

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- 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 $C_{15}H_{11}BrN_2O_6$: 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.

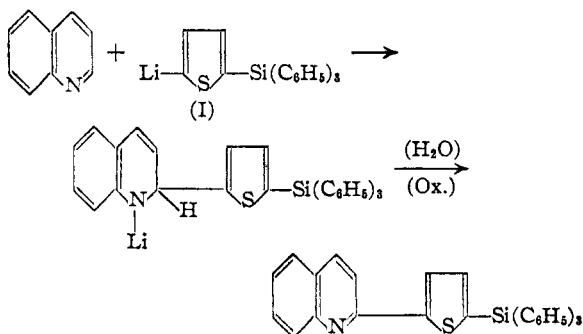
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED NOVEMBER 10, 1948

Some Anil Additions Involving Organosilicon Compounds

BY HENRY GILMAN AND MARY ALYS PLUNKETT¹

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.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-thienylsilane³ under nitrogen in a mixture of equal parts of benzene and anhydrous ether was added 0.016 mole of *n*-butyllithium⁴ 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 $C_{31}H_{23}N_2SSi$: 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 Ethanamine¹

BY LOUIS H. GOODSON AND HOPE CHRISTOPHER

In studying the reaction of ethanamine with salicylaldehyde and with *o*-chlorobenzaldehyde, M. Meltzner, E. Waldman and Chester B. Kremers² report that in these two cases addition com-

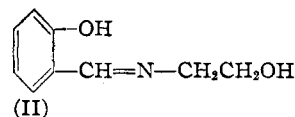
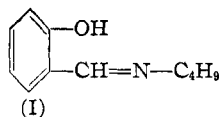
(1) This investigation was supported in part by a research grant from the National Cancer Institute of the National Institute of Health, U. S. Public Health Service.

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

pounds are formed without the elimination of water. They suggest that the failure of these two aldehydes to yield oxazolidines is due to chelation. We have found that water is eliminated in both of these reactions and that salicylaldehyde gives a Schiff base and that *o*-chlorobenzaldehyde yields an oxazolidine derivative.

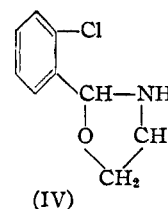
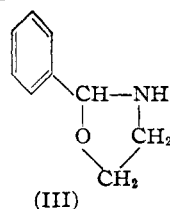
In our initial experiments, salicylaldehyde was dissolved in an excess of benzene and treated with ethanolamine whereupon a mildly exothermic reaction took place and a water layer separated. Azeotropic distillation of the mixture effected the separation of one mole of water from one mole of each of the reactants. It was thought that perhaps the elimination of water in our experiment was due to the use of conditions differing from those used by Meltsner and co-workers.² Accordingly, we followed their procedure as carefully as possible but noted a layer of water in the receiver on removal of the butyl alcohol from the reaction mixture by slow distillation. The analyses and refractive indices of the products obtained from salicylaldehyde and ethanolamine show that the products are the same whether the reaction is carried out in benzene or in butyl alcohol. The intense yellow color of the material, even in thin layers, suggests that the Schiff base structure is the probable one. This structure is further supported by the ultraviolet absorption spectra (Fig. 1) of this and related compounds. Curve A is the absorption spectrum for *N*-*n*-butyl-2-hydroxybenzalimine (I) which was prepared by the reaction of salicylaldehyde and *n*-butylamine. Its absorption spectrum confirms the fact that it is a Schiff base possessing a double bond conjugated with a benzene ring. Curve B represents the absorption spectrum of the reaction product obtained

from salicylaldehyde and ethanolamine. The similarity of these two curves indicates that this product is then the *N*-(2-hydroxyethyl)-2-hydroxybenzalimine (II), which is a Schiff base containing a double bond conjugated with the benzene ring.



The structure, 2-(2-hydroxyphenyl)-oxazolidine, is eliminated because it would be expected to have an absorption spectrum resembling curves C and D (Fig. 1).

Similarly the reaction of *o*-chlorobenzaldehyde with ethanolamine in benzene yielded the theoretical quantity of water necessary for the formation of the Schiff base or the oxazolidine. However, this colorless product is thought to be the 2-(2-chlorophenyl)-oxazolidine (IV) in spite of Meltsner's report that his analysis agreed with a chelation compound formed without the elimination of water. Curve D (Fig. 1) gives the ultraviolet absorption spectrum of 2-phenyloxazolidine³ (III)



whose assigned structure was based on an analogy with known oxazoles and on its method of preparation. Because the oxazolidine ring system is relatively unstable, compounds bearing this structure react in the same manner as the open chain Schiff bases. For example, treatment of 2-phenyloxazolidine with dilute acid readily gives benzaldehyde and ethanolamine hydrochloride. Further, treatment of 2-(4-methoxyphenyl)-oxazolidine² with benzylmagnesium chloride gives a product similar to that obtained with Grignard reagents on various Schiff bases.⁴ For these and other reasons it is difficult in most cases to distinguish between the Schiff base and the oxazolidine structures by their chemical reactivities. Curve C gives the ultraviolet absorption spectrum of 2-(2-chlorophenyl)-oxazolidine, (IV). Comparison of this curve with Curve D indicates the absence of the Schiff base structure and also a similarity with the known oxazolidine spectrum.

The molecular refractivities of four compounds discussed in this paper have been reported. In each case there appears to be an exaltation ranging from 2.57 to 3.35 units. Other Schiff bases and oxazolidines to be reported later in connection with other work, show exaltations of similar magnitudes. An attempt to differentiate between

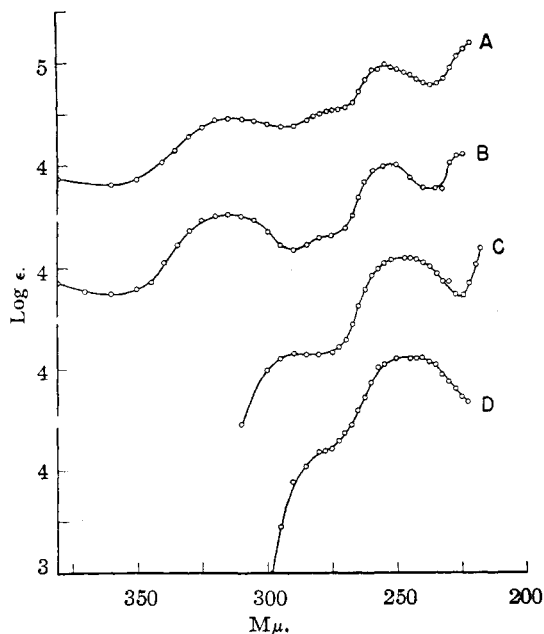


Fig. 1.

(3) Knorr and Matthes, *Ber.*, **34**, 3487 (1901).

(4) R. B. Moffett and W. M. Hoebe, *This Journal*, **69**, 1792 (1947); K. N. Campbell, C. H. Helbing and Sr. M. Patricia, O.S.F., and B. K. Campbell, *ibid.*, **70**, 3868 (1948).

oxazolidine and Schiff base structures on the basis of their molecular refractivities was unsuccessful.

Experimental⁵

N-Butyl-*o*-hydroxybenzalimine (I).—Azeotropic distillation of a mixture of 91.6 g. of salicylaldehyde, 54.7 g. of butylamine and an excess of benzene for two hours gave the theoretical quantity of water in the distillate. The benzene was removed under reduced pressure and the residue was distilled. The fraction, b. p. 84° at 0.1 mm., was yellow and weighed 127 g., n_D^{25} 1.5442; d_4^{25} 0.9919; MR_D (calcd.) 53.76; MR_D (obsd.) 56.43.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.55; H, 8.51; N, 7.91. Found: C, 74.70; H, 8.48; N, 7.92.

N-(2-Hydroxyethyl)-2-hydroxybenzalimine (II).—Method (a): A mixture of 61 g. of salicylaldehyde, 30.5 g. of ethanolamine and 200 ml. of benzene was refluxed using a water-trap (9 ml. of water was collected in two hours). The residue was distilled and the fraction b. p. 110–120° at 0.2 mm. was yellow and weighed 74 g.; n_D^{25} 1.6052; d_4^{25} 1.1608; MR_D (calcd.) 46.04; MR_D (obsd.) 49.02.

Anal. Calcd. for $C_9H_{11}NO_2$: N, 8.48. Found: N, 8.48.

Method (b): To a solution of 30.5 g. of salicylaldehyde in 68 ml. of reagent grade *n*-butanol was added 15.2 g. of ethanolamine. An exothermic reaction caused the temperature to rise from 28 to 63°. The clear deep-yellow solution was boiled for four hours and then distilled. During the early part of the distillation a water layer was visible under the butanol. The fraction b. p. 110–115° at 0.2 mm. weighed 36 g.; n_D^{25} 1.6050; d_4^{25} 1.1608.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.31; H, 6.80; N, 8.46.

2-Phenyloxazolidine (III).—This compound, prepared by the method of Knorr and Matthes,³ was colorless, b. p. 86–88° at 0.1 mm.; n_D^{25} 1.5729; d_4^{25} 1.0707; MR_D (calcd.) 43.36; MR_D (obsd.) 45.93.

2-*o*-Chlorophenyloxazolidine (IV).—A mixture of 70.3 g. of *o*-chlorobenzaldehyde, 30.5 g. of ethanolamine and 200 ml. of benzene (exothermic on mixing) was refluxed for two hours using a water-trap (9 ml. of water collected). The material was distilled and the fraction b. p. 102–104° at 0.2 mm., weighed 82 g. After redistillation it was a colorless oil weighing 78 g.; n_D^{25} 1.5793; d_4^{25} 1.2073; MR_D (calcd.) 47.22; MR_D (obsd.) 50.57.

Anal. Calcd. for C_9H_9ClNO : C, 58.86; H, 5.49; N, 7.63. Found: C, 58.82; H, 5.46; N, 7.66.

Ultraviolet Absorption Spectra.—The data given in Fig. 1 were obtained using a Beckman quartz spectrophotometer with the hydrogen discharge lamp and quartz cells with a light path of 1 cm. A solution of 2.45 mg. of compound (I) in 100 ml. of absolute alcohol showed maxima at 255 $m\mu$, ϵ = 95,500 and 315 $m\mu$, ϵ = 30,000 (Curve A). A solution of 2.28 mg. of compound (II) in 100 ml. of absolute alcohol showed maxima at 252.5 $m\mu$, ϵ = 100,000 and at 315 $m\mu$, ϵ = 34,100 (Curve B). A solution of 2.53 mg. of compound (III) in 100 ml. of abs. alcohol showed maxima at 247.5 $m\mu$, ϵ = 127,400 and 290 $m\mu$, ϵ = 14,480 (Curve C). A solution of 2.28 mg. of compound (IV) in 100 ml. of abs. alcohol showed a maximum at 245 $m\mu$, ϵ = 127,600 (Curve D).

(5) Nitrogen analyses done by semi-micro Kjeldahl procedure. Carbon and hydrogen analyses by Micro-Tech Laboratories of Skokie, Ill.

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RECEIVED AUGUST 9, 1948

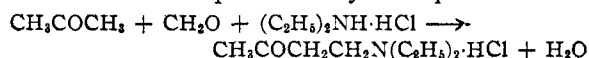
Preparation of Anhydrous Methyl Vinyl Ketone and Methyl Isopropenyl Ketone

By HUGH J. HAGEMEYER, JR.

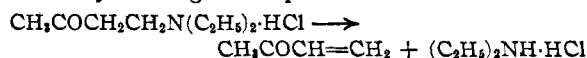
The preparation of methyl isopropenyl ketone by the aldol condensation of methyl ethyl ketone

with formaldehyde and an evaluation of the method was reported by Landau and Irany.¹ In both the liquid phase aldol condensation and in the catalytic vapor phase condensation of formalin with methyl ketone^{2,3} considerable difficulty is encountered in drying the unsaturated ketone and in removing traces of formaldehyde.

An alternate method of preparing methyl vinyl ketone and methyl isopropenyl ketone has now been evolved using the Mannich Reaction.^{4,5,6,7} The Mannich base is prepared by treating a ketone with a secondary amine hydrochloride and formalin or paraformaldehyde. With acetone, diethylamine hydrochloride and formalin the reaction can be represented by the equation

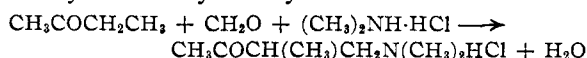


The tertiary base is separated from the reaction mixture by treating the reaction product with 50% caustic. After drying and distillation it is suspended in an inert medium such as Dowtherm and an equivalent of anhydrous hydrogen chloride is added. The tertiary amine salt is then deaminated by heating to temperatures of 145–160°



The secondary amine hydrochloride can be recovered from the inert medium by filtration or extraction with water and reused in a subsequent batch. In practice it is preferred to add the tertiary amine hydrochloride gradually to the deaminating flask and the unsaturated ketone is distilled off continuously.

It is significant that with methyl ethyl ketone only methyl isopropenyl ketone was formed and there was no evidence for the formation of ethyl vinyl ketone. This indicates the mono-tertiary amine formed to be exclusively α -methyl- β -dimethylaminoethyl methyl ketone.



The methyl isopropenyl ketone prepared by deamination of this tertiary amine hydrochloride had the same constants as those reported for pure methyl isopropenyl ketone by Brant.⁸

Experimental

General Procedure.—A mixture of ketone, dialkylamine hydrochloride and formaldehyde is refluxed for eight to twelve hours. A large excess of ketone is preferred in order to minimize the formation of di-tertiary amine products. In some instances the addition of a small amount of ethanol or isopropyl alcohol is advantageous in order to give a homogeneous mixture. At the end of the reaction excess ketone is removed by distillation. An excess

- (1) Landau and Irany, *J. Org. Chem.*, **12**, 422 (1946).
- (2) Brant, U. S. Patent 2,245,567.
- (3) McMahon, Roper, Utermohlen, Hasek, Harris and Brandt, *THIS JOURNAL*, **70**, 2971 (1948).
- (4) Defeu, McQuillan and Robinson, *J. Chem. Soc.*, 3089 (1931).
- (5) Mannich, *Arch. Pharm.*, **255**, 261 (1917).
- (6) Mannich and Salzmann, *Ber.*, **72**, 506 (1949).
- (7) Mannich and Haf, *Arch. Pharm.*, **265**, 589 (1927).
- (8) Brant, *THIS JOURNAL*, **64**, 2224 (1942).