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.

(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

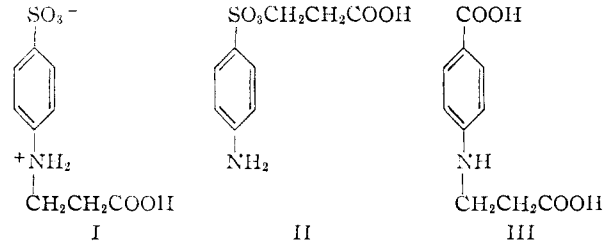
BY CHARLES D. HURD AND SHIN HAYAO

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.

As evidence against the first formulation there is

(1) C. D. Hurd and S. Hayao, THIS JOURNAL, **74**, 5889 (1952).



I II III

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

$$Ar—NNa—SO_2C_6H_4CH_3 \longrightarrow Ar—N(CH_2CH_2COOH)—SO_2C_6H_4CH_3$$

When Ar represented BrC_6H_4– the product formed was identical with 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%)

of the bromoaniline was recovered. The alkaline solution was acidified to congo red with 20% hydrochloric acid but there was no precipitation of a β-amino acid.

Second Experiment.—Propiolactone (7.2 g.) was added dropwise to a solution of 18 g. of sodium benzenesulfonate in 100 ml. of water at 10°. The clear solution was stirred at 0–10° for 2 hours and then at 26° overnight. Then a solution of 17.2 g. of bromoaniline in 100 ml. of acetone was added to this slightly acidic solution. The clear solution was stirred at 26° for 2 hours after which time the acetone was removed under diminished pressure. With processing similar to the above there was recovered 16.6 g. (91%) of bromoaniline and there was formed no β-amino acid.

N-2-Carboxyethyl-N-*p*-bromophenyl-*p*-toluenesulfonamide.—Propiolactone (10.8 g.) was added dropwise and with stirring during five minutes to a solution of 35.9 g. of *p*-toluenesulfone-(*p*-bromoanilide), m.p. 143–146°, in 200 ml. of water containing 5.6 g. of sodium hydroxide. The turbid solution clarified immediately with evolution of heat. Stirring was continued for an hour and then the mixture was kept at 25° overnight. After acidification (HCl) the resulting precipitate was extracted with benzene. The organic layer was then extracted with aqueous sodium bicarbonate. The cloudy alkaline extract (A) was washed with ether to clarify it and the ether extract was combined with the benzene layer. The organic layer was dried, solvent removed and the remaining light tan oil was stirred with aqueous sodium bicarbonate (B). The insoluble solid (25.14 g.) was collected, m.p. 137–142°. This was the original starting material. Its recovery was 59.5%.

Extract A was acidified (HCl) to give 12.65 g. of a white solid. From the alkaline washing (B), another 1.6 g. of product was secured: total 14.25 g., m.p. 127–131°. This is a 100% yield, based on the unrecovered sulfonanilide. It was recrystallized four times from aqueous methanol to give colorless prisms of m.p. 133–134°.

The same compound was prepared from N-*p*-bromophenyl-β-alanine[1] (11.6 g.) and *p*-toluenesulfonyl chloride (9.1 g.) dissolved in 30 ml. of dry pyridine and 150 ml. of benzene. After 3 hours of refluxing and conventional processing operations there was isolated 9 g. of crystalline product, m.p. 134–135°, after crystallization from ether–hexane. The mixture of this with that obtained above melted at 133–135°.

Anal. Calcd. for $C_{16}H_{16}BrNO_4S$: N, 3.52. Found: N, 3.39.

N-2-Carboxyethyl-N-*p*-nitrophenyl-*p*-toluenesulfonamide.—A solution of 56.4 g. of *p*-toluenesulfone-(*p*-nitroanilide) (m.p. 189°), 500 ml. of water and 7.8 g. of sodium hydroxide was warmed to about 50°. To it was added 14.0 g. of propiolactone dropwise with stirring during 5 minutes. When about half of the lactone was added a yellow precipitate began to separate from the clear red-brown solution. The mixture was stirred at this temperature for 1.5 hours and then set at 25° overnight. Processing followed the method given above for the *p*-bromo analog. There was a 77% recovery (43.5 g., m.p. 185–186°) of starting nitroanilide. The desired product originally appeared as a yellow sticky gum on acidification of the alkaline solution. It slowly solidified to give 11.5 g. of the product. This is a 93% yield, based on the nitroanilide which reacted. One recrystallization from aqueous methanol (Norit) gave yellow, sandy crystals of m.p. 147–151°, weight 9.5 g. After 4 crystallizations from aqueous methanol and vacuum drying for 3 hours over phosphorus pentoxide the substance appeared in colorless needles melting at 150–151°.

Anal. Calcd. for $C_{16}H_{16}N_2O_6S$: N, 7.68. Found: N, 7.61.

N-*p*-Thiocyanophenyl-β-alanine.—A solution of 0.04 mole each of propiolactone and *p*-thiocyanoaniline[2] in 60 ml. of acetone was refluxed for 3 hours. After distillation of solvent, the residue was worked up as usual[1] to give 1.95 g. (32% recovery) of the thiocyanoaniline and 5.6 g. (61% yield) of a product melting at 156–158°. After 2 recrystallizations from aqueous methanol a pure sample melted at 159–160°.

Anal. Calcd. for $C_{10}H_{10}N_2O_2S$: C, 54.0; H, 4.50; N, 12.6. Found: C, 54.0; H, 4.53; N, 12.4.

N,N-Bis-(trichlorophenyl)-β-alanine.—Dry chlorine gas was bubbled for an hour into a cold solution (10°) of 4.9 g. of N,N-diphenyl-β-alanine[3] in 50 ml. of chloroform. The solution was then washed with water and shaken with 10% sodium hydroxide solution to cause separation of 2.75 g. of sodium salt. This salt was treated with dilute hydrochloric acid to form 1.4 g. of colorless prisms of m.p. 168–168.5°. After two recrystallizations from methanol a pure sample, m.p. 169.5–170°, resulted. That it contained chlorine was proved by sodium fusion. It was insoluble in dilute acid or base or in boiling water; however, it was soluble in hot methanol or in boiling sodium hydroxide solution.

Anal. Calcd. for $C_{15}H_9Cl_6NO_2$: C, 40.2; H, 2.01; N, 3.13. Found: C, 40.5; N, 2.07; N, 3.21.

2,3-Dibromopropiono-*p*-toluidide.—A solution of 4.2 g. of bromine in 30 ml. of acetic acid was added dropwise during 15 minutes into a warm (90°) solution of 4.2 g. of acryl-*p*-toluidide in 70 ml. of glacial acetic acid. The clear solution, light yellow in color, was heated at 100° for an hour and with stirring. It was maintained at room temperature overnight. Dilution with water yielded 7.7 g. (87.5%) of product, m.p. 147–149°. Two recrystallizations from benzene–hexane and two from aqueous acetone gave rise to white needles of m.p. 152°.

Anal. Calcd. for $C_{10}H_{11}Br_2NO$: C, 37.4; H, 3.43; N, 4.36. Found: C, 37.35; H, 3.68; N, 4.41.

(2) H. P. Kaufmann and W. Oehring, *Ber.*, **59**, 187 (1926).

(3) T. L. Gresham and collaborators, THIS JOURNAL, **73**, 3168 (1951).

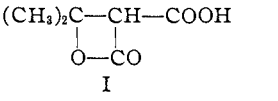
CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

Carboxy β-Lactones

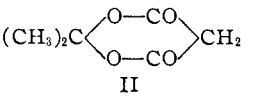
BY CHARLES D. HURD AND SHIN HAYAO

RECEIVED JUNE 1, 1954

An extensive series of recent papers by Vul'fson deals[1] with the formation of β-lactones by reaction of aldehydes or ketones with malonic acid under dehydrating conditions. He used either malonic acetic anhydride, $CH_2(COOCOCH_3)_2$, or a mixture of malonic acid, acetic anhydride and a trace of sulfuric acid. The structure given for the product of reaction with acetone as the ketone is I. Since this is a β-lactone our interest in this field prompted us to investigate these claims. If the compounds



I



II

were indeed β-lactones then they should react chemically in the manner of propiolactone[2a] or of β-isovalerolactone.[2b] The synthesis in question actually was discovered in 1908 by Meldrum[3] who used acetone, malonic acid, acetic anhydride and sulfuric acid, and it was he who assigned structure I to it. He found that the compound was acidic and that if it was heated with aniline it yielded acetone, carbon dioxide and acetanilide.

Meldrum's work was extended by Ott,[4] by Michael and Ross,[5] and it has been considered acceptable in recent reviews.[6] The interpretation was ques-

(1) N. S. Vul'fson and M. M. Shemyakin, *J. Gen. Chem.* (*U.S.S.R*), **13**, 436, 448 (1943); Vul'fson, *ibid.*, **20**, 425, 435, 595, 600, 603 (1950).

(2) (a) C. D. Hurd and S. Hayao, THIS JOURNAL, **74**, 5889 (1952); (b) T. L. Gresham, J. E. Jansen, F. W. Shaver and W. L. Beear, *ibid.*, **76**, 486 (1954).

(3) A. N. Meldrum, *J. Chem. Soc.*, **93**, 598 (1908).

(4) E. Ott, *Ann.*, **401**, 159 (1913).

(5) A. Michael and J. Ross, THIS JOURNAL, **55**, 3684 (1933).

(6) W. E. Hanford and J. C. Sauer in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 108.