an authentic sample, and no bands attributable to deuterium could be detected. The allylbenzene fraction, however, showed —C—D stretching bands at 4.7μ as well as differences in the 7–13μ region[3,4] when compared with an authentic undeuterated sample of allylbenzene. The strong absorption bands at 10.04μ and 10.91μ[7] were identical in the deuterated and undeuterated samples of allylbenzene indicating the absence of any appreciable =CHD in the former compound. Oxidative degradation of the deuterated allylbenzene (630 mg.) with ozone in ethyl acetate afforded phenylacetic acid (m.p. 74–76°) whose infrared spectrum—compared with authentic undeuterated phenylacetic acid—exhibited differences in the 7–12μ region characteristic of deuterium containing analogs.

*Octene-1-1-d* (V). Lithium metal (1.38 g.) and 1-bromooctene[8] (20 g.) were allowed to react in ether solution as previously described.[1] The resulting lithium octenyl solution was decomposed with deuterium oxide (4 ml.). The ether solution was dried (sodium sulfate) and fractionated to give octen-1-1-*d*. Yield 7 g. (60%); b.p. 121°; $n_D^{25}$ 1.4078. Reported[9] for 1-octene, b.p. 121–122°; $n_D^{19}$ 1.4085. The intensity of the out-of-plane bending vibrations at 10.1μ and 10.9μ for octen-1-1-*d* were approximately one half of those found in 1-octene. Our sample of octen-1-1-*d* showed the expected —C—D stretching band at 4.5μ.[3]

*Pyrolysis of cyclohexen-3-ol-1* (*VI*). The procedure of Owen and Robins[10] was used in the preparation of this unsaturated alcohol. Cyclohexen-3-ol-1 (7.5 g.) was added dropwise to the pyrolysis tube at 500° in an atmosphere of nitrogen using the procedure normally employed.[1] The infrared spectrum of the condensate showed no carbonyl bands. Fractionation of this material gave a small forerun (0.6 g., 9%)—presumably a mixture of cyclohexadienes and starting material (5.45 g., 73%, b.p. 160–163°, $n_D^{25}$ 1.4840). The nonvolatile residue weighed 0.45 g.

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## An Attempt to Synthesize 3,5-Diphenylbenzocyclopentatriene, a Cyclic Allene

C. F. KOELSCH

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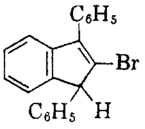
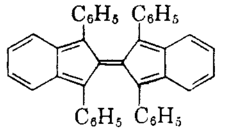
1,2-Cycloheptadiene has been prepared, but attempts to obtain 1,2-cyclohexadiene have led only to polymers.[1]

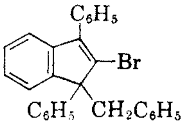
Considerable distortion, both bending and twisting, would be involved if the allenic system were present in the still smaller five-membered ring. In spite of this, it was considered of interest to discover what would happen if the sodio derivative of 2-bromo-1,3-diphenylindene (I) were prepared, for the heavy substitution might inhibit polymerization of the expected cyclic allene. If the allene could not be isolated, it was considered possible that a dimer (II) might be isolated, and this would be of interest since such a dimer has the structure originally proposed for rubrene,[2] and unsuccessful attempts to synthesize a compound having this structure have been reported.[3]



I



II



III

Surprisingly, it has now been found that the anion of 2-bromo-1,3-diphenylindene shows no tendency to eliminate a bromide anion. When the indene was added to sodium *iso*-propoxide in *iso*-propyl alcohol, a bright yellow solution resulted, and no sodium bromide was formed when this solution was boiled for thirty minutes. That the anion was present was shown by addition of benzyl chloride. This caused immediate disappearance of the yellow color and formation of 1-benzyl-2-bromo-1,3-diphenylindene (III) in nearly quantitative yield. The benzyl derivative was identical with the product of bromination of 1-benzyl-1,3-diphenylindene.

The author thanks the Graduate School of the University of Minnesota for a grant supporting this research, and Mrs. O. Hamerston for the analytical work.

### EXPERIMENTAL

*2-Bromo-1,3-diphenylindene* (I). Bromination of 1,3-diphenylindene has been investigated previously[4] but the 2-bromo derivative has not been reported. It was obtained easily in nearly quantitative yield by adding 3.2 g. of bromine in 5 ml. of carbon tetrachloride to a cooled solution of 5.3 g. of 1,3-diphenylindene in 20 ml. of carbon tetrachloride. The solvent was then removed by distillation and the residue was heated at 100° under reduced pressure for a few minutes. Solution in hexane and chromatography over alumina gave 6.55 g. of colorless oil which solidified completely when it was rubbed with ether-hexane at −70°. Recrystallization from hexane furnished prisms, m.p. 66–68°.

*Anal.* Calcd. for $C_{21}H_{15}Br$: C, 72.6; H, 4.3. Found: C, 72.5; H, 4.5.

Oxidation of the bromo compound with chromic acid in acetic acid gave *o*-dibenzoylbenzene identified by mixed melting point and infrared spectrum.

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*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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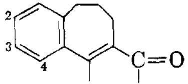
In previous investigations[1] the condensation of benzosuberones with oxalate esters was found to yield cyclic enol esters (I) of the expected glyoxylates, provided that the 4-position of the benzosuberone contained no substituent. In a search for precursors which would be convertible to 4-substituted 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 $\gamma$-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 $\delta$-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°. *$\gamma$-4-Hydroxy-3-methoxyphenylpropylmalonic acid* was iso-

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