(lit.[21] m.p. 155°). Fraction iii was found to be pure by v.p.c. and was analyzed as V [lit.[22] b.p. 129–130° (1 mm.)].

Anal. Calcd. for $C_{19}H_{29}NO_4$: C, 74.58; H, 8.47; N, 7.91. Found: C, 73.91; H, 8.56; N, 7.63.

The semicarbazone of V melted at 160° (lit.[22] m.p. 158°).

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The Acyloin Condensation. II. The Conjugate Addition of Some α,β-Unsaturated Esters Followed by a Dieckmann Cyclization[1]

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The acyloin-type condensation with ethyl *p*-methylcinnamate, ethyl *o*-chlorocinnamate, and ethyl *p*-chlorocinnamate gave the respective phenyl-substituted cyclopentane carboxylic acid, ethyl 5-oxo-2,3-diphenylcyclopentane carboxylate, when refluxed with sodium in ether. These were hydrolyzed, respectively, with 48% hydrobromic acid and 10% sodium hydroxide to give the respective diphenyl-substituted cyclopentanones and the diphenyl-substituted adipic acids. The treatment of the following esters of cinnamic acids, *n*-propyl, *n*-butyl, *n*-amyl, isopropyl, isobutyl, isoamyl, *sec*-butyl, *t*-butyl, cyclohexyl, benzyl, and β-phenylethyl, with sodium in ether gave the corresponding 5-oxo-2,3-diphenylcyclopentane carboxylic acid esters. The course of these reactions and products, respectively corresponded to the course of the reactions and products obtained with ethyl cinnamate.[3]

The need for certain starting compounds for the syntheses of potential physiologically active compounds inspired this work. The acyloin condensation with α,β-unsaturated esters of the cinnamic acid variety have been shown to proceed by way of conjugate addition followed by a Dieckmann ring closure.[3–5] The results obtained in this work extend the generality of this reaction.

Ethyl *p*-methylcinnamate, ethyl *o*-chlorocinnamate, and ethyl *p*-chlorocinnamate were prepared by the Claisen condensation by the treatment of the respective aldehydes with ethyl acetate and sodium.[6] The acyloin-type condensation was carried out by refluxing the esters with powdered sodium in dry ether. Ethyl *p*-methylcinnamate gave a 25% yield of the condensation product. Ethyl *o*-chlorocinnamate and ethyl *p*-chlorocinnamate gave 9% yields of the corresponding condensation products. In consideration of the evidence for the proposed mechanism for this reaction,[3,5] ethyl cinnamate with a methyl substituent in the *ortho* or *para* position in the phenyl moiety would be expected to give a higher yield of the condensation product I than the unsubstituted ethyl cinnamate, as a positive methyl group would be expected to enhance the electron density of the carbonyl oxygen in the cinnamate ester, facilitating reduction by sodium and thus favoring the increase of the yield of I. The yield was found to be slightly higher. Ethyl cinnamate in this reaction gave a 20% yield of the corresponding product.[7] The chloro substituent being a negative group would be expected to decrease the electron density on the carbonyl oxygen of the cinnamate ester making reduction by sodium more difficult, and thus favoring lower yields of II and III. This was found to be the case.

The structures for I, II, and III were demonstrated by their analysis, acid hydrolysis and basic hydrolysis products, and their characteristic infrared spectra (see Table I).

Although for compounds VIII and IX, the carbon and hydrogen values were high and the chlorine values were low, the correct values of carbon, hydrogen, and chlorine for compounds II and III together with the infrared spectra of VIII and IX help to make these values acceptable.

The 2-carbethoxycyclopentanone group has been shown to absorb strongly in the carbonyl region giving a very characteristic doublet at about 5.7–5.8 μ.[3] Compounds I, II, and III absorbed strongly in the carbonyl region, giving a doublet at 5.72–5.83 μ. The hydrolysis products gave absorption maxima in the infrared region characteristic of ketones and dibasic acids.

The preparation of compounds X through XX was important for finding if the ester group in the α,β-unsaturated ester would affect the yield of the 5-oxo-2,3-diphenylcyclopentane carboxylic acid nucleus in the acyloin-type condensation, and also to produce model compounds of this class to learn if large ester groups in these β-keto esters would decrease ring opening by basic reagents in the syntheses of pyrimidines.

No complete uniform effect regarding yields could be observed; however, yields of 24, 31, 35, and 41% were obtained, respectively, from the butyl, isoamyl, isobutyl, and cyclohexyl cinnamic esters, while the ethyl ester gave a 20% yield.[3,7]

The evidence for the demonstration of the structures of the compounds X through XX was furnished by their carbon and hydrogen analyses and their infrared spectra (see Table II). Compounds X through XX absorbed strongly at about 5.7–5.8 μ, giving a doublet.

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(2) Taken in part from theses submitted to North Carolina College in partial fulfillment of the requirements for M.S. degrees, June 1962, by G R. Kilpatrick and, June 1963, by N. Horton and S. A. Blakeney.

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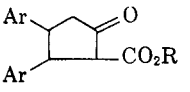
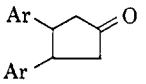
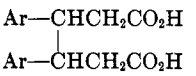
(7) We wish to report a correction: the yield of 2-carbethoxy-3,4-diphenylcyclopentanone[3] was 20%, not 10%.

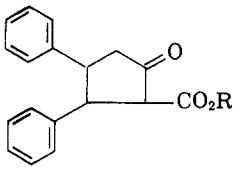
TABLE I

Compd.	Structure	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% Cl Calcd.	% Cl Found	M.p., °C.	% yield	λ_{max}, μ	Recrystn. solvent
												
I	Ar = *p*-tolyl	$C_{32}H_{34}O_3$	78.54	78.32	7.19	7.27			99–100	25	5.72–5.83	Ether
Ia	Oxime of I	$C_{32}H_{35}NO_3$	74.96	75.18	7.25	7.17			132–133			Alc. and H_2O
II	Ar = *o*-chlorophenyl	$C_{30}H_{18}Cl_2O_3$	63.67	63.36	4.81	5.00	18.80	18.77	116–117	9	5.75–5.83	Ether
III	Ar = *p*-chlorophenyl	$C_{30}H_{18}Cl_2O_3$	63.67	63.94	4.81	4.98	18.80	17.96	129–130	9	5.72–5.83	Ether
												
IV	Ar = *p*-tolyl	$C_{19}H_{20}O$	86.32	85.87	7.63	7.49			80	Quant.	5.83	2-Ethoxyethanol–acetone, 1:1
V	Ar = *o*-chlorophenyl	$C_{17}H_{14}Cl_2O$	66.90	66.95	4.62	4.56	23.24	22.75	94–95	Quant.	5.76	2-Ethoxyethanol, acetone, and H_2O
VI	Ar = *p*-chlorophenyl	$C_{17}H_{14}Cl_2O$	66.90	66.48	4.62	5.45	23.24	23.50	93	Quant.	5.8	2-Ethoxyethanol, acetone, and H_2O
												
VII	Ar = *p*-tolyl	$C_{20}H_{22}O_4$	73.59	73.73	6.79	6.94			245[a]	Quant.	2.9–3.45 5.85–5.92	Alc. and H_2O
VIII	Ar = *o*-chlorophenyl	$C_{18}H_{16}Cl_2O_4$	58.87	59.17	4.39	4.98	19.32	18.69	189	Quant.	2.95–3.85 5.85–5.92	Alc. and H_2O
IX	Ar = *p*-chlorophenyl	$C_{18}H_{16}Cl_2O_4$	58.87	60.53	4.39	4.65	19.32	18.57	280[a]	Quant.	2.95–3.85 5.85–6.92	Alc. and H_2O

[a] Sublimed.

TABLE II

5-OXO-2,3-DIPHENYLCYCLOPENTANE CARBOXYLIC ACID ALKYL ESTERS



Compd.	R	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	M.p., °C.	% yield	λ_{max}, μ	Recrystn. solvent
X	*m*-Propyl	$C_{21}H_{22}O_3$	78.23	78.40	6.88	6.89	95–96	17	5.7–5.8	Alc. and H_2O
XI	*m*-Butyl	$C_{22}H_{24}O_3$	78.54	78.38	7.19	7.31	110–111	24	5.7–5.8	Alc. and H_2O
XII	Isobutyl	$C_{22}H_{24}O_3$	78.54	78.66	7.19	7.36	127–128	35	5.7–5.8	Alc. and H_2O
XIII	*n*-Amyl	$C_{23}H_{26}O_3$	78.82	78.98	7.48	7.61	95–96	18	5.69–5.79	Alc. and H_2O
XIV	Cyclohexyl	$C_{24}H_{26}O_3$	79.52	78.79	7.23	7.53	164–165	41	5.7–5.82	2-Ethoxyethanol
XV	Isoamyl	$C_{23}H_{26}O_3$	78.82	78.67	7.48	7.38	107–108	31	5.7–5.8	Alc. and H_2O
XVI	Benzyl	$C_{25}H_{22}O_3$	81.05	81.03	5.99	6.22	100–101	9	5.7–5.79	95% alc.
XVII	Isopropyl	$C_{21}H_{22}O_3$	78.23	78.42	6.88	7.02	107–108	15	5.7–5.8	59% alc.
XVIII	*sec*-Butyl	$C_{22}H_{24}O_3$	78.54		7.19		111–112	27	5.7–5.82	95% alc.
XIX	*t*-Butyl	$C_{22}H_{24}O_3$	78.54	78.02	7.19	7.10	140–141	12	5.7–5.8	95% alc.
XX	Phenylethyl	$C_{26}H_{24}O_3$	81.21	81.45	6.29	6.40	107	13	5.72–5.83	Petr. ether (30–60°)

Experimental[8]

The procedure described for the syntheses of I is general and was used to prepare the condensation products described in this work.

Ethyl 5-Oxo-2,3-di-*p*-tolylcyclopentane Carboxylate (I).—In a three-necked flask, 23.48 g. (1.03 g.-atoms) of freshly powdered sodium and 190.10 g. (1.00 mole) of ethyl *p*-methylcinnamate in 900 ml. of dry ether was stirred and refluxed for 5 hr. after the dropwise addition of the ester which took a period of 3 hr. The reaction mixture, a dark slurry, was cooled in an ice bath and carefully acidified with 37% H_2SO_4, which was added from a dropping funnel with stirring. The ether layer was separated, the aqueous layer was extracted with 100 ml. of ether, and the ether layers were combined. The combined ether layers were washed successively with four 50-ml. portions of 20% Na_2CO_3 solution and then with 100 ml. of water. The ether layer was dried over 100 g. of anhydrous $MgSO_4$. The filtered dry ether solution was concentrated to about 100 ml. and placed in the deepfreeze and allowed to remain for 3 hr. A practically pure product separated which weighed 42.4 g., a yield of 25% of theory. Recrystallization from ether gave a pure product which melted at 99–100°.

The acid hydrolysis and decarboxylation of I, II, and III were effected as described for the preparation of IV.

3,4-Di-*p*-tolylcyclopentanone (IV).—One gram of I was refluxed in 50 ml. of 48% HBr for 1 hr. The dark amorphous precipitate which formed was purified from 2-ethoxyethanol–acetone, 1:1, and water. The pure product melted at 80°.

The basic hydrolysis of I, II, and III was effected as described for the preparation of VII.

3,4-Di-*p*-tolyladipic Acid (VII).—One gram of I was refluxed in 50 ml. of 10% NaOH for 1 hr. The solution was cooled and acidified with dilute HCl, and the product was purified from hot alcohol and water. The pure product sublimed at 245°.

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(8) (a) Melting points were taken on a Fisher-Johns apparatus. (b) Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.