Anal. Calcd. for $C_{15}H_{12}O_6$: C, 62.50; H, 4.16. Found: C, 62.57; H, 4.04.

Eriodictyol acetate was prepared from acetic anhydride and pyridine without heating; colorless needles, m.p. 138°.

Eriodictyol trimethyl ether was obtained as colorless needles, m.p. 136°.

Anal. Calcd. for $C_{15}H_9O_3(OCH_3)_3$: OCH_3, 27.19. Found: OCH_3, 27.90.

The yield from 3 kg. of wood chips was 23 g. of naringenin, 6.5 g. of taxifolin and 7.4 g. of eriodictyol.

Oxidation of Eriodictyol.—Eriodictyol (0.1 g.) was fused for 10 minutes at 230° with 1.5 g. of potassium hydroxide in 3 drops of water, and the reaction product dissolved in water, after acidification with 25% sulfuric acid; the solution was exhaustively extracted with ether; the ether extract was washed with 1% sodium bicarbonate solution and then evaporated to dryness.

These two fractions were paper chromatographed. The bicarbonate-soluble fraction gave one spot (R_f 0.35) which corresponds to that of protocatechuic acid; the ether soluble fraction gave one spot (R_f 0.16) which corresponds to that of phloroglucinol.[8]

Acknowledgment.—We wish to thank Dr. Masataka Ohmasa, Director of the Government Forest Experiment Station and Prof. Shizuo Hattori of the University of Tokyo for their advice. We are grateful to Mrs. Hrauko Nakamura for her help with the chromatograms. We are grateful to Dr. Simon H. Wender, of the University of Oklahoma, for his kindness in arranging for revision of the manuscript.

[8] Developing solvent, *m*-cresol:water:glacial acetic acid = 25:24:1; detecting agent, 2% methanolic ferric chloride.

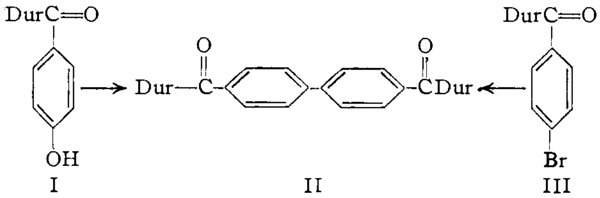
GOVERNMENT FOREST EXPT. STATION OF JAPAN
MEGURO, TOKYO, JAPAN

Bimolecular Reduction of *p*-Duroylphenoxide by Grignard Reagents

BY REYNOLD C. FUSON AND GEORGE W. PARSHALL[1]

RECEIVED JUNE 25, 1954

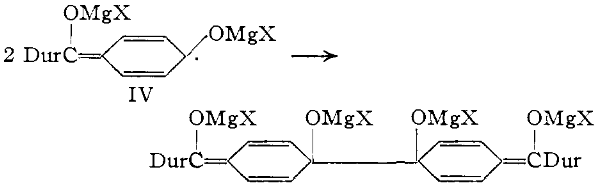
In the preceding paper,[2] it was reported that *p*-duroylphenol (I) reacts with tertiary alkyl Grignard reagents to give addition products in good yields. An attempt to employ primary and secondary Grignard reagents has disclosed a remarkable new reaction. When *p*-duroylphenol was treated with isopropylmagnesium bromide, none of the expected addition product could be isolated. Instead *p,p′*-diduroylbiphenyl (II) was obtained in a 19% yield. The same product was also formed by the action of benzylmagnesium chloride on *p*-duroylphenol. With methylmagnesium iodide and *p*-duroylphenol neither addition nor coupling occurred; however addition of cobaltous chloride to the reaction mixture brought about the formation of the biphenyl derivative.



I II III

The structure of *p,p′*-diduroylbiphenyl was proved by an independent synthesis. *p*-Bromophenyl duryl ketone (III) was coupled by treatment with the binary mixture, magnesium–magnesium iodide,[3] according to the method previously described for the synthesis of *p,p′*-dimesitoylbiphenyl.[4] The reaction of *p*-bromophenyl duryl ketone with methylmagnesium iodide in the presence of cobaltous chloride also gave *p,p′*-diduroylbiphenyl.

The favorable effect of cobaltous chloride on the reaction of *p*-duroylphenol with methylmagnesium iodide suggests that a free radical mechanism is involved.[5] In this respect the reaction resembles the formation of acyloins by the reaction of carboxylate ions with the binary mixture, magnesium–magnesium iodide.[6] The *p*-duroylphenoxide ion formed by the reaction with one mole of Grignard reagent is attacked probably by the magnesious halide to give a free radical IV. Dimerization of the radical IV would give a complex V which might be expected to decompose directly to the diketone II or to yield a hydrolysis product which could form the diketone by loss of two molecules of water.



IV

V

Experimental[7]

Action of Grignard Reagents on *p*-Duroylphenol. (a) Isopropylmagnesium Bromide.—The Grignard reagent prepared from 1.5 g. of magnesium and 4.8 ml. of isopropyl bromide in 50 ml. of ether was filtered and added rapidly to a solution of 2.54 g. of *p*-duroylphenol in 50 ml. of hot benzene. The mixture, which became purple immediately, was boiled under reflux for 45 minutes and poured into dilute hydrochloric acid. The organic layer became cherry-red, but the color faded to yellow after a few minutes. The organic layer was washed with water, dried over magnesium sulfate and freed of solvent by evaporation. A yellow solid was deposited when the gummy residue was extracted with methanol. Recrystallization from benzene converted the solid to light yellow flakes which melted at 322–326°, yield 0.45 g. (19%). A mixed melting point with an authentic sample of *p,p′*-diduroylbiphenyl was not depressed.

Anal.[8] Calcd. for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22. Found: C, 85.90; H, 7.42.

The infrared spectrum[9] contains bands assignable to a hindered conjugated carbonyl group (1667 cm.$^{-1}$), to an aromatic system (1558, 1606 cm.$^{-1}$) and to a *para*-substituted phenyl radical (822 cm.$^{-1}$).

(b) Benzylmagnesium Chloride.—A solution of 2.56 g. of *p*-duroylphenol in 30 ml. of hot benzene was added to the Grignard reagent prepared from 1.2 g. of magnesium and 5.5 ml. of benzyl chloride in 30 ml. of ether. After being heated under reflux overnight, the reaction mixture was poured into cold dilute hydrochloric acid and the product was isolated as in the preceding experiment. Recrystallization from petroleum ether gave yellow flakes of *p,p′*-diduroylbiphenyl, m.p. 320–322°. The infrared spectrum

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[1] National Science Foundation Fellow, 1952–1953; Allied Chemical and Dye Fellow, 1953–1954.

[2] R. C. Fuson, W. D. Emmons and G. W. Parshall, THIS JOURNAL, **76**, 5466 (1954).

[3] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

[4] R. C. Fuson and M. D. Armstrong, *ibid.*, **63**, 2650 (1941).

[5] M. S. Kharasch and E. K. Fields, *ibid.*, **63**, 2316 (1941).

[6] M. Gomberg and W. E. Bachmann, *ibid.*, **50**, 2762 (1928).

[7] All melting points are corrected.

[8] The microanalyses were performed by Mrs. Esther Fett, Mrs. Katherine Pih and Mrs. Lucy Chang.

[9] The infrared spectra were determined and interpreted by Miss Helen Miklas.

was identical with that of the product obtained in the preceding experiment.

Anal. Calcd. for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22. Found: C, 86.20; H, 7.49.

(c) **Methylmagnesium Iodide–Cobaltous Chloride.**—A slurry of 0.65 g. of anhydrous cobaltous chloride in 25 ml. of ether was added to the Grignard reagent prepared from 2.4 g. of magnesium and 7.4 ml. of methyl iodide in 50 ml. of *n*-butyl ether. A slurry of 2.54 g. of *p*-duroylphenol in 50 ml. of *n*-butyl ether was added and the mixture was boiled under reflux for 5 hours. During this time, the color changed from reddish-brown to a deep reddish-violet. The reaction mixture was hydrolyzed with cold dilute hydrochloric acid and the organic layer was washed with dilute aqueous sodium hydroxide, dried over magnesium sulfate and freed of solvent by evaporation. Addition of methanol to the residual brown oil gave light yellow flakes of *p*,*p*′-diduroylbiphenyl, m.p. 323–326°. A mixed melting point with an authentic sample was not depressed.

When this experiment was carried out in the absence of cobaltous chloride, the *p*-duroylphenol was recovered unchanged.

p,*p*′-**Diduroylbiphenyl.**—The binary mixture, magnesium–magnesium iodide, was prepared by treating 2.4 g. of magnesium with 2.5 g. of iodine in 30 ml. of ether. The flask was swept with nitrogen and a solution of 3.2 g. of *p*-bromophenyl duryl ketone[10] in 60 ml. of benzene was added rapidly. After 5 minutes, the surface of the magnesium became red. The color soon spread throughout the solution and deepened to an intense purple. The reaction mixture was heated for 2.5 hours and hydrolyzed with cold dilute hydrochloric acid. The yellow solid which precipitated was collected by filtration. The organic layer of the filtrate was washed with water and the solvents were distilled. More yellow solid precipitated when methanol was added to the oily residue. The *p*,*p*′-diduroylbiphenyl crystallized from benzene in yellow flakes, m.p. 323–326°, yield 1.45 g. (61%).

Anal. Calcd. for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22. Found: C, 85.95; H, 7.40.

Reaction of *p*-Bromophenyl Duryl Ketone with Methylmagnesium Iodide in the Presence of Cobaltous Chloride.—A slurry of 0.7 g. of anhydrous cobaltous chloride in 20 ml. of ether was added to the Grignard reagent prepared from 1.2 g. of magnesium and 4.1 ml. of methyl iodide in 30 ml. of ether. Addition of a solution of 3.2 g. of *p*-bromophenyl duryl ketone in 60 ml. of benzene gave the mixture a dark purple color. The reaction mixture was heated under a nitrogen atmosphere for 3 hours and poured into cold dilute hydrochloric acid. The *p*,*p*′-diduroylbiphenyl, isolated as in the preceding experiment, crystallized from benzene in yellow flakes, m.p. 324–328°, yield 0.75 g. (32%). A mixed melting point with an authentic sample showed no depression.

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[10] R. C. Fuson, W. S. Friedlander and G. W. Parshall, This Journal, **76**, 5119 (1954).

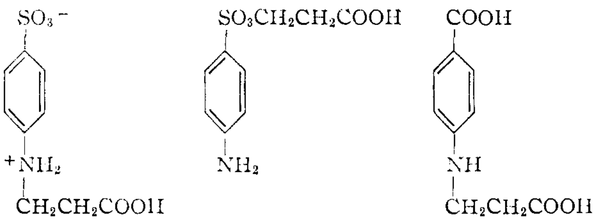
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Reaction of Propiolactone with Arylamines and with Sulfonamides

BY CHARLES D. HURD AND SHIN HAYAO

RECEIVED MAY 17, 1954

In an earlier paper[1] it was shown that propiolactone reacted with sulfanilic acid to yield N-(2-carboxyethyl)-sulfanilic acid (I). It was considered possible that the lactone reacted first at the sulfonate ion to form a sulfonic ester II, which then alkylated the amino group. This now appears improbable, and direct reaction at the amino position is suggested instead.

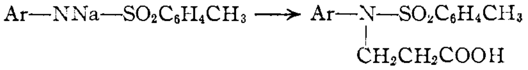


I II III

As evidence against the first formulation there is the fact that no II was ever isolated. This could be explained only if the subsequent alkylation was rapid. Hence, it was decided to treat sodium *p*-aminobenzoate with the lactone because if reaction occurred at the carboxylate ion the resulting carboxylic ester, $H_2N-C_6H_4-COOCH_2CH_2COOH$, would be stable and should show no tendency to alkylate the amino group. No such ester was found. Instead, reaction occurred directly at the amino group to give III.

Finally, if the sulfonic ester in II could alkylate an amine then the reaction product of propiolactone and sodium benzenesulfonate should be able to alkylate *p*-bromoaniline, but in such an operation which was carried out the amine was practically all recovered.

Sodium salts of sulfonamides were found to react readily in aqueous solution with propiolactone



$$Ar{-}NNa{-}SO_2C_6H_4CH_3 \longrightarrow Ar{-}\underset{\displaystyle CH_2CH_2COOH}{\underset{|}{N}}{-}SO_2C_6H_4CH_3$$

When Ar represented BrC_6H_4- the product formed was identical to that obtained[1] by reaction of *p*-bromoaniline with propiolactone followed by acylation with *p*-toluenesulfonyl chloride.

These new reactions also are of interest to report: (1) *p*-thiocyanoaniline and propiolactone, reacting to form N-(*p*-thiocyanophenyl)-β-alanine; (2) acrylo-*p*-toluidide (made from the lactone *via* hydracrylotoluidide) and bromine, adding to yield 2,3-dibromopropiono-*p*-toluidide; (3) N,N-diphenyl-β-alanine and chlorine, substituting to form N,N-bis-(trichlorophenyl)-β-alanine. Presumably the chlorine atoms are at the 2,4,6-positions.

Experimental

Propiolactone and Sodium *p*-Aminobenzoate. Fifteen-hundredths mole (10.8 g.) of propiolactone was added dropwise to 0.1 mole of sodium *p*-aminobenzoate in 100 ml. of water maintained at 0° during 10 minutes. The mixture was stirred at 0° for an hour and then was kept at 25° for 3 hours. On acidifying the mixture to congo red with hydrochloric acid there was obtained 15.3 g. (73%) of product, m.p. 190° dec.; colorless powder, m.p. 197–198.5° dec. from aqueous methanol. The mixed m.p. with N-(*p*-carboxyphenyl)-β-alanine,[1] m.p. 198.5° dec. was not depressed; neut. equiv. obsd. 102.9, calcd. 104.5.

Propiolactone, Sodium Benzenesulfonate and *p*-Bromoaniline. First Experiment.—Eight grams (0.11 mole) of propiolactone was added dropwise during 5 minutes to a solution of 18.0 g. (0.1 mole) of sodium benzenesulfonate in 100 ml. of water maintained at −5 to 0°. Stirring was continued for a half-hour at 0°, but then the ice-bath was removed because freezing of the contents made stirring difficult. The clear, slightly acidic solution was stirred at 25° for 1.5 hours and then was made basic to litmus using 20% sodium hydroxide solution. Then 17.2 g. (0.1 mole) of *p*-bromoaniline in 100 ml. of ether was added and the mixture was stirred at 25° overnight to let the ether evaporate slowly. The mixture was filtered to collect the bromoaniline. The filtrate was extracted with ether. In all, 16.4 g. (95%)

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[1] C. D. Hurd and S. Hayao, This Journal, **74**, 5889 (1952).