1-Benzyl-2-bromo-1,3-diphenylindene (III). (a) A solution of sodium *iso*-propoxide from 0.2 g. of sodium in 5 ml. of *iso*-propyl alcohol was treated with 0.7 g. of I and then with 1 g. of benzyl chloride. Volatile materials were removed with steam, and the colorless residue (0.85 g.) was crystallized from ligroin, giving 0.8 g. of prisms, m.p. 117–118°.

(b) A solution of 0.5 g. of 1-benzyl-1,3-diphenylindene[5] in 5 ml. of carbon tetrachloride was treated with 0.2 g. of bromine. The solvent and hydrogen bromide were then removed by short warming at 100° under reduced pressure. Crystallization from ligroin gave 0.5 g. of prisms, m.p. 117–118° alone or mixed with (a); the infrared spectra of the two samples were identical.

Anal. Calcd. for $C_{26}H_{21}Br$: C, 76.9; H, 4.8. Found: C, 76.8; H, 5.1.

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Seven-Membered Ring Compounds. X. Hydroxy- and Methoxybenzosuberones

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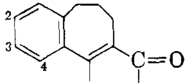
In previous investigations[1] the condensation of benzosuberones with oxalate esters was found to yield cyclic enol esters (I) of the expected glyoxylates, provided that the 4-position of the benzosuberone contained no substituent. In a search for precursors which would be convertible to 4-substituted benzosuberones, we have prepared a number of hydroxybenzosuberones.



I

The condensations of the benzyl ethers of hydroxyaldehydes with diethyl ethylidenemalonate[2] (Table I) proceeded in better yields than the hydroxyaldehydes themselves. Reduction of the cinnamylidenemalonic acids by means of Raney alloy and alkali[3] gave γ-phenylpropylmalonic acids with hydrogenolysis of the benzyl group. The crude malonic acids were heated without purification to obtain the phenylvaleric acids (Table I). As a second usable method, catalytic hydrogenation of several benzyloxycinnamylidenemalonic acids followed by decarboxylation gave benzyl ethers which were hydrolyzed to hydroxyphenyl valeric acids.

The cyclization of hydroxyphenylvaleric acids in polyphosphoric acid (PPA) proceeded in low yield. A cyclization of δ-4-acetoxy-3-methoxyphenylvaleric acid gave material which resisted purification and the attempted cyclization of 4-benzyloxy-3-methoxyphenylvaleric acid gave polymeric material. The cyclization of the benzoates of 2- and 4-hydroxy-3-methoxyphenylvaleric acids by means of PPA gave yields of 51% and 42% respectively.

The assistance of a grant from the National Science Foundation is gratefully acknowledged.

EXPERIMENTAL[5]

4-Benzyloxy-3-methoxycinnamylidenemalonic acid. The following illustrates a convenient modification of the reported method[2] for the condensation of aromatic aldehydes with ethylidenemalonic ester. The cinnamylidenemalonic acids in Table I were obtained by this procedure.

Benzyltrimethylammonium chloride was prepared by the addition of 190 g. of benzyl chloride over a 10 min. period to 350 g. of 25% aqueous trimethylamine at a temperature below 40° maintained by stirring and cooling in an ice bath. After stirring for 3 hr. and standing overnight, the solution was distilled on the water bath at aspirator pressure. The residual solid, after drying for 1 week in a vacuum dessicator, weighed 193 g. (70%).

A solution containing 17 g. of sodium hydroxide in 164 ml. of methanol was added to a flask containing 77.6 g. of benzyltrimethylammonium chloride. After the solution of the salt and standing overnight, the material was filtered by suction and the sodium chloride pressed and washed with a small portion of methanol. To the base was added 23.6 g. (0.0975 mol) of benzylvanillin[6] and 36.6 ml. of ethylidenemalonic ester.[7] The flask was swirled without cooling and stored for 48 hrs. It was diluted with 500 ml. of water, refluxed for 1 hr., cooled, and acidified with 1:1 hydrochloric acid. After standing at 5° for 24 hr. the crystals were filtered, washed with cold water and dried on the steam bath. The orange-yellow solid weighed 26.1 g. (75%) (see Table I).

4-Benzyloxy-3-methoxycinnamylideneacetic acid. A solution of 3.20 g. of the above cinnamylidenemalonic acid in 6.3 ml. of acetic anhydride and 2.7 ml. of pyridine was warmed on the water bath and allowed to stand at room temperature overnight.[8] After dilution with water and decomposition of the acetic anhydride, the solution was extracted with benzene yielding 2.21 g. (79%) of orange-brown crystals m.p. 184–192°. Further purification from ethyl acetate–petroleum ether (b.p. 60–71°) gave fine pale yellow crystals m.p. 203.0–204.0°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.36; H, 5.93.

Phenylvaleric acids. The acids in Table I were obtained by reduction with Raney alloy as described[2,3] with subsequent decarboxylation of the crude malonic acids at 180°. *γ-4-Hydroxy-3-methoxyphenylpropylmalonic acid* was iso-

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TABLE I

CINNAMYLIDENEMALONIC ACIDS

	Yield, %	M.P.[a]	M.P. (Cor.)[a] for Anal.	Compound	Calcd. C	Calcd. H	Found C	Found H
3-CH_3O	100	189–196	201.6–202.0[b]	$C_{13}H_{12}O_5$	62.91	4.88	62.88	4.72
3-$C_6H_5CH_2O$	89	162–176	192.0[c]	$C_{19}H_{16}O_5$	70.36	4.97	70.71	5.01
2-$C_6H_5CH_2O$-3-CH_3O	95	130–139	162.3–163.9[d]	$C_{20}H_{18}O_6$	67.79	5.12	68.05	5.15
4-$C_6H_5CH_2O$-3-CH_3O	75	140–154	195.0–195.5[e]	$C_{20}H_{18}O_6$	67.79	5.12	68.10	5.03
PHENYLVALERIC ACIDS								
3-HO	81.5	89–112	115.2–117.0[f]	$C_{11}H_{14}O_3$	68.02	7.27	68.21	7.27
3-CH_2O	79	B.p. 200–220 (1 mm.-bath)	B.p. 142–143 (0.17 mm.)	$C_{12}H_{16}O_3$	69.20	7.75	70.22	7.79
2-HO-3-CH_3O	42	81–88	86.2–88.2[g]	$C_{12}H_{16}O_4$	64.27	7.19	64.61	7.24
4-HO-3-CH_3O	74	86–89	90.5–92.5[h]	$C_{12}H_{16}O_4$	64.27	7.19	63.66	7.31
4-$C_6H_5CH_2O$-3-CH_3O	81[i]	93.5–100	100.5–102[j]	$C_{19}H_{22}O_4$	72.59	7.06	72.62	7.17
BENZOSUBERONES								
2-HO	18[k]	156.5–163.5	164.4–166.1[l]	$C_{11}H_{12}O_2$	74.97	6.87	75.06	6.95
2-CH_3O	94	54–58	58.9–60.3[m]	$C_{12}H_{14}O_2$	75.76	7.42	75.81	7.42
1-$C_6H_5CO_2$-2-CH_3O	51	124–139	138.0–141.4	$C_{19}H_{18}O_4$	73.53	5.85	73.39	5.89
1-HO-2-CH_3O	(82)[n]	88–95	98.4–100.6	$C_{12}H_{14}O_3$	69.88	6.84	69.83	6.84
3-$C_6H_5CO_2$-2-CH_3O	42[o]	119–124	126–127.4[p]	$C_{19}H_{18}O_4$	73.53	5.85	73.65	5.68
3-HO-2-CH_3O	30	106–109	112.0–113.2[q]	$C_{12}H_{14}O_3$	69.88	6.84	70.24	7.04

[a] All cinnamylidenemalonic acids melted with gas evolution. [b] From benzene–ethyl acetate, canary yellow. [c] Instantaneous; from benzene–ethyl acetate, canary yellow. [d] From benzene–ethyl acetate, canary yellow. [e] Golden yellow clumps of spears from methanol. [f] From benzene. [g] From cyclohexane–acetone or aqueous methanol; dark green ferric chloride test. The *benzoate* melted at 98–99.6° (cor.). Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.39; H, 6.10. [h] From cyclohexane; green ferric chloride test. The *acetate*, from benzene–petroleum ether (b.p. 65–110°) melted at 76.5–78.1° (cor.). Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.27; H, 6.85. [i] From the catalytic reduction of the cinnamylidenemalonic acid followed by heating at 180° and extraction with hot cyclohexane. [j] From cyclohexane. [k] Cyclization time 30 min. (95°). [l] From benzene-cyclohexane; identical to the compound obtained (by Mr. Irwin Schmeltz) from 2-methoxybenzosuberone by cleavage with aluminum chloride. The *benzoate* from methanol melted at 60.2–61.2° (cor.). Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.24; H, 5.65. [m] From cyclohexane and sublimed at 0.16 mm. (90° bath). The *oxime*, from cyclohexane and sublimed at 0.12 mm. (140° bath) melted at 127.0–128.8° (cor.). Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37. Found: C, 70.35; H, 7.55. [n] By saponification of the benzoate; deep green ferric chloride test. [o] Cyclization time 25 mins. (90°). [p] From benzene-petroleum ether (b.p. 60–71°). Saponification of the benzoate gave 3-hydroxy-2-methoxybenzosuberone which was methylated to 2,3-dimethoxybenzosuberone, identical to known material.[4] [q] From benzene-petroleum ether (b.p. 60–71°); green ferric chloride test. The *acetate* from petroleum ether (b.p. 90–110°) melted at 104.8–106.4° (cor.). Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.96; H, 6.57.

lated prior to decarboxylation in virtually quantitative yield m.p. 112–119° (gas evol.). From benzene–petroleum ether (b.p. 65–110°) and ethyl acetate–petroleum ether, material melting at 122.8–124.0° (gas evol.) was obtained.

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.15; H, 6.01.

The catalytic reduction of 4-benzyloxy-3-methoxycinnamylidenemalonic acid in alcohol over platinum gave a malonic acid with retention of the benzyl group. Decarboxylation gave the benzyl ether of the valeric acid (Table I). Debenzylation[9] gave δ-4-hydroxy-3-methoxyphenylvaleric acid (93.2%) identical to the material produced *via* Raney alloy–sodium hydroxide.

δ-4-Benzoyloxy-3-methoxyphenylvaleric acid. The dried mixture of the benzoate and benzoic acid, m.p. 89–102°, obtained by treatment with benzoyl chloride in aqueous sodium hydroxide was either (a) sublimed 24 hr. at 70° (0.3 mm.) to yield material (76%) m.p. 118–123° which depressed the melting point of benzoic acid or (b) digested three times with water at 90°, filtering after each digestion, to yield product (77%) m.p. 121–124°, similarly depressing the melting point of benzoic acid. By repeated crystallization from benzene–petroleum ether (b.p. 90–110°) 1:10, colorless material m.p. 126.0–127.8° was obtained.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.51; H, 6.13.

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2,4′-Diphenylbiphenyl

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Of the nine possible $C_{24}H_{18}$ hydrocarbons consisting of four linked benzene rings, eight are recorded.[1–8] We now report the synthesis of the re-

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