which, after removal of the excess diazomethane and the solvent, was obtained as a light yellow liquid (5 g.). The crude ester was allowed to react overnight at room temperature with chloroacetic anhydride (4.5 g.) in benzene solution. The reaction mixture was warmed on a steam-cone for an hour and then the solvent was removed. On pouring the residue into water and stirring, crystals (5.95 g., 83.2%), m.p. 92–100°, separated. By recrystallization from a mixture of benzene and ligroin, the amide was obtained as colorless, stout prisms (5.6 g., 94%), m.p. 95–98°. After further recrystallization from ligroin, the m.p. was constant at 96–97°.

Anal. Calcd. for $C_{13}H_{14}O_3NClS$: C, 52.09; H, 4.71; N, 4.67. Found: C, 52.24; H, 4.84; N, 4.75.

2-Phenyl-3-chloroacetyl-4-carbomethoxythiazolidinesulfoxide. (a).—A solution of III (1.2 g.) in dioxane (15 ml.) was treated with potassium permanganate (0.17 g.) dissolved in glacial acetic acid (5 ml.). After one hour the reaction mixture was decolorized by the addition of a few drops of hydrogen peroxide. By pouring the colorless solution into water 0.54 g. of crystalline material was obtained. This was washed with ether to remove the starting material and then crystallized thrice from ethanol and twice from chloroform–ether. The m.p. was constant at 211–213° (dec.).

Anal. Calcd. for $C_{13}H_{14}O_4NClS$: C, 49.45; H, 4.47; N, 4.44. Found: C, 49.31; H, 4.44; N, 4.83.

(b).—To a solution of III (1.5 g.) in acetic acid was added 1.5 ml. of 35% hydrogen peroxide. After two weeks the solution was poured into water, 1.26 g. of crystalline material, yield 79.6%, m.p. 195–205°, was obtained. Recrystallization from ethanol raised the m.p. to 210–212°.

No reaction was observed when a solution of the sulfoxide in dry dioxane was treated with triethylamine.

2,4-Dicarbethoxythiazolidine (IV).—Cysteine ethyl ester hydrochloride (4.2 g.) and sodium acetate (2.7 g.) were dissolved in 20 ml. of water. Ethyl glyoxalate alcoholate (3.35 g.) in 80 ml. of alcohol was added and the reaction mixture was stored for two days. After removal of most of the alcohol by distillation, the oily layer which separated was collected in ether. The dried (sodium sulfate) ether extract was concentrated to a yellow liquid (4.5 g.). By evaporative distillation 2.8 g. (53%) of the thiazolidine was obtained. An analytical sample, $n^{25}D$ 1.4880, d^{25}_4 1.1991, was prepared by a second evaporative distillation.

Anal. Calcd. for $C_9H_{15}O_4NS$: C, 46.34; H, 6.48; N, 6.00; *MR*, 56.44. Found: C, 46.57; H, 6.50; N, 6.04; *MR*, 56.05.

2,4-Dicarbethoxy-3-chloroacetylthiazolidine (VI).—A mixture of IV (0.87 g.) and chloroacetic anhydride (0.8 g.) was allowed to react overnight at 60–70°. The reaction mixture was then poured into water and extracted with ether. The ether extract was washed successively with sodium bicarbonate solution and water. Removal of ether from the dried (sodium sulfate) solution left a slightly yellow, viscous oil (1.15 g., 81%). Evaporative distillation (120–130° (0.4 mm.)) gave a colorless, viscous oil (90% recovery). A second evaporative distillation afforded an analytical sample, $n^{25}D$ 1.5090.

Anal. Calcd. for $C_{11}H_{16}O_5ClNS$: C, 42.65; H, 5.21; N, 4.52. Found: C, 42.74; H, 5.18; N, 4.67.

2-Carbethoxy-4-carbomethoxy-5,5-dimethylthiazolidine (V).—To a solution of D-penicillamine methyl ester hydrochloride (3 g.) and sodium acetate (2 g.) in 20 ml. of water was added ethyl glyoxalate alcoholate (2.3 g.) in 50 ml. of alcohol. After two days the alcohol was removed, leaving oily droplets in an aqueous suspension. The oil was collected with ether, washed, and the dried ethereal solution was concentrated to a pale yellow liquid (3.71 g.). An evaporative distillation (60–70° (0.07 mm.)) of 1.85 g. of this liquid afforded 1.51 g. of colorless distillate—part of which crystallized. The crystalline material (0.8 g., 35%), m.p. 48–50°, is readily soluble in organic solvents but can be recrystallized from dilute alcohol.

Anal. Calcd. for $C_{10}H_{17}O_4NS$: C, 48.56; H, 6.93; N, 5.66. Found: C, 48.60; H, 7.03; N, 5.79.

The liquid fraction of the distillate (0.71 g., 31.3%) was thrice distilled for analysis.

Anal. Calcd. for $C_{10}H_{17}O_4NS$: C, 48.56; H, 6.93; N, 5.66. Found: C, 48.38; H, 6.77; N, 5.62.

Both the crystalline and liquid fractions were optically active, the specific rotations in alcohol, $[\alpha]^{25}D$ were −20.7° and +28.2°, respectively.

In another experiment using 5 g. of D-penicillamine methyl ester hydrochloride, the undistilled reaction mixture was seeded. After two days in a refrigerator, 3.3 g. (37.3%) of crystalline product, m.p. 43–45°, was obtained.

2-Carbethoxy-3-benzoyl-4-carbomethoxy-5,5-dimethylthiazolidine.—To a suspension of 2-carbethoxy-4-carbomethoxy-5,5-dimethylthiazolidine (0.5 g.) in 10% sodium hydroxide solution was added benzoyl chloride (0.25 ml.) with vigorous shaking. After one hour, the reaction mixture was warmed on a steam-cone to destroy excess benzoyl chloride and was then extracted with ether. The dried (sodium sulfate) ethereal solution was concentrated to an oil which was purified by an evaporative distillation (130–140° (0.5 mm.)); a colorless and very viscous oil (0.27 g., 38%) was obtained. The infrared spectrum has an amide band at 6.02 μ in addition to the carbonyl band (a double peak at 5.73 and 5.77 μ).

Anal. Calcd. for $C_{17}H_{21}O_5NS$: C, 58.10; H, 6.02; N, 3.99. Found: C, 57.95; H, 6.02; N, 3.86.

2-Carbethoxy-3-chloroacetyl-4-carbomethoxy-5,5-dimethylthiazolidine (I).—A mixture of 2-carbethoxy-4-carbomethoxy-5,5-dimethylthiazolidine (0.8 g.) and chloroacetic anhydride (1 g.) was kept overnight at 70–75°. The ethereal extract of the melt was washed successively with water, dilute hydrochloric acid, water, sodium bicarbonate solution and water. The dried ethereal solution gave a reddish brown oil (0.88 g.) after concentration. A faintly yellow and very viscous oil (0.77 g., 73.6%) was obtained by an evaporative distillation (130–140° (0.5 mm.)). A colorless analytical sample was prepared by two more evaporative distillations.

Anal. Calcd. for $C_{12}H_{18}O_5NClS$: C, 44.52; H, 5.64; N, 4.33. Found: C, 44.66; H, 5.68; N, 4.13.

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The Reaction of Azomethines with Methylmagnesium Iodide[1]

BY PAUL M. MAGINNITY AND THOMAS J. GAIR

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The classical investigations of Busch[2] and his co-workers indicated that Schiff bases reacted with the Grignard reagent in a manner analogous to aldehydes, but only one example involving a keto anil was reported. Such reactions were used by subsequent workers, notably Moffett and Hoehn,[3] and Campbell and co-workers[4] to prepare substituted aromatic secondary amines, but the problem of isolating the intermediate Grignard addition compound and determining its composition was not studied.

Sachs and Sachs[5] attempted the isolation of the compounds resulting from the action of phenylmagnesium bromide and ethylmagnesium bromide on quinoline in ethyl ether. Their analyses indicated that one mole of the organomagnesium compound and one mole of quinoline had reacted, although the

(1) Taken from a thesis submitted by Thomas J. Gair to the Graduate School of Boston College in partial fulfillment of the requirements of the degree of Master of Science.

(2) (a) M. Busch, *Ber.*, **37**, 2691 (1904); (b) M. Busch and A. Rinck, *ibid.*, **38**, 1761 (1905); (c) M. Busch and H. Leefhelm, *J. prakt. Chem.*, **77**, 20 (1908).

(3) R. B. Moffett and W. M. Hoehn, THIS JOURNAL, **69**, 1792 (1947).

(4) K. N. Campbell, C. H. Helbing, M. P. Florkowski and B. K. Campbell, *ibid.*, **70**, 3868 (1948).

(5) F. Sachs and L. Sachs, *Ber.*, **37**, 3086 (1904).

TABLE I

METHYLMAGNESIUM IODIDE–AZOMETHINE ADDITION COMPOUNDS

Compound	Formula	N, % Calcd.	N, % Found	Mg, % Found	Mg, % Found	I, % Calcd.	I, % Found
Benzophenone anil[a]	$C_{20}H_{18}NMgI$	3.30	2.77	5.74	6.69	29.96	30.27
Benzylideneaniline[b]	$C_{14}H_{14}NMgI$	4.03	3.65	7.00	7.21	36.52	36.98
Benzylidenebenzylamine[c]	$C_{15}H_{16}NMgI$	3.87	3.00	6.72	6.45	35.11	35.18
Benzylidene-*n*-butylamine[d]	$C_{12}H_{18}NMgI$	4.27	3.47	7.43	7.04	38.75	39.23
Benzylidenecyclohexylamine[c]	$C_{14}H_{20}NMgI$	3.96	3.63	6.88	8.04	35.90	34.48
Benzylidene-ethylamine[d]	$C_{10}H_{14}NMgI$	4.68	4.26	8.12	8.33	42.38	43.88
Benzylideneisopropylamine[d]	$C_{11}H_{16}NMgI$	4.47	4.18	7.76	7.32	40.49	40.71
Butylidenebenzylamine[d]	$C_{12}H_{18}NMgI$	4.27	3.53	7.43	7.06	38.75	39.44

[a] Prepared by the method of G. Reddelien, *Ber.*, **43**, 2476 (1910). [b] Prepared as described in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 80. [c] Prepared by the method of A. T. Mason and G. R. Winder, *J. Chem. Soc.*, **65**, 191 (1894). [d] Prepared by the method of H. Zauschirm, *Ann.*, **245**, 281 (1888).

hygroscopic nature of the compounds made analyses difficult.

A quantitative study of the reactions between certain azomethines and 2-substituted Δ^1-pyrrolines and methylmagnesium iodide using the Zerevitinov method[6] indicated that these compounds, all containing the >C=N— group, reacted with one mole of the reagent in butyl ether, while analyses of addition compounds of 2-phenyl-Δ^1-pyrroline pointed to the same conclusion.

In order to determine the exact nature of the compounds resulting when such reactions take place with azomethines, a series of methylmagnesium iodide–azomethine compounds was prepared and analyzed by a method similar to that of Sachs and Sachs, except that butyl ether was used as a solvent, a modification which enabled the compounds to be more easily separated and dried. The analytical data listed in Table I show that equimolar quantities of the azomethine and Grignard reagent had reacted to form the addition compound.

Experimental

The azomethines were prepared as described in the literature (see Table I). The methylmagnesium iodide solution was prepared in the usual manner from 62.7 g. of methyl iodide, 10.8 g. of magnesium and 250 ml. of anhydrous butyl ether. To 1 g. of the azomethine, dissolved in 25 ml. of the butyl ether, was added slightly more than the theoretical quantity of the methylmagnesium iodide solution. The ether was decanted from the tarry precipitate first formed (generally yellowish in color) and more butyl ether added. The precipitate was then rubbed until it separated out as a powder, whereupon it was removed by filtration and dried in a vacuum desiccator.

Benzylidene-*n*-butylamine and methylmagnesium iodide yielded an oil, which solidified eventually when immersed in an ice-bath.

When the procedure of Sachs and Sachs was used, namely, preparing the compound in ethyl ether, washing four times with fresh ether, and rubbing until the tar turned to powder, the compound was never obtained completely dry and the analyses were not satisfactory.

The reaction of benzophenone anil with the Grignard reagent in benzene as described by Short and Watt[7] was repeated, but although a gas was evolved, no separation of an addition compound was observed.

The data of Table I summarize the analytical results obtained for the addition compounds thus prepared. Magnesium was determined as the sulfate and nitrogen was determined by the Dumas method, both as described by Niederl and Niederl.[8] Iodine was determined gravimetrically as silver iodide.

(6) P. M. Maginnity with J. B. Cloke, THIS JOURNAL, **73**, 49 (1951).

(7) W. F. Short and J. S. Watt, *J. Chem. Soc.*, 2293 (1930).

(8) J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942.

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Preparatory Method for N-Vinyl-2-pyrrolidone

BY BRUNO PUETZER, LEON KATZ AND LESTER HORWITZ

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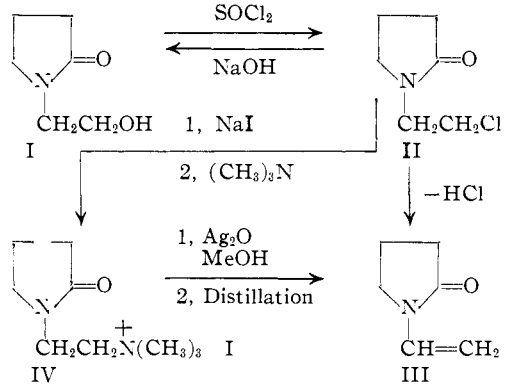
The present commercial process for the preparation of N-vinyl-2-pyrrolidone is based on the high pressure reaction of acetylene with 2-pyrrolidone.[1a,b] The extensive interest in the polymer, polyvinylpyrrolidone,[2] as a blood plasma extender[3] prompted us to consider alternative syntheses of the monomer avoiding the use of acetylene and pressure. Two such syntheses are outlined in the flow sheet.

The preparation of N-(β-hydroxyethyl)-2-pyrrolidone (I) by the passage of 2-aminoethanol and butyrolactone over dehydration catalysts has been reported.[1a,4] The corresponding chloro derivative, (β-chloroethyl)-2-pyrrolidone (II), was reported[1a] as being formed by the action of thionyl chloride on I. We have prepared I by heating a solution of butyrolactone in excess 2-aminoethanol to 180–190° so that the water liberated was entrained by the slowly distilling 2-aminoethanol. The yields

FLOW SHEET



(1) (a) J. W. Reppe, "Acetylene Chemistry," PB Report No. 18852-S, U. S. Department of Commerce, New York, N. Y., Charles A. Meyer & Co., Inc. (1949); (b) French Patent 865,354 (May 21, 1941).

(2) An excellent summary on polyvinylpyrrolidone is "PVP," General Aniline and Film Corporation, New York, March, 1951.

(3) PVP (Macrose) is the trade name for the Schenley Laboratories blood plasma extender.

(4) In this connection see C. Schuster and A. Seib, German Patent 694,043; E. Spath and J. Lintner, *Ber.*, **69**, 2727 (1936).