*4,4'-Dimethoxystilbene. Procedure B.* A round-bottom flask, equipped with an air condenser, was charged with 25 g. (0.076 mole) of 4,4'-dimethoxydiphenyl fumarate and 125 g. of Dowtherm. The mixture, becoming homogeneous on warming, was refluxed for 36 hr. The contents were cooled to 20°, filtered on a Büchner funnel, and either funnel-washed or slurry-washed twice with 25-ml. portions of cold ethanol. The yield of almost white to pale tan, nacreous crystals of 4,4'-dimethoxystilbene, melting at 211-212°, was 12 g. (65.6%).

*Halogen analyses.* The halogenated compounds of Tables I and II were decomposed for analyses by the Parr bomb technique instead of by the Carius method. In all cases but one, the found halogens were equal to or less than the theoretical. The data suggest a condition which may not be so much a reflection of the purity of the compounds as it is a limitation on the Parr decomposition, especially for compounds high in halogen. As a control, a sample of tetrabromophthalic anhydride, characterized by a theoretical bromine content of 69.1%, showed a 67.8% content by Parr combustion *versus* a 69.3, 69.4% content by Carius combustion.

*Acknowledgment.* The author is indebted to Audrey K. Lord and Emily A. Bundy for their assistance with this work.

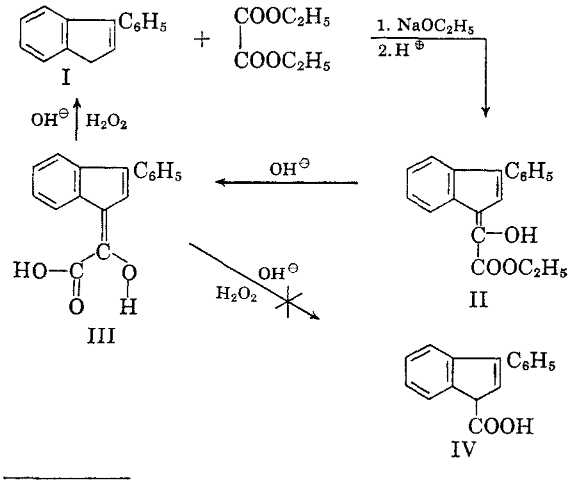
ALLIED CHEMICAL CORP.
NATIONAL ANILINE DIVISION
BUFFALO 5, N. Y.

# Condensation and Addition Reactions of 3-Phenylindene

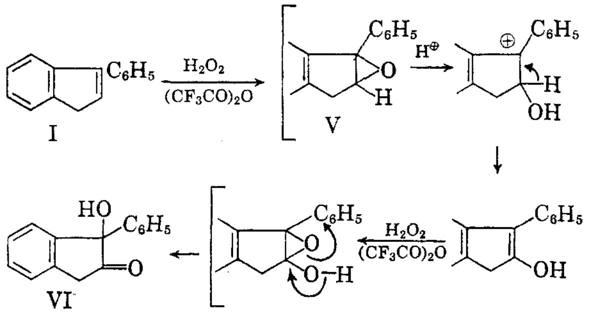
BORIS WEINSTEIN[1]

*Received March 23, 1961*

Some time ago we had occasion to study the condensation of 3-phenylindene (I) with diethyl oxalate in the presence of sodium ethoxide. The product of the reaction, ethyl 3-phenylindenylglyoxylate (II), exhibited an intense hydroxyl absorption at 2.91 $\mu$ and a single carbonyl band at 5.91 $\mu$. Therefore, it probably existed in the enol form in the solid state. On hydrolysis with cold aqueous alkali, the ester afforded 3-phenylindenylglyoxylic acid (III). The free acid possessed a weak hydroxyl peak at 2.86 $\mu$, which could be due to a hydrogen bonding effect, as well as a carbonyl absorption at 5.97 $\mu$. An attempted decarbonylation of III with hot alkali and hydrogen peroxide gave the parent compound I instead of the expected 3-phenylindenecarboxylic acid (IV).



In addition 3-phenylindene was treated with hydrogen peroxide and trifluoroacetic anhydride[2] in the expectation of obtaining 3-phenylindene-2,3-epoxide (V). However, a compound believed to be 3-phenyl-3-hydroxylindan-2-one (VI) was isolated from the reaction. The infrared spectrum showed a hydroxyl absorption at 2.85 $\mu$ as well as a cyclopentanone band at 5.70 $\mu$. The structure assigned to VI was supported by its lack of reactivity to the Sarett reagent (chromium trioxide–pyridine). A suggested mechanism for the conversion of I to VI is as follows:



Finally I was hypobrominated to produce 1-phenyl-2-bromoindan-1-ol (VII). This compound was synthesized previously by treatment of I with *N*-bromosuccinimide in aqueous acetone to yield a mixture of stereoisomeric bromohydrins.[3] The sharp melting point of our VII indicated that it may be a single *dl*-isomer pair. A *trans* relationship between the bromo- and hydroxyl-groups is probable on the basis of the analogous hypobromination of indene.[4] Compound VII exhibited at 2.95 $\mu$ the expected hydroxyl absorption.

## EXPERIMENTAL[5]

*3-Phenylindene* (I). To a 1-l. three-neck flask equipped with addition funnel, stirrer, and condenser capped with a calcium chloride drying tube were added magnesium turnings (7.3 g., 0.30 g.-atom), an iodine crystal, bromobenzene (3.0 g.), and dry ether (150 ml.). As soon as the reaction began, the remainder of the bromobenzene (34.5 g., 0.22 mole) in ether (150 ml.) was added over a half-hour period

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[1] Present address: Stanford Research Institute, Menlo Park, Calif.

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[3] A. S. Kende, *Chemistry & Industry*, 1053 (1956).

[4] C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.*, **62**, 3473 (1940).

[5] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were determined as potassium bromide disks using the Baird Model B spectrophotometer.

with stirring. The final mixture was refluxed for a similar period.

The indan-1-one (26.4 g., 0.20 mole) in ether (150 ml.) was added to the phenylmagnesium bromide solution over a half-hour period and the combined contents were refluxed for a second half-hour. The reaction mixture was poured into a stirred slush of iced water (400 g.) and ammonium chloride (3 g.). The ether layer was removed and the residual aqueous solution was extracted with three portions of ether (100 ml. each). The combined organic extracts were filtered through magnesium sulfate and the ether was removed *in vacuo*. The oily residue was distilled to give 34.5 g. (89.6%) of a yellow liquid, b.p. 118–119° (0.45 mm.), $n_D^{20}$ 1.6320 [lit. value,[6] b.p. 200–201° (29 mm.), $n_D^{24}$ 1.6313].

*Anal.* Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.80; H, 6.27.

*Ethyl 3-phenyl-1-indenylglyoxylate* (II). A mixture of 3-phenylindene (9.61 g., 0.05 mole) and diethyloxalate (8.77 g., 0.06 mole) in dry ether (25 ml.) was added with stirring and under nitrogen to a sodium ethoxide solution, previously prepared from sodium (1.61 g., 0.07 g.-atom) and anhydrous ethanol. The solution was stirred for 3 hr. and was then poured into a chilled mixture of ether (100 ml.) and aqueous sulfuric acid (7%, 100 ml.) and was stirred for 0.5 hr. The ethereal layer was separated and the acidic solution was extracted again with ether (50 ml.). The combined ethereal extracts were washed with aqueous sodium bicarbonate, and water and were filtered through magnesium sulfate. The ether was stripped off and the residue was crystallized from benzene-petroleum ether to give 12.9 g. (88.3%) of orange needles, m.p. 104.0–104.5°. Infrared absorptions were at 2.91 and 5.91 μ.

*Anal.* Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.41.

*3-Phenylindenylglyoxylic acid* (III). A solution of ethyl 3-phenyl-1-indenylglyoxylate (12.9 g., 0.044 mole) in ether (100 ml.) was stirred with aqueous sodium hydroxide (2%, 100 ml.) for 12 hr. The ether layer was discarded and the red basic solution was treated with a mixture of ether (100 ml.) and aqueous hydrochloric acid (5%, 100 ml.) and was stirred for 1 hr. The ethereal layer was removed and the acidic solution was extracted twice with ether (100-ml. portions). The combined ether extracts were washed twice with water, were filtered through magnesium sulfate and the ether was stripped off. The residue was crystallized from benzene to give 11.45 g. (98.4%) of reddish orange needles, m.p. 188–189° dec. Infrared absorptions at 2.86 and 5.97 μ.

*Anal.* Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.52; H, 4.75.

*Attempted preparation of 3-phenylindene-1-carboxylic acid* (IV). The glyoxylic ester (63 mg.) was added to a mixture of ammonium hydroxide (2 ml.), ethanol (2 ml.), water (10 ml.), and hydrogen peroxide (30%) (0.50 ml.), and the resulting solution was warmed on the steam bath for 1.5 hr. An additional portion of hydrogen peroxide (0.1 ml.) was added and the solution was heated for a final 0.5 hr. The cold solution was acidified with hydrochloric acid and was extracted with ether. The ethereal extract was washed with water, dried and was evaporated. The residue was identified as starting material by infrared comparison.

The glyoxylic acid (1.32 g.) was dissolved in aqueous sodium hydroxide solution (20 ml., 0.5*N*) and hydrogen peroxide (30%, 7.5 ml.) in water (10 ml.) and heated on the steam bath for 5 hr. The solution was neutralized with dilute sodium bicarbonate solution and extracted with ether to furnish a yellow oil (0.5 g.) whose infrared spectrum was identical with that of authentic 3-phenylindene.

*2-Phenyl-3-hydroxyl-indan-2-one* (VI). To a chilled suspension of hydrogen peroxide (90%, 0.82 ml., 0.03 mole) in methylene chloride (5 ml.) was added trifluoroacetic anhydride (5.08 ml., 0.036 mole) over a 10-min. period. The resulting solution was stirred further in the cold for 15 min. and was added to a stirred mixture of sodium carbonate (9.54 g., 0.09 mole), 3-phenylindene (3.85 g., 0.02 mole) and methylene chloride (30 ml.) over a half-hour period. The reaction was refluxed for an additional hour, the inorganic salts were filtered off, and the salt cake was triturated with fresh methylene chloride (30 ml.) and sucked dry. The combined organic extracts were evaporated to furnish an oily residue. A methylene chloride–petroleum ether (b.p. 60–68°) solution furnished 3.34 g. (80.1%, based on unrecovered starting material) of white crystals, m.p. 127.5–128.5°. Infrared-absorptions were at 2.85 and 5.70 μ. A sample of this compound was unaffected after 5 hr. by chromium trioxide-pyridine.

*Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 79.99; H, 5.32.

*1-Phenyl-2-bromo-indan-1-ol* (VII). In a 1-l. three-neck flask equipped with stirrer, thermometer, and dropping funnel was placed water (150 ml.), Tide (0.70 g.), and 3-phenylindene (4.81 g., 0.025 mole). After warming to 80° and complete emulsification had occurred, a saturated solution of bromine in aqueous sodium bromide (bromine, 4.0 g., sodium bromide, 10.0 g., water, 150 ml.) was added dropwise over 0.5 hr. Since the reaction solution had not turned a permanent yellow, an additional small quantity of brominating solution was added to the flask.

After stirring for 4 hr., the solution was decanted and the residual yellow gum was stirred with fresh, cold water for a further similar period. The gum was collected and dried, wt. 5.5 g., and was triturated with petroleum ether to furnish 2.1 g. (50.0%, based on unrecovered starting material) of white needles, m.p. 131.0–132.0. Infrared absorption was at 2.95 μ.

*Anal.* Calcd. for $C_{15}H_{13}BrO$: C, 62.28; H, 4.53; Br, 27.65. Found: C, 62.53; H, 4.61; Br, 27.28.

*Acknowledgment.* I wish to thank Dr. Michael P. Cava for his interest and suggestions in connection with this work.

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

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## Oxidation of *p*-Nitrotoluene to 4,4′-Dinitrobibenzyl and 4,4′-Dinitrostilbene

HARRY A. STANSBURY, JR., AND WILLIAM R. PROOPS

*Received March 24, 1961*

The preparation of 4,4′-dinitrobibenzyl by the oxidative coupling of *p*-nitrotoluene has been described by House[1] and was based on the method of Green *et al.*[2] In this method the solid *p*-nitrotoluene was added to a methanolic potassium hydroxide solution and air was passed through the mixture for 8 hours to form 4,4′-dinitrobibenzyl. The kinetics of the oxidation have been studied in methanolic potassium hydroxide[3] and in a solution of potassium *t*-butoxide in *t*-butyl alcohol.[4] In the

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