

### Experimental

A suspension of 19.5 g. of *N*-bromosuccinimide in 30 cc. of carbon tetrachloride was mixed with 12.0 g. of ethyl tetrolate and 0.5 g. of freshly recrystallized dibenzoyl peroxide. After fifty minutes at reflux temperature the pale yellow solution was decanted from 15 g. of dark tarry material, the solvent evaporated and the residue distilled. In addition to 6.6 g. (55%) of ethyl tetrolate there was obtained 3.5 g. (12%) of a fraction boiling at 68–75° at 2 mm. This product was combined with those from other experiments and carefully fractionated to yield pure ethyl  $\alpha,\beta$ -dibromocrotonate b. p. 58.5–60° at 0.8 mm.,  $n_D^{20}$  1.5175,  $d_4^{20}$  1.744.

*Anal.* Calcd. for  $C_8H_9O_2Br_2$ : C, 26.50; H, 2.96; Br, 58.77. Found: C, 26.60; H, 3.05; Br, 58.62.

For further identification a sample was saponified by refluxing with 10% aqueous potassium hydroxide. From the highly colored product there was isolated by extraction with ligroin pure  $\alpha,\beta$ -dibromocrotonic acid, m. p. 118.5–119.5°. Michael reported the melting point of this substance as 120°.<sup>5</sup>

(5) A. Michael, *Ber.*, **34**, 4221 (1901).

STERLING CHEMISTRY LAB.  
YALE UNIVERSITY  
NEW HAVEN, CONN.

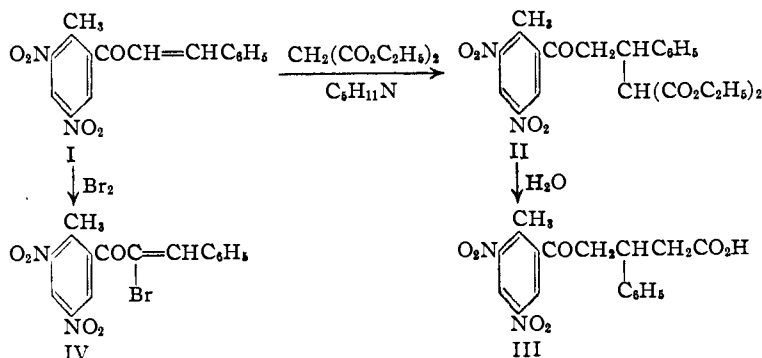
RECEIVED NOVEMBER 17, 1948

## The Condensation of 2'-Methyl-3',5'-dinitrochalcone with Ethyl Malonate

BY REYNOLD C. FUSON AND GEORGE MUNN

2'-Methyl-3',5'-dinitrochalcone (I) was prepared in the hope that it might undergo an intramolecular Michael condensation to yield the corresponding substituted  $\alpha$ -tetralone. However, under the conditions ordinarily employed for Michael condensations no ring closure occurred. That this chalcone is capable of undergoing reactions of the Michael type was demonstrated by condensing it intermolecularly with ethyl malonate.

The product (II) which was obtained when the chalcone was allowed to react with ethyl malonate was hydrolyzed and the resulting acid decarboxylated to form 2-phenyl-3-(2-methyl-3,5-dinitrobenzoyl)-butyric acid (III).



The 2'-methyl-3',5'-dinitrochalcone yielded a monobromo derivative when it was allowed to react with bromine in acetic acid solution. Oxidation of the bromochalcone with permanganate produced 3,5-dinitro-*o*-toluic acid, showing that the bromine was not attached to the methyl group.

It thus seems probable that the addition of bromine to the double bond is followed by the loss of hydrogen bromide, forming 2'-methyl-3',5'-dinitro- $\alpha$ -bromochalcone (IV).

### Experimental

**2-Methyl-3,5-dinitroacetophenone.**—2-Methyl-3,5-dinitrobenzoyl chloride was prepared by heating a mixture of 45 g. of 3,5-dinitro-*o*-toluic acid,<sup>1</sup> 35 ml. of purified thionyl chloride, and 200 ml. of dry benzene under reflux until the acid completely dissolved. The solvents were then removed by distillation under diminished pressure, and the residue was dissolved in 250 ml. of dry ether. This ether solution was used without further purification.

An ether solution of the ethoxymagnesium salt<sup>2</sup> of malonic ester was made in the following manner: Five milliliters of absolute ethanol, 0.5 ml. of carbon tetrachloride, and 5.25 g. of magnesium turnings were placed in a flask and allowed to react for a few minutes. Seventy-five milliliters of anhydrous ether was then added and to this mixture a solution of 35.2 g. of ethyl malonate, 20 ml. of absolute ethanol and 25 ml. of dry ether was added at a rate such that mild refluxing was maintained.

When the magnesium had dissolved, the solution of 2-methyl-3,5-dinitrobenzoyl chloride was added with stirring over a period of thirty minutes. The contents of the flask were then heated under reflux for an additional thirty minutes and then acidified with dilute sulfuric acid. The ether layer and an ether extract of the water layer were combined and the solvent was removed by distillation. The residual liquid was heated under reflux for four hours in a mixture of 60 ml. of acetic acid, 7.5 ml. of concentrated sulfuric acid and 40 ml. of water. The mixture was cooled, diluted with water and extracted with ether. The ether was washed with sodium bicarbonate solution, dried over calcium chloride, and the solvent was removed by distillation. The residue was distilled under diminished pressure at 150–152° (2 mm.). The yield was 27 g. (60%). When recrystallized from methanol, the 2-methyl-3,5-dinitroacetophenone melted at 72–73°.

*Anal.* Calcd. for  $C_9H_9N_2O_5$ : C, 48.24; H, 3.60; N, 12.50. Found: C, 48.47; H, 3.79; N, 12.40.

**2'-Methyl-3',5'-dinitrochalcone (I).**—Dry hydrogen chloride was bubbled slowly over a period of two days into a solution of 22.6 g. of 2-methyl-3,5-dinitroacetophenone and 12 ml. of benzaldehyde in 150 ml. of glacial acetic acid. During this time a crystalline precipitate appeared. The mixture was then heated under reflux for two hours and poured on ice. The white precipitate which formed was collected on a filter and recrystallized from ethanol.

Twenty-one grams of 2'-methyl-3',5'-dinitrochalcone was obtained; m. p. 128–129°; 67%.

*Anal.* Calcd. for  $C_{16}H_{12}N_2O_5$ : C, 61.53; H, 3.88; Found: C, 61.65; H, 3.90.

**Condensation of 2'-Methyl-3',5'-dinitrochalcone with Ethyl Malonate.**—A mixture of 3.1 g. of 2'-methyl-3',5'-dinitrochalcone, 2 ml. of ethyl malonate, 100 ml. of absolute ethanol, and 5 drops of piperidine was heated under reflux for twenty-four hours. It was then diluted with water, acidified and extracted with ether. The ether layer was dried over calcium chloride, and the solvent was removed by distillation. The residue was recrystallized several times from

methanol with the use of charcoal; 1.8 g. of white crystals (II) was obtained; m. p. 96–97°.

*Anal.* Calcd. for  $C_{23}H_{24}N_2O_9$ : C, 58.47; H, 5.12; N, 5.93. Found: C, 58.78; H, 5.16; N, 6.09.

(1) McGookin, Swift and Tittensor, *J. Soc. Chem. Ind. (Trans.)*, **59**, 92 (1940).

(2) Walker and Hauser, *THIS JOURNAL*, **68**, 1386 (1948).

**2-Phenyl-3-(2-methyl-3,5-dinitrobenzoyl)-butyric Acid.**—One gram of the malonic ester adduct was heated under reflux for four hours in a mixture of 10 ml. of glacial acetic acid, 7 ml. of water, and 1.5 ml. of concentrated sulfuric acid. The reaction mixture was then poured into 100 ml. of cold water; the acid precipitated as a brown gum. When this substance was recrystallized from methanol with the use of charcoal, it yielded 2-phenyl-3-(2-methyl-3,5-dinitrobenzoyl)-butyric acid (III) as white crystals melting at 137–138°.

*Anal.* Calcd. for  $C_{18}H_{18}N_2O_7$ : C, 58.06; H, 4.33; N, 7.53. Found: C, 58.32; H, 4.42; N, 7.78.

**2'-Methyl-3',5'-dinitro- $\alpha$ -bromochoalcone.**—A solution of 3.1 g. of 2'-methyl-3',5'-dinitrochoalcone and 5 ml. of bromine in 100 ml. of glacial acetic acid was allowed to stand at room temperature for twenty-four hours. At the end of this time the reaction mixture was poured into ice water and the excess bromine was destroyed by the addition of sodium sulfite solution. The white precipitate which formed was collected on a filter and recrystallized from ethanol. The bromochoalcone (IV) formed white crystals which melted at 137°; yield 3 g.

*Anal.* Calcd. for  $C_{15}H_{11}BrN_2O_6$ : C, 49.12; H, 2.83. Found: C, 49.44; H, 2.79.

When the bromochoalcone was oxidized with potassium permanganate in aqueous acetone, 3,5-dinitro-*o*-toluic acid was formed.

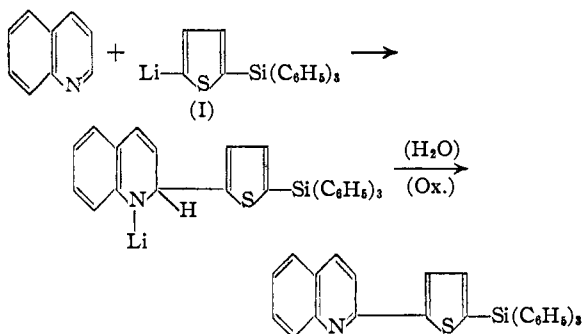
NOYES CHEMICAL LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS

RECEIVED NOVEMBER 10, 1948

## Some Anil Additions Involving Organosilicon Compounds

BY HENRY GILMAN AND MARY ALYS PLUNKETT<sup>1</sup>

In connection with studies on pharmacological action and chemical constitution, it seemed of interest to make a molecule containing both silicon and the quinoline nucleus. Consequently, compounds were prepared in which a lithiosilane was added to the anil linkage of a quinoline compound, as in the reaction



Triphenyl-[2-(5-lithio)-thienyl]-silane (I) reacted with quinoline, 6-methoxyquinoline and 4,7-dichloroquinoline. It is very probable that the substance isolated in each case was the 2-substituted quinoline, and not the 1,2-dihydro compound initially formed by hydrolysis of the N-Li intermediate from the addition of I across the azomethine linkage. Isolation through the picrates often leads to the oxidation of 1,2-dihydro-

(1) Present address: Vassar College, Poughkeepsie, N. Y.

quinolines by the picric acid.<sup>2</sup> The 1,2-dihydro compounds show an instability toward purification by crystallization, and cannot usually be obtained with a definite melting point range, as were the compounds described in this communication.

The preparation of I and a typical anil addition reaction are given in the experimental.

The authors are grateful to William Meikle for assistance, and particularly to Parke, Davis and Company for arranging for pharmacological testing, the results of which will be reported elsewhere.

### Experimental

**Triphenyl-[2-(5-lithio)-thienyl]-silane (I).**—To a solution of 5.5 g. (0.016 mole) of triphenyl-2-thienylsilane<sup>3</sup> under nitrogen in a mixture of equal parts of benzene and anhydrous ether was added 0.016 mole of *n*-butyllithium<sup>4</sup> in ether; the reaction mixture was refluxed for five hours. The solution gave a negative color test II.<sup>5</sup> It was used on the basis of an 80% yield, but the RLi compound was not, of course, isolated.

**Triphenyl-[5-(2'-quinolyl)-2-thienyl]-silane.**—To approximately 0.012 mole of I under nitrogen was added 1.5 g. (0.012 mole) of freshly distilled quinoline (previously dried over potassium hydroxide). A very slow reflux set in as the addition was made and the reaction mixture changed from red to dark yellow. After refluxing for one hour, the mixture was hydrolyzed and worked up to give 5 g. of crude solid, which was dissolved in dioxane and treated with a hot alcoholic solution of picric acid. The red picrate which precipitated was decomposed by boiling with a 5% solution of sodium hydroxide. After recrystallization from dilute dioxane, 40% of product melting at 168–170° was obtained.

*Anal.* Calcd. for  $C_{31}H_{23}N_2SSi$ : N, 2.98; S, 6.82. Found: N, 2.86; S, 6.61.

Addition of I to 4,7-dichloroquinoline gave triphenyl-[5-(4',7'-dichloro-2'-quinolyl)-2-thienyl]-silane, m. p. 200–203°.

*Anal.* Calcd. for  $C_{31}H_{21}NCl_2SSi$ : S, 5.95; Cl, 13.03. Found: S, 6.26; Cl, 13.30.

Addition of I to 6-methoxyquinoline gave triphenyl-[5-(6'-methoxy-2'-quinolyl)-2-thienyl]-silane, m. p. 227–228°.

*Anal.* Calcd. for  $C_{32}H_{25}ONSSi$ : N, 2.80. Found: N, 3.14.

(2) Gilman, Towle and Spatz, *THIS JOURNAL*, **68**, 2017 (1946); Gilman and Benkeser, *ibid.*, **69**, 123 (1947).

(3) R. A. Benkeser, unpublished studies, Iowa State College.

(4) The titer of the *n*-butyllithium solution was determined by the procedure of Gilman and Haubein, *THIS JOURNAL*, **66**, 1515 (1944).

(5) Gilman and Swiss, *ibid.*, **62**, 1847 (1940).

DEPARTMENT OF CHEMISTRY  
IOWA STATE COLLEGE  
AMES, IOWA

RECEIVED OCTOBER 29, 1948

## The Reaction of *o*-Hydroxy and *o*-Chlorobenzaldehyde with Ethanalamine<sup>1</sup>

BY LOUIS H. GOODSON AND HOPE CHRISTOPHER

In studying the reaction of ethanalamine with salicylaldehyde and with *o*-chlorobenzaldehyde, M. Meltsner, E. Waldman and Chester B. Kremers<sup>2</sup> report that in these two cases addition com-

(1) This investigation was supported in part by a research grant from the National Cancer Institute of the National Institute of Health, U. S. Public Health Service.

(2) M. Meltsner, E. Waldman and Chester B. Kremers, *THIS JOURNAL*, **62**, 3494 (1940).