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 $C_{18}H_{16}N_2O_7$: C, 58.06; H, 4.33; N, 7.53. Found: C, 58.32; H, 4.42; N, 7.78.

2′-Methyl-3′,5′-dinitro-α-bromochalcone.—A solution of 3.1 g. of 2′-methyl-3′,5′-dinitrochalcone 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 bromochalcone (IV) formed white crystals which melted at 137°; yield 3 g.

Anal. Calcd. for $C_{16}H_{11}BrN_2O_5$: C, 49.12; H, 2.83. Found: C, 49.44; H, 2.79.

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

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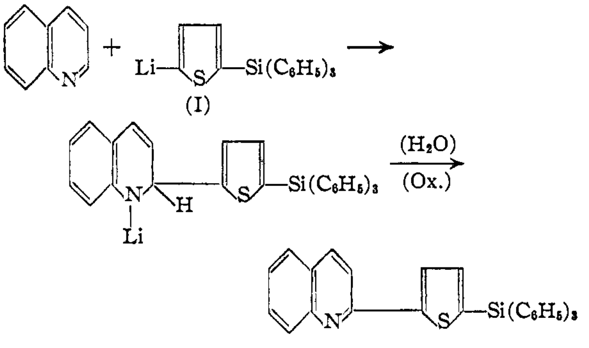
RECEIVED NOVEMBER 10, 1948

Some Anil Additions Involving Organosilicon Compounds

BY HENRY GILMAN AND MARY ALYS PLUNKETT[1]

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-dihydroquinolines by the picric acid.[2] 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[3] under nitrogen in a mixture of equal parts of benzene and anhydrous ether was added 0.016 mole of *n*-butyllithium[4] in ether; the reaction mixture was refluxed for five hours. The solution gave a negative color test II.[5] 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 $C_{31}H_{23}NSSi$: 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.

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[1] Present address: Vassar College, Poughkeepsie, N. Y.

[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).

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RECEIVED OCTOBER 29, 1948

The Reaction of *o*-Hydroxy and *o*-Chlorobenzaldehyde with Ethanolamine[1]

BY LOUIS H. GOODSON AND HOPE CHRISTOPHER

In studying the reaction of ethanolamine with salicylaldehyde and with *o*-chlorobenzaldehyde, M. Meltsner, E. Waldman and Chester B. Kremers[2] report that in these two cases addition com-

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[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).