

Anal. Calcd. for $C_{19}H_{14}O_3 + H_2O$: C, 74.0; H, 5.2. Found: C, 73.7; H, 5.4.

The quinol also separates from dilute methanol or dilute acetic acid in needles that contain water. From toluene it is obtained in the form of pale tan prisms which are solvent free and melt at 160–163° with darkening.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.8. Found: C, 78.4; H, 4.7.

Boiling with sodium hydroxide transforms the quinol into an amorphous brown substance. On boiling with alkaline sodium hydrosulfite it gives a clear orange-brown solution from which acids precipitate the hydroxy com-

pound (V), identified by mixed melting point and by its conversion to the methoxy ketone (III) on methylation with methyl sulfate and alkali.

Summary

The condensation of β -naphthol with cinnamic acid yields a dihydrocoumarin which has been converted into a *peri*-naphthindene derivative. Some reactions of this latter substance are described.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

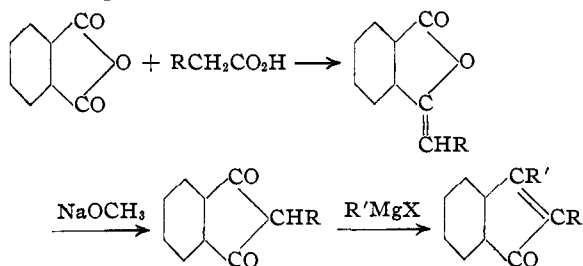
Some Applications of the Rosenmund-v. Braun Nitrile Synthesis

BY C. FREDERICK KOELSCH

When an aromatic bromide is heated in a sealed tube with water, sodium cyanide and cuprous cyanide, the halogen is replaced by carboxyl.¹ Hydrolysis of the intermediate nitrile may be avoided by omitting the water and sodium cyanide, this procedure making the use of a sealed tube or an autoclave unnecessary.² The importance of this reaction has been demonstrated in a recent synthesis of phenanthrene-9-carboxylic acid.³

In the present research the reaction has been applied to the preparation of some derivatives of 2,3-diphenylindone, and the cyano group has been introduced into each of the three benzenoid rings of this compound. Likewise it has been found that β,γ,γ -triphenylacrylonitrile and β -phenyl- γ -diphenyleneacrylonitrile are readily obtainable from the corresponding vinyl bromides. However, when α -*p*-bromophenyl- β,β -diphenylvinyl bromide is heated with cuprous cyanide under the usual conditions, it is completely resinified; at lower temperatures it is recovered unchanged.

The halogenated indones were prepared by the following series of reactions, the last step of the se-



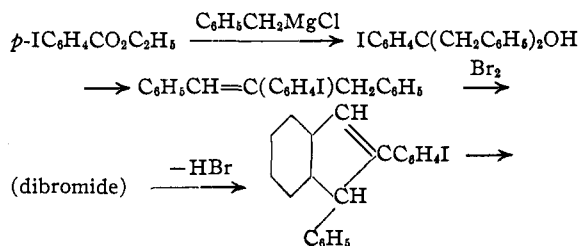
- (1) Rosenmund and Struck, *Ber.*, **52**, 1749 (1919).
 (2) Von Braun and Manz, *Ann.*, **488**, 111 (1931).
 (3) Mosettig and van de Kamp, *This Journal*, **54**, 3334 (1932).

ries constituting a hitherto undescribed diarylindone synthesis.

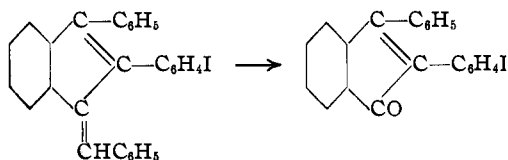
When 4-bromophthalic anhydride was used, a mixture of benzal bromophthalides was obtained which was converted quantitatively into 1,3-diketo-2-phenyl-5-bromoindane. This with phenylmagnesium bromide gave an easily separable mixture of the isomeric 5- and 6-bromodiphenylindones; thus enolization of this unsymmetrical β -diketone involves either of the carbonyl groups.

It is noteworthy that although solid 2-phenylindandione is obtainable in only the white keto form,⁴ the halogenated derivatives of this substance prepared in this research were each easily obtainable in two forms: by crystallization from non-polar solvents in a white modification (keto), and from polar solvents in a violet-black modification (enol).

The structure of 5-bromo-2,3-diphenylindone was proved by oxidation to the known 4-bromo-2-benzoylbenzoic acid, and that of 2-*p*-iodophenyl-3-phenylindone by a separate synthesis according to the scheme⁵



- (4) Hantzsch, *Ann.*, **392**, 286 (1912).
 (5) Compare Orechhoff, *Ber.*, **47**, 89 (1914); Ruggli, *Ann.*, **414**, 125 (1917).



Experimental

Substitution in the 2-Phenyl of 2,3-Diphenylindone

***p*-Iodobenzaldehyde.**—*p*-Iodobenzaldehyde was prepared from phenylacetic acid by direct iodination,⁶ from *p*-aminophenylacetic acid by diazotization, and from *p*-iodotoluene through *p*-iodobenzyl bromide and cyanide.⁷ The last method is much the better.

A mixture of 80 g. of *p*-iodophenylacetic acid, 46 g. of phthalic anhydride and 1 g. of sodium acetate is heated for two hours at 225–235°. The melt is dissolved in hot acetic acid and cooled. The product (70 g.) is deposited in the form of yellow needles. Recrystallized from acetic acid, the compound melts at 172–173°.

Anal. Calcd. for C₁₅H₉O₂I: C, 51.7; H, 2.62. Found: C, 51.7; H, 2.58.

2-*p*-Iodophenylindandione-1,3.—A solution of 4.7 g. of sodium in 100 ml. of methanol is added to a suspension of 68 g. of *p*-iodobenzaldehyde in 300 ml. of methanol. After the mixture has been boiled for five minutes, water is added, the diketone is precipitated with hydrochloric acid, dried and recrystallized (64 g.). From acetic acid it separates in red-violet prisms, and from non-polar solvents in colorless needles. Both of these forms melt at 145–146° to a red liquid.

Anal. Calcd. for C₁₅H₉O₂I: C, 51.7; H, 2.62. Found: C, 51.9; H, 2.61.

2-*p*-Iodophenyl-3-phenylindone.—A solution of 100 g. of iodophenylindandione in hot benzene is added to a phenylmagnesium bromide solution containing 17 g. of magnesium. The mixture is boiled for one hour and decomposed with iced sulfuric acid. Washing the organic solution with dilute sodium carbonate removes unchanged diketone (17 g.). The neutral product is distilled under reduced pressure and crystallized from acetic acid. There is obtained 61 g. of bright orange-red needles that melt at 141–143°.

Anal. Calcd. for C₂₂H₁₃ON: C, 86.0; H, 4.23. Found: C, 86.1; H, 4.35.

2-*p*-Cyanophenyl-3-phenylindone.—Iododiphenylindone (20 g.) and cuprous cyanide (10 g.) are mixed and heated for three hours at 240°. The melt is pulverized and extracted in a Soxhlet with acetone. The product, obtained in a nearly quantitative yield, is distilled at 15 mm. and crystallized from acetic acid, when it forms orange plates that melt at 142–144°.

Anal. Calcd. for C₂₂H₁₃ON: C, 86.0; H, 4.23. Found: C, 86.1; H, 4.35.

α,γ -Diphenyl- β -*p*-iodophenylpropanol- β .—This carbinol, obtained from ethyl *p*-iodobenzoate and benzylmagnesium chloride in a yield of about 75%, after crystallization from ether-petroleum ether and then from ethanol, forms white needles that melt at 117–117.5°.

Anal. Calcd. for C₂₁H₁₉OI: C, 60.9; H, 4.61. Found: C, 60.9; H, 4.54.

α,γ -Diphenyl- β -*p*-iodophenylpropene.—This hydrocarbon is obtained in a good yield by boiling a solution of the above carbinol in acetic acid containing a little sulfuric acid. It forms colorless prisms from a mixture of ethanol and ethyl acetate that melt at 92–92.5°.

Anal. Calcd. for C₂₁H₁₇I: C, 63.6; H, 4.32. Found: C, 63.7; H, 4.25.

1-Phenyl-2-*p*-iodophenylindene.—The above iodotriphenylpropene dissolved in 2.5 times its weight of acetic acid is treated with the calculated amount of bromine, and the solution is boiled for twenty minutes. The product can be separated by crystallization from ligroin into nearly equal amounts of a yellow substance that melts at 165–168° with decomposition (probably α -bromo- α,γ -diphenyl- β -*p*-iodophenylpropene; C₂₁H₁₈BrI requires: C, 53.1; H, 3.4. Found: C, 54.2; H, 3.02) and the indene, which forms microscopic white needles that melt at 184–185°.

Anal. Calcd. for C₂₁H₁₆I: C, 63.9; H, 3.83. Found: C, 63.5; H, 3.82.

1-Benzal-2-*p*-iodophenyl-3-phenylindene.—To a suspension of 7 g. of 1-phenyl-2-*p*-iodophenylindene in 70 ml. of absolute ethanol is added 3 ml. of benzaldehyde and a solution of 0.3 g. of sodium in 5 ml. of ethanol. The mixture is boiled for five minutes and cooled, giving 6 g. of the benzal compound. The substance separates from acetic acid in the form of yellow needles that melt at 173–174°.

Anal. Calcd. for C₂₈H₁₈I: C, 69.7; H, 3.98. Found: C, 69.9; H, 3.91.

This benzal compound is oxidized by the calculated amount of chromic acid in acetic acid to 2-*p*-iodophenyl-3-phenylindone, which melts at 141–143° alone or mixed with the same substance prepared from iodophenylindandione.

Substitution in the 3-Phenyl of 2,3-Diphenylindone

2-Phenyl-3-*p*-bromophenylindone.—A benzene solution of 2-phenylindandione-1,3 is added to a solution of *p*-bromophenylmagnesium bromide containing 7 g. of magnesium. After boiling for one hour, the mixture is hydrolyzed with iced acid, and the unchanged diketone (20 g.) is extracted with sodium carbonate. The neutral product is distilled under reduced pressure and crystallized from acetic acid and then from toluene. There is obtained 9 g. of the bromodiphenylindone which forms orange prisms that melt at 172–174°.

Anal. Calcd. for C₂₁H₁₃OBr: C, 69.8; H, 3.6. Found: C, 69.9; H, 3.82.

2-Phenyl-3-*p*-cyanophenylindone.—The preceding bromodiphenylindone is heated with half its weight of cuprous cyanide at 250° for four hours, the melt is powdered and extracted with acetone, and the product is distilled under reduced pressure and crystallized from acetic acid. The cyano compound forms bright red prisms that melt at 184–187°.

Anal. Calcd. for C₂₂H₁₃ON: C, 86.0; H, 4.23. Found: C, 85.6; H, 4.34.

(6) Datta and Chatterjee, *THIS JOURNAL*, **41**, 292 (1919).

(7) Wheeler and Clapp, *Am. Chem. J.*, **40**, 460 (1908).

Substitution in the Indene Nucleus of 2,3-Diphenylindone

2 - Phenyl - 5 - bromoindandione - 1,3.—4 - Bromophthalic anhydride⁸ (29 g.) is mixed with phenylacetic acid (17.5 g.) and sodium acetate (1 g.) and heated at 220–240° for three hours. The product (23 g.), a mixture of the two possible benzal bromophthalides, is crystallized from acetic acid, when it melts at 145–170°. This mixture is suspended in methanol and treated with a solution of 2 g. of sodium in the same solvent. The solution is boiled for five minutes, water is added, and the diketone is precipitated with hydrochloric acid. From acetic acid, the product (20 g.) is deposited in the form of violet-black needles, and from benzene in the form of white needles. Both of these forms melt to a red liquid at 166–167°.

Anal. Calcd. for $C_{15}H_9O_2Br$: C, 59.8; H, 2.99. Found: C, 59.4; H, 2.84.

5- and 6-Bromo-2,3-diphenylindones.—The above diketone (19 g.) suspended in benzene is added to a solution of phenylmagnesium bromide containing 4 g. of magnesium. The mixture is boiled for one hour, hydrolyzed, and the unchanged diketone (3 g.) is removed with sodium carbonate. The neutral product is distilled under reduced pressure and fractionally crystallized from ether-petroleum ether. The less soluble part (8.5 g.) is 6-bromo-2,3-diphenylindone, which forms orange-red plates from acetic acid that melt at 192–194°.

Anal. Calcd. for $C_{21}H_{13}OBr$: C, 69.8; H, 3.6. Found: C, 69.7; H, 3.4.

The more soluble part is 5-bromo-2,3-diphenylindone, which forms orange needles from acetic acid that melt at 167–168°.

Anal. Calcd. for $C_{21}H_{13}OBr$: C, 69.8; H, 3.6. Found: C, 69.8; H, 3.4.

The structure of the latter 5-bromodiphenylindone is indicated by its oxidation by chromic acid in acetic acid to 2-benzoyl-4-bromobenzoic acid which melts at 189–191° alone or mixed with a known sample of this same melting point, kindly furnished by Dr. Stephens.

6 - Cyano - 2,3 - diphenylindone.—6 - Bromodiphenylindone is treated with cuprous cyanide and the product is worked up as described for 2-phenyl-3-*p*-cyanophenylindone. The product forms orange red plates that melt at 209–211°.

(8) Stephens, *THIS JOURNAL*, **43**, 1953 (1921).

Anal. Calcd. for $C_{22}H_{13}ON$: C, 86.0; H, 4.23. Found: C, 85.6; H, 4.2.

The Vinyl Compounds

α - *p* - Bromophenyl - β , β - diphenylvinyl Bromide.—An ether solution of benzophenone (28 g.) is added to a solution of *p*-bromobenzylmagnesium bromide containing 7.3 g. of magnesium. The solution is hydrolyzed with iced ammonium chloride, and the product is crystallized from ether-petroleum ether. There is obtained 35 g. of *p*-bromobenzylidiphenylcarbinol, which forms white needles that melt at 124–126°. (Found: C, 68.4; H, 5.0. $C_{20}H_{17}OBr$ requires: C, 68.0; H, 4.7.) This carbinol (7 g.) is dissolved in acetic acid (30 ml.) and treated with bromine (3.2 g.). The bromine is rapidly absorbed, and the solution soon deposits crystals of the vinyl bromide. The product is best purified by distillation under reduced pressure followed by crystallization from acetic acid. It forms colorless needles that melt at 109–110°.

Anal. Calcd. for $C_{20}H_{14}Br_2$: C, 58.0; H, 3.4. Found: C, 57.8; H, 3.4.

Under the usual conditions for the replacement of bromine by cyanogen (240°) this dibromo compound is converted into a black resin. At lower temperatures it is partly resinified and partly recovered unchanged.

Triphenylacrylonitrile.—Triphenylvinyl bromide heated with cuprous cyanide in the usual way gives a quantitative yield of triphenylacrylonitrile which melts at 163–165°.⁹

α - Phenyl - β - diphenyleneacrylonitrile.— α - Phenyl - β -diphenylenevinyl bromide¹⁰ and cuprous cyanide at 240° give a good yield of the corresponding nitrile which forms yellow needles that melt at 188–189°.

Anal. Calcd. for $C_{21}H_{13}N$: C, 90.2; H, 4.66. Found: C, 90.1; H, 4.68.

Summary

The synthesis of some halogenated diphenylindones is described, and it is shown that the Rosenmund-v. Braun method for the replacement of halogen by cyanogen is applicable to these compounds and to certain triarylvinyl bromides.

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(9) Hobbe and Feitschel, *Ber.*, **34**, 1967 (1901).

(10) Koelsch, *THIS JOURNAL*, **54**, 3387 (1932).