[CONTRIBUTION FROM THE RESEARCH LABORATORIES, NATIONAL DRUG CO.]

Derivatives of 1,4-Benzodioxan. II.[1,2]
3-Methyl-1,4-benzodioxan-2-carboxamides and Corresponding Amines

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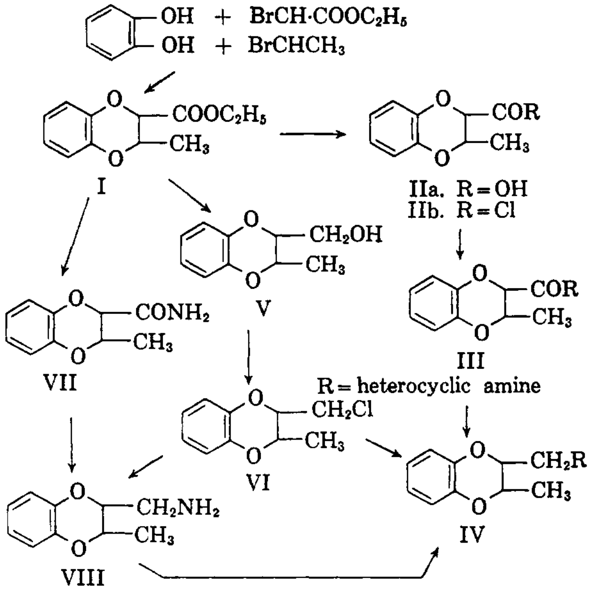
The syntheses of a series of 3-methyl-1,4-benzodioxan-2-carboxamides (III) and of their corresponding amines (IVa) are reported. Two alternative routes in the preparation of *N*-substituted 2-aminomethyl-3-methyl-1,4-benzodioxans (IVb and IVc) are also described. The lithium aluminum hydride reduction of benzodioxancarboxamides (III, VII, and IXa) to the corresponding amines (IVa, VIII, and Xa) offers a new and improved method for the synthesis of compounds of this type.

In the first publication[1] of this series, a new synthesis of 1,4-benzodioxan derivatives, chiefly the 2-carboxamides, was described. As a continuing effort in the search for new therapeutic agents from compounds of this type, it became interesting to synthesize 3-methyl-1,4-benzodioxan-2-carboxamides and their corresponding amines for pharmacological evaluation. Also, subsequent reports that benzodioxan derivatives were found to possess potential central nervous depressing[4] and orally effective adrenergic blocking activities[5] prompted an extensive study of compounds in this field.

Ethyl 3-methyl-1,4-benzodioxan-2-carboxylate (I) was prepared according to the method[1] given for ethyl 1,4-benzodioxan-2-carboxylate by condensation of ethyl α,β-dibromobutyrate, instead of ethyl α,β-dibromopropionate, with catechol in the presence of anhydrous potassium carbonate. However, it was not surprising that the yield (30%) of I was considerably lower than that of its nonmethyl substituted analog (76%).

In order to obtain an excellent yield (90%) of 3-methyl-1,4-benzodioxancarboxylic acid (IIa), it was found necessary to saponify the ester I carefully under very mild conditions. Otherwise, the yield of the acid was greatly decreased. Treatment of the acid (IIa) with thionyl chloride afforded the acid chloride (IIb), which upon reaction with heterocyclic amines smoothly produced, in good yields, the amides (III) which are listed in Table I. Lithium aluminum hydride reduction of the amides (III) promptly formed the corresponding 3-methyl-1,4-benzodioxan-2-ylmethylamines (IVa), which are listed in Table II. In fact, in earlier experiments, several 1,4-benzodioxan-2-carboxamides[1] (IXa) were similarly reduced to amines (Xa), which are listed in Table III, in satisfactory yields. This process seemed to offer a new and general route to the synthesis of aminomethylbenzodioxans. Some of the above amides and amines yielded two diastereoisomers, which were separated by fractional crystallization whenever possible.



IVa. R = heterocyclic amine
IVb. R = $NHCH_2CON(C_2H_5)_2$
IVc. R = $NHCH_2CONHCH(CH_3)_2$

IXa. R = heterocyclic amine
IXb. R = NH_2

Xa. R = heterocyclic amine
Xb. R = NH_2

By another route, lithium aluminum hydride reduction of the ester I afforded two isomers of 2-hydroxymethyl-3-methyl-1,4-benzodioxan (V). The yield of one, melting at 94–95°, was 33%, and the second, boiling at 107–109°/0.1 mm., was 37%. However, treatment of either of the isomers of V with thionyl chloride in pyridine provided the same 2-chloromethyl-3-methyl-1,4-benzodioxan (VI). Subsequently, *N*,*N*-diethyl-(3-methyl-1,4-benzodioxan-2-ylmethylamino)acetamide (IVb) was ob-

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(1) For the preceding article of this series see J. Koo, S. Avakion, and G. J. Martin, *J. Am. Chem. Soc.*, **77**, 5373 (1955).

(2) Part of this work has been published in preliminary form; J. Koo, *et al.*, *Chem. and Ind.*, 832 (1958).

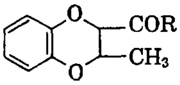
(3) Present address: Geigy Research Laboratories, Ardsley, N. Y.

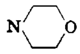
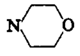
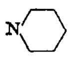
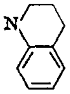
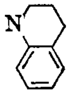
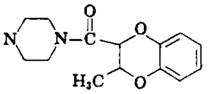
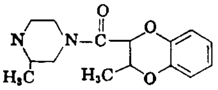
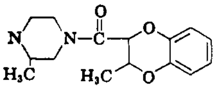
(4) J. Mills, M. M. Boren, W. E. Buting, W. N. Cannon, and M. J. Martell, Abstracts, 132nd Meeting, *Am. Chem. Soc.*, New York, September 1957, 7-O.

(5) G. V. Rossi and T. H. F. Smith, *J. Am. Pharm. Assoc.*, **46**, 472 (1957).

TABLE I

3-METHYL-1,4-BENZODIOXAN-2-CARBOXAMIDES



R	M.P.	Yield, %	Recryst. from	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
	125–126	52[a]	Ethanol-water	$C_{14}H_{17}O_4N$	5.32	5.41				
 (High melting isomer)	132–133	28[a]	Ethanol-water	$C_{14}H_{17}O_4N$	5.32	5.15				
	95–96	14[d]	Ethanol-water	$C_{15}H_{17}O_3N$	5.36	5.28				
	86–88	58[b]	Ethanol-water	$C_{19}H_{19}O_3N$	4.53	4.47	73.76	74.74	6.19	6.25
 (High melting isomer)	128–130	40[b]	Ethanol	$C_{19}H_{19}O_3N$	4.53	4.29	73.76	73.51	6.19	6.34
	206–208	28	Benzene	$C_{24}H_{26}O_6N_2$	6.39	6.41				
	196–200	51[c]	Benzene-ligroin	$C_{25}H_{28}O_6N_2$	6.19	6.16				
 (High melting isomer)	235–236	12[c]	Benzene	$C_{25}H_{28}O_6N_2$	6.19	6.16				

[a] The combined yield of the two isomers was 80%; [b] 98%; [c] 63%. [d] Evidence indicated that another low melting isomer existed, which was not purified. Thus, the combined yield of the two isomers should be considerably higher.

tained by heating the chloride VI with glycine *N*,*N*-diethylamide around a temperature of 140°.

Alternatively, when the ester I was mixed with concentrated aqueous ammonia-ethanol at room temperature, it yielded smoothly the 3-methyl-1,4-benzodioxan-2-carboxamide (VII), which, upon reduction with lithium aluminum hydride, readily provided the corresponding amine VIII as a colorless oil in 70% yield. Its hydrochloride was obtained and separated in two isomers, one melting at 205–207°; the other at 178–180°. Earlier, the 2-aminomethyl–1,4-benzodioxan (Xb) a key intermediate in this series, was formed in higher yield (82%) by reduction of its corresponding amide (IXb) in a similar manner.

Bovet and coworkers[6] prepared 2-aminomethyl-1-4-benzodioxan in low yields by prolonged heating of 2-chloromethyl-1,4-benzodioxan with alcoholic ammonia or gaseous ammonia under pressure. According to this procedure, 2-aminomethyl-3-methyl-1, 4-benzodioxan (VIII) was also obtained in low yield (21%) and with some difficulty by the reaction of 2-chloromethyl-3-methyl-1,-4-benzodioxan (VI) with alcoholic ammonia. Therefore, our application of lithium aluminum hydride reduction to produce 2-aminomethyl-1, 4-benzodioxans seemed superior because of easier operation and considerably higher yields.

Finally, condensation of the amine VIII with *N*-isopropylchloroacetamide afforded the *N*-isopropyl-(3-methyl-1,4-benzodioxan-2-ylmethylamino)acetamide (IVc) as a thick lemon oil in 65% yield.

EXPERIMENTAL[7]

Ethyl 3-methyl-1,4-benzodioxan-2-carboxylate (I). Anhydrous potassium carbonate (200 g.) was added in portions to a stirred solution of 220 g. of catechol in 800 ml. of dry acetone followed by the dropwise addition of 137.5 g. of ethyl 2,3-dibromobutyrate. Another 200 g. of potassium carbonate and 137.5 g. of the dibromoester were added similarly and this was repeated twice more using a total of 800 g. of potassium carbonate and 550 g. of ester. Stirring and refluxing was continued for another 15 hr. The reaction mixture was then filtered and the solid washed several times with acetone. The filtrate was concentrated to about

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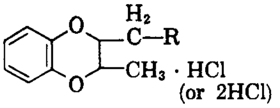
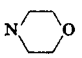
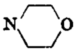
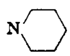
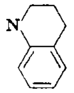
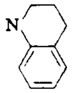
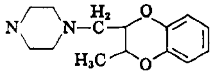
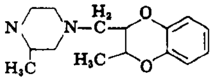
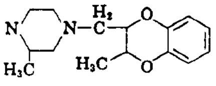
[6] G. B. Marini-Betolo, R. Landi-Victory and D. Bovet, *Gass. Chim. Ital.*, **83**, 144 (1953).

[7] All melting and boiling points are uncorrected.

TABLE II

3-METHYL-1,4-BENZODIOXAN-2-YLMETHYLAMINE HYDROCHLORIDES



R	M.P.	Yield, %	Recryst. from	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chloride, % Calcd.	Chloride, % Found
	228–229	27[a]	Ethanol-ether	$C_{14}H_{20}O_3NCl$	4.90	4.84	12.41	12.61
 (High melting isomer)	252–253	51[a]	Ethanol	$C_{14}H_{20}O_3NCl$	4.90	4.90	12.41	12.54
	205–207	59[b]	Ethanol-ether	$C_{15}H_{22}O_2NCl$	4.94	4.81	12.49	12.67
 (High melting isomer)	257–258	23[b]	Ethanol	$C_{15}H_{22}O_2NCl$	4.94	4.74	12.49	12.55
	142–143	37[c]	Ethanol-ether	$C_{19}H_{22}O_2NCl$	4.22	4.33	10.69	10.80
 (High melting isomer)	184–185	10[c]	Ethanol-ether	$C_{19}H_{22}O_2NCl$	4.22	4.29	10.69	10.78
	315 dec.	47	Water	$C_{24}H_{33}O_4N_2Cl_2$	5.80	5.75		
	250–255	33[d]	Ethanol-ether	$C_{25}H_{34}O_4N_2Cl_2$	5.63	5.44		
 (High melting isomer)	278–280	18[d]	Ethanol-ether	$C_{25}H_{34}O_4N_2Cl_2$	5.63	5.49		

[a] The combined yield of the two isomers was 78%; [b] 82%; [c] 47%; and [d] 51%.

300 ml. and the residue was diluted with 400 ml. of cold water. The oil layer was separated from the aqueous layer, the latter which was extracted repeatedly with ether. The combined oil layer and ether extracts were washed with water, dried over magnesium sulfate, and evaporated. The dark residue was distilled at 96–97° (0.1 mm.) to yield 135 g. (30%) of ester I as a colorless oil, n_D^{25} 1.5157.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.39; H, 6.31.

3-Methyl-1,4-benzodioxan-2-carboxylic acid (IIa). A mixture of 90 g. of ester I, 100 ml. of ethanol, and 250 ml. of 10% sodium hydroxide was gently heated on a steam bath with stirring until the internal temperature was around 65°. At this point, a dark but clear solution resulted. Cracked ice was added to the alkaline solution, which was then acidified with hydrochloric acid. Upon cooling, the acid which separated was filtered and dried, yield 71 g. (91%), m.p. 126–129°. A small portion was recrystallized from dilute ethanol to give colorless fine needles, m.p. 130–131°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.05; H, 5.26.

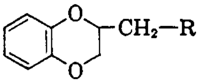
3-Methyl-1,4-benzodioxan-2-carbonyl chloride (IIb). Thionyl chloride (20 g.) was added to a solution of 10 g. of acid IIa in 60 ml. of dry benzene and the solution was gently heated on steam bath for 1 hr. The excess of thionyl chloride and benzene was evaporated under reduced pressure. Dry benzene, 50 ml., was added to the residue and then evaporated as before and this operation was repeated twice more. The yield of crude acid chloride as a dark oil was 9.3 g. (85%)-which was not further purified but used for the next reaction.

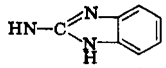
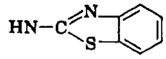
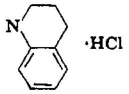
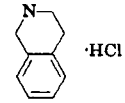
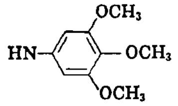
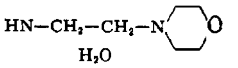
Preparation of 3-methyl-1,4-benzodioxan-2-carboxamides (III. R = A heterocyclic amine listed in Table I). The acylation of heterocyclic amines with 3-methyl-1,4-benzodioxan-2-carbonyl chloride is illustrated by the preparation of *4-(3-methyl-1,4-benzodioxan-2-carbonyl)morpholine.* The chloride (9.3 g.) from the above experiment in 30 ml. of benzene was added dropwise to 12 g. of morpholine in 60 ml. of benzene with stirring and refluxing for 3 hr. The salt which separated was filtered off and the benzene solution was washed with dilute sodium hydroxide solution, then with dilute hydrochloric acid, and finally with water. The benzene was dried, evaporated to about 50 ml., and petroleum ether (b.p. 00–00°) was added. The colorless material formed was filtered, weighing 6.1 g., m.p. 117–120°. It was recrystallized from dilute ethanol to give colorless fine needles, m.p. 125–126°. Evaporation of the benzene-petroleum ether filtrate yielded a solid, 3 g., m.p. 125–129°. Recrystallization twice from dilute ethanol gave the higher melting isomer, m.p. 132–133°. The combined yield of two isomers was 79%.

Lithium aluminum hydride reduction of 1,4-benzodioxan-2-carboxamides (III *and* IXa) *to the corresponding amines* (IVa *and* Xa, *R = a heterocyclic amine listed in* Table II *and* III). The reduction of 1,4-benzodioxan-2-carboxamides and 3-methyl analogs to the corresponding amines is illus-

TABLE III

1,4-Benzodioxan-2-ylmethylamines



R	M.P.	Yield, %	Recryst. from	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chloride, % Calcd.	Chloride, % Found
	200–201	75	Ethanol	$C_{16}H_{15}O_2N_3$	14.94	14.82		
	147–149	75	Benzene-ligroin	$C_{16}H_{14}O_2N_2S$	9.39	9.07		
	159–161	72	Ethanol-ether	$C_{12}H_{20}O_2NCl$	4.41	4.36	11.16	11.25
	239–241	79	Ethanol	$C_{18}H_{20}O_2NCl$	4.41	4.30	11.16	11.22
	99–101	59	Ether-petroleum ether (b.p. 00–00°)	$C_{18}H_{21}O_5N$	4.23	4.10		
	65–66	95	Ethyl acetate–ethanol	$C_{15}H_{22}O_3N_2H_2O$	9.46	9.43		

trated by the preparation of *4-(3-methyl-1,4-benzodioxan-2-ylmethyl)morpholine hydrochloride.* A solution of 8 g. of 4-(3-methyl-1,4-benzodioxan-2-ylcarbonyl)morpholine (a mixture of isomers) in ether was added dropwise to a mixture of 5 g. of lithium aluminum hydride in 200 ml. of ether with stirring and refluxing during a period of 5 hr. The reaction mixture was then decomposed with 20 ml. of ethyl acetate followed by 200 ml. of 20% sodium potassium tartrate solution. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether extracts was washed twice with water, dried, and evaporated. The oil residue which failed to crystallize was dissolved in 200 ml. of dry ether and hydrogen chloride gas was introduced. The colorless precipitate which separated was filtered and dried. The crude product was recrystallized once from absolute ethanol to give 4.3 g. of colorless needles, m.p. 252–253°. Absolute ether was added to the ethanolic filtrate and 2.3 g. of the second isomer was obtained, m.p. 228–229°. *The combined yield of two isomers was 88%.*

2-Hydroxymethyl-3-methyl-1,4-benzodioxan (V). Eighty grams of the ester I was added dropwise to a well stirred suspension of 15 g. of lithium aluminum hydride in 500 ml. of dry ether. The reaction mixture was stirred and refluxed for 5 hr., cooled, and then decomposed by adding 60 ml. of ethyl acetate dropwise, followed by 600 ml. of 20% sodium potassium tartrate. The ether layer was separated from the aqueous layer which was extracted several times with ether. The combined oil layer and extracts was washed with 5% sodium bicarbonate solution, then with water, dried over magnesium sulfate, and evaporated. The residue, which was partially solid, was recrystallized from benzene–petroleum ether to give 21.5 g. (33%) of colorless needles, m.p. 94–95°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.74; H, 6.48.

The filtrate contained the other diastereoisomer, an oil, b.p. 107–109° (0.1 mm.) and weighing 24 g. (37%).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.79; H, 6.88.

2-Chloromethyl-3-methyl-1,4-benzodioxan (VI). Thirty-five milliliters of thionyl chloride was added dropwise to a stirred and cooled solution of 23 g. of V (the low melting isomer) in 100 ml. of benzene containing 30 ml. of dry pyridine. The next day the mixture was poured onto chopped ice and extracted with ether. The ether solution was washed with dilute sodium bicarbonate solution and then with water, dried over anhydrous sodium sulfate, and evaporated. The residue was distilled to yield 12 g. (47%) colorless oil, b.p. 86–88° (0.1 mm.).

In another experiment the higher melting isomer of V was used and the same chloride was obtained.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: Cl, 17.85. Found: Cl, 17.74.

N,N-Diethyl(3-methyl-1,4-benzodioxan-2-ylmethylamino)-acetamide (IVb). A mixture of 9.5 g. of 2-chloromethyl-3-methyl-1,4-benzodioxan and 30 g. of aminodiethylacetamide was heated in an oil bath at 135–145° for 16 hr. The dark red paste was diluted with ice water and the oil that separated was extracted with ether. The ether extracts were washed with cold water, dried, and evaporated. The red oil residue, 12 g., was distilled at 173–175°/0.1 mm. to give the thick pale yellow oil. The yield was 9.5 g. (67%).

Anal. Calcd. for $C_{16}H_{24}O_3N_2$: N, 9.58. Found: N, 9.71.

3-Methyl-1,4-benzodioxan-2-carboxamide (VII). To a mixture of 36 g. of ethyl 3-methyl-1,4-benzodioxan-2-carboxylate and 150 ml. of concd. aqueous ammonia in a glass stoppered flask ethanol was gradually added with shaking until a clear solution resulted. It was allowed to stand at room temperature for 4 days with occasional shaking. Evaporation of most of the excess ammonium hydroxide and ethanol and cooling the flask caused a light pink product to separate. It was filtered, washed with cold water, and dried, weighing 25 g. (80%), m.p. 120–135°. The material was then recrystallized from dilute ethanol to give colorless needles which started to melt at 125° but which would not become a clear solution until 140°. Presumably, it was a mixture of isomers.

Anal. Calcd. for $C_{10}H_{11}O_3N$: N, 7.25. Found: N, 7.21.

2-Aminomethyl-3-methyl-1,4-benzodioxan (VIII). (*a*) *By lithium aluminum hydride reduction of the amide* VII. Twenty grams of VII (isomer mixture) was added portionwise to a well stirred suspension of 6 g. of lithium aluminum hydride in 400 ml. of dry ether. The mixture was stirred and refluxed for 8 hr. and then allowed to stand overnight. It was decomposed by the dropwise addition of 30 ml. of ethyl acetate followed by 300 ml. of 20% sodium potassium tartrate solution. The ether layer was separated from the aqueous layer, which was extracted twice with ether. The combined oil and ether extracts were washed with water, dried and evaporated. The residue was distilled at 95–96 (0.1 mm.) to give 12.5 g. (70%) of a colorless oil, n_D^{30} 1.5430.

Anal. Calcd. for $C_{10}H_{13}NO_2$: N, 7.82. Found: N, 7.84.

The *hydrochloride* salt was recrystallized from absolute ethanol to give a colorless material, m.p. 205–207°.

Anal. Calcd. for $C_{16}H_{14}O_2NCl$: N, 6.49. Found: N, 6.49.

Addition of ether to the above ethanol filtrate caused an isomer of the hydrochloride salt to separate, which after recrystallization from absolute ethanol and ether, melted at 178–180°.

Anal. Calcd. for $C_{10}H_{14}O_2N$: N, 6.49. Found: N, 6.49.

(*b*) *By the reaction of chloride* VI *with ammonia.* According to the procedure of Martini-Betolo, Landi-Victory and Bovet[6] heating 2-chloromethyl-3-methyl-1,4-benzodioxan with 12% ethanolic ammonia at 120° for 12 hr., provided an oily product, b.p. 95–97° (0.1 mm.), n_D^{30} 1.5435, in 21% yield.

Anal. Calcd. for $C_{10}H_{13}O_2N$: N, 7.82. Found. N, 7.76.

2-Aminomethyl-1,4-benzodioxan (Xb). This compound was obtained by lithium aluminum hydride reduction of 1,4-benzodioxan-2-carboxamide (IXb) in a similar manner as that of VIII. Starting with 24 g. of amide, 19 g. (82%) of pure product was provided as a colorless liquid, b.p. 82–83° (0.75 mm.), n_D^{25} 1.5554. The reported[6] b.p. 127–137° (4 mm.) but no per cent of yield mentioned.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.18; H, 6.96; N, 8.35.

N-Isopropyl-(3-methyl-1,4-benzodioxan-2-ylmethylamino)-acetamide (IVc). To 9 g. of 2-aminomethyl-3-methyl-1,4-benzodioxan in 200 ml. of toluene was added dropwise 3.4 g. of *N*-isopropylchloroacetamide with stirring and refluxing for a period of 22 hr. The colorless salt which separated was filtered and washed with a little toluene. The toluene solution was evaporated under reduced pressure and the residue was distilled at 175–180°/0.03 mm. to give 4.1 g. (65%) of a thick lemon colored oil.

Anal. Calcd. for $C_{13}H_{22}O_3N$: N, 10.06. Found: N, 9.83.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTH CAROLINA COLLEGE AT DURHAM AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

The Acyloin Condensation. I. The Syntheses of 1,6-Diphenylhexanedione-3,4 and 2-Carbethoxy-3,4-diphenylcyclopentanone[1]

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The acyloin condensation with ethyl β-phenylpropionate in toluene and xylene under the atmosphere and under nitrogen gave 1,6-diphenylhexanedione-3,4 (hydrocinnamil) (I) in 61% yield; no acyloin could be isolated. The structure was demonstrated by its quinoxaline, dioxime, diphenylhydrazone, and dihydro derivatives and its infrared spectrum. Ethyl *p*-nitrocinnamate under similar conditions was recovered unchanged. Ethyl cinnamate in ether gave a 10% yield of 2-carbethoxy-3,4-diphenylcyclopentanone (III) accompanied by a large amount of high boiling substance. The proof of structure of this product was demonstrated by its 3,5-dinitrobenzoate, phenylhydrazones, and oxime derivatives and by its infrared spectrum. The product was degraded to the known *dl*-3,4-diphenyladipic acid and a mixed melting point taken with a prepared sample. The chromophore of this compound and its derivatives gave very characteristic absorption bands in the carbonyl region.

The acyloin condensation has been carried out with a variety of esters but little has been reported on the acyloin condensation with esters of the type used in this work. The acyloin condensation with ethyl β-phenylpropionate was expected to give the corresponding acyloin, but the product obtained was a low melting yellow ketone. A considerable amount of sodium remained at the end of the reaction. The product was not further reduced when retreated with sodium under similar conditions. Bredereck and Theilig[4] reported that the acyloin condensation with ethyl β-phenylpropionate gave the corresponding acyloin. These workers, however, did not isolate an acyloin but assigned a structure on the basis that an imidazole was formed by treating the reaction mixture with formamide, since this was a general reaction for acyloins. The product obtained in this work, however, would not form an imidazole when treated with formamide according to the procedure of Bredereck and Theilig.[4] The acyloin condensation was carried out according to a procedure described by Snell and McElvain.[5] The condensation was run in toluene and xylene, under nitrogen and under the atmosphere; the same product was obtained under each condition. The pure product melted at 90–91°. The product gave no acetate or benzoate derivative, but readily gave dioxime, diphenylhydrazone, and quinoxaline derivatives. The product was reduced with sodium borohydride; a compound was ob-

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