (m, 9 H, aromatic)
6g	benzene/petroleum ether	201–202	white needles	Cl	H	CH_3	$C_{16}H_{13}ClO_2$	2.49 (s, 3 H, $-CH_3$), 6.8 (s, 1 H, H-3), 7.8 (m, 7 H, aromatic)
6h	benzene/petroleum ether	168–169 (170) (*10*)	white needles	OCH_3	H	CH_3	$C_{17}H_{16}O_3$	2.45 (s, 3 H, $-CH_3$), 3.9 (s, 3 H, $-OCH_3$), 6.7 (s, 1 H, H-3), 7.6 (m, 7 H, aromatic)
8e	benzene/petroleum ether	181–182 (179) (*11*)	white crystals	H	Br	CH_3	$C_{16}H_{11}BrO_2$	2.32 (s, 3 H, $-CH_3$), 6.76 (s, 1 H, H-3), 7.8 (m, 7 H, aromatic)
8f	benzene/petroleum ether	220–222	white	Cl	Br	CH_3	$C_{16}H_{10}BrClO_2$	2.2 (s, 3 H, $-OCH_3$), 6.7 (s, 1 H, H-3), 7.5 (m, 6 H, aromatic)
8k	EtOH	235	white	Cl	Br	H	$C_{15}H_8BrClO_2$	6.79 (s, 1 H, H-3), 7.7 (m, 7 H, aromatic)
9b	EtOH	192–193	white	H	H	Br	$C_{15}H_{10}Br_2O_2$	7.6 (m, 7 H, aromatic), 8.4 (d, 1 H, H-5)
9c	EtOH	189–190	white	H	Br	Br	$C_{15}H_9Br_3O_2$	7.7 (m, 6 H, aromatic), 8.3 (d, 1 H, H-5)
9e	benzene/petroleum ether	232–233	white needles	H	Br	CH_3	$C_{16}H_{12}Br_2O_2$	2.4 (s, 3 H, $-CH_3$), 7.7 (m, 7 H, aromatic)
9f	benzene/petroleum ether	249–250	white needles	Cl	Br	CH_3	$C_{16}H_{11}Br_2ClO_2$	2.5 (s, 3 H, $-CH_3$), 7.7 (m, 6 H, aromatic)
9h	EtOH	136–137 (138) (*12*)	white needles	OCH_3	H	CH_3	$C_{17}H_{15}O_3Br$	2.4 (s, 3 H, $-CH_3$), 3.85 (s, 3 H, $-OCH_3$), 7.6 (m, 7 H, aromatic)
9l	benzene/petroleum ether	231	white	Cl	Br	Br	$C_{15}H_8Br_3ClO_2$	8.3 (d, 1 H, H-5), 8.0 (d, 1 H, H-7), 7.5 (m, 4 H, aromatic)

Scheme I



9e were formed (Scheme I). **1e** gave **8e** and **9e** on heating the reaction mixture and **8e**, **9e**, and **3e** at room temperature. On the other hand, **9f**, **6g**, **8f**, and **3f** were obtained from **1g** under hot condition; **2g** and **3f** were formed when the same reaction was performed at room temperature. **1h** gave **9h**, whereas, at room temperature the reaction products were **2h**, **3i**, in addition to **6h** and **9h**. In the case of **1i**, **8i** was the only product. **1j** gave **3k**, **8k**, **8i**, **9i**, and **6j** when the reaction mixture was heated for 3 h. Authentic samples of **2a**, **8b**, **6a**, **3e**, **8e**, **3f**, **6f**, **3i**, **8i**, and **6h** were prepared by the methods reported earlier (3).

Experimental Section

Melting points are uncorrected. Reaction mixtures were separated by column chromatography using silica gel and the purity was checked by thin-layer chromatography (TLC).

Reaction of 2'-Hydroxychalcone Dibromides (1a) with Me_2SO. (*a*) The chalcone dibromide (**1a**) in Me_2SO (20 mL) was heated on a water bath for 3 h and the reaction mixture was allowed to cool to room temperature. It was diluted with water and the precipitate was filtered off, washed with water, and dried. TLC showed six spots. By column chromatography **8b**, **9c**, **3b**, **6a**, and **2a** were separated using petroleum ether, benzene, and other as eluotropic solvents.

(*b*) A mixture of the chalcone dibromide (**1a**) and Me_2SO (20 mL) was kept at room temperature for 5 days. It was then worked up as described above to give **3b**, **2a**, and **6a**.

Similarly, the reactions of other chalcone dibromides (**1b**–**1**) with Me_2SO were carried out and data of the reaction products are given in Table I. Satisfactory C, H, and halogen analyses were obtained for all the compounds.

Registry No. **1a**, 39729-11-8; **1b**, 35820-37-2; **1c**, 10372-55-1; **1d**, 22219-26-7; **1e**, 29976-68-9; **1f**, 102260-70-8; **1g**, 75227-44-0; **1h**, 22129-40-4; **1i**, 29976-70-3; **1j**, 43016-14-4; **1k**, 102260-69-5; **1l**, 75767-98-5; **2a**, 1214-47-7; **2g**, 16635-10-2; **2h**, 16635-13-5; **3b**, 1218-22-0; **3e**, 29976-64-5; **3f**, 102260-59-3; **3i**, 29976-66-7; **3k**, 102260-60-6; **6a**, 487-26-3; **6g**, 14166-18-6; **6h**, 102260-61-7; **8e**, 29976-76-9; **8f**, 102260-62-8; **8k**, 102260-63-9; **9b**, 102260-64-0; **9c**, 102280-65-1; **9e**, 102260-66-2; **9f**, 102260-67-3; **9h**, 72149-92-9; **9i**, 102260-68-4; Me_2SO, 67-68-5.

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Reaction of Acetylenedicarboxaldehyde Bis(diethyl acetal) with Bis(azidomethyl)benzene

Sultan T. Abu-Orabi*

Chemistry Department, Yarmouk University, Irbid, Jordan

Robert E. Harmon

Chemistry Department, Western Michigan University, Kalamazoo, Michigan 49001

Three 1,1'-[phenylenebis(methylene)]bis(triazole-4,5-dicarboxaldehyde) tetrakis(ethyl acetals) (IIIa–c) were synthesized by the condensation of acetylenedicarboxaldehyde bis(diethyl acetal) with 1,2-, and 1,3-, and 1,4-bis(azidomethyl)benzene.

In continuation of our previous work on the condensation reaction of 1-benzyl-1*H*-triazole-4,5-dicarboxaldehyde with cyclic ketones to form polymethylene-bridged benzyl triazoletropones (*1*), we report in the present paper details on the preparation of the three bis(azidomethyl)benzenes (IIa–c) and on their reactions with acetylenedicarboxaldehyde bis(diethyl acetal) to give the phenylenebis(methylene)bis(triazole-4,5-dicarboxaldehyde) tetrakis(ethyl acetals) (IIIa–c). (See Scheme I.)

Experimental Section

Acetylenedicarboxaldehyde bis(diethyl acetal) was prepared from acetylene gas and triethyl orthoformate by the method described by Whol (*2*). Melting points were determined by using a Thomas-Hoover Unimelt instrument and are uncorrected. The nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer using tetramethylsilane as an internal reference, and shifts (δ) are reported in ppm.

Preparation of the Bis(azidomethyl)benzene (IIa–c). To a solution of 13.0 g (0.2 mol) of sodium azide in 70 mL of water and 70 mL of methanol was added 17.5 g (0.1 mol) of the bis(chloromethyl)benzene. The mixture was heated in a bomb flask at 100 °C for 2 days. The methanol was removed on a rotary evaporator at diminished pressure. The residue was

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