

cyanate and 3-methyl-1-pentyne-3-ol according to ref. 1. Heating larger quantities of these reactants gave an uncontrollable exothermic reaction.

**3-*p*-Chlorophenyl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Methyl-1-butyne-3-ol).**—A mixture of 15 g. (0.1 mole) of *p*-chlorophenyl isocyanate, 10 g. (0.12 mole) of 3-methyl-1-butyne-3-ol, and 0.1 g. of sodium acetate was warmed on a steam bath. After warming for about 0.5 hr., a vigorous reaction occurred. After heating an additional 4 hr. on the steam bath, chloroform was added; the mixture was filtered, and the chloroform was distilled at reduced pressure. After recrystallization from methanol, a 65% yield of product, m.p. 98–99°, was obtained.

*Anal.* Calcd. for  $C_{12}H_{12}ClNO_2$ : C, 60.63; H, 5.10; N, 5.89. Found: C, 60.65; H, 5.12; N, 5.84.

**3-Phenyl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Methyl-1-butyne-3-ol).**—A mixture of 30 g. (0.36 mole) of 3-methyl-1-butyne-3-ol, 30 g. (0.28 mole) of phenyl isocyanate, and 1 g. of sodium acetate was heated on a steam bath for 4 hr. Ether was added to the cooled mixture, and the insoluble salt was removed by filtration. The solvent was removed by vacuum distillation. After recrystallization from a mixture of ether–petroleum ether (b.p. 30–60°) the 1,1-dimethylpropargyl-*N*-phenylcarbamate melted at 94–95°.

*Anal.* Calcd. for  $C_{12}H_{13}NO_2$ : C, 70.91; H, 6.45. Found: C, 70.95; H, 6.50.

The infrared curve showed a band at 3.03  $\mu$  for the acetylenic hydrogen.

An alcoholic solution of the 1,1-dimethylpropargyl-*N*-phenylcarbamate from the above reaction was added slowly to a solution of 2 g. of sodium in ethanol. After the ensuing exothermic reaction had subsided, water was added to the solution, and the resulting mixture was extracted with ether. After drying over magnesium sulfate, the ether solution was concentrated at reduced pressure. Recrystallization of the resulting solid from ethanol gave a product that melted at 94–95°. An over-all yield of 38 g. (68%) was obtained.

*Anal.* Calcd. for  $C_{12}H_{13}NO_2$ : C, 70.91; H, 6.45; N, 6.89. Found: C, 70.63; H, 6.76; N, 6.94.

**3-Aryl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Hydroxy-3-methyl-2-butanone).**—One-tenth mole of aryl isocyanate was added slowly to 10 g. (0.10 mole) of 3-hydroxy-3-methyl-2-butanone with swirling. The mixture became warm and was heated on the steam bath for 4 hr. The infrared spectrum of the crude product showed this material to be, at least in part, the substituted 4-hydroxyoxazolidinone (VI). The material was then refluxed in toluene containing 0.5 g. of *p*-toluenesulfonic acid, and the water was separated with a Dean-Stark trap. After cooling, the mixture was poured into water; the organic layer was separated, dried over magnesium sulfate, and the solvent was distilled under reduced pressure. The residue was crystallized from methanol. These products were obtained in 80–90% yield and were identical in all respects to those prepared from the acetylenic alcohols.

**3-Phenyl-4,5,5-trimethyloxazolidine-2-one.**—3-Phenyl-4-methylene-5,5-dimethyloxazolidine-2-one (15 g.) was hydrogenated at 50 p.s.i. in the presence of 5 g. of 5% palladium-on-carbon, using 250 ml. of ethanol as the solvent and warmed by a heat lamp. The product (13 g., 86% yield) was crystallized from methanol and melted at 98–99°.

*Anal.* Calcd. for  $C_{12}H_{15}NO_2$ : C, 70.22; H, 7.37; N, 6.82. Found: C, 70.54; H, 7.57; N, 7.09.

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### An *N*-Methylpyrrolidone–Diacetylene Complex. Its Use in the Isolation of Diacetylene

NORMAN SHACHAT

Research Laboratories, Rohm & Haas Company, Philadelphia, Pennsylvania

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During an investigation of certain reactions of diacetylene (1,3-butadiyne) in which *N*-methylpyrrolidone was employed as the solvent, it was observed that the hydrocarbon and the solvent formed a colorless crystalline 1:1 molecular complex which precipitated from the solution. The complex appeared to be quite stable while kept under a solution of diacetylene in *N*-methylpyrrolidone; however, a pure sample of the solid could not be isolated by filtration, presumably owing to the high vapor pressure of diacetylene in the complex and the low vapor pressure of *N*-methylpyrrolidone. The best samples, obtained by filtration under slight positive nitrogen pressure, still contained some excess *N*-methylpyrrolidone. Analyses of these samples for acetylenic hydrogen by the method of Barnes and Molinini<sup>1</sup> showed a molar ratio of *N*-methylpyrrolidone: diacetylene of  $1.2 \pm 0.1:1$ . Efforts to prepare a similar solid complex with other solvents, namely *N*-vinylpyrrolidone, *N*-ethylpyrrolidone, pyrrolidone, butyrolactone, and *N,N*-dimethylformamide, were unsuccessful.

The *N*-methylpyrrolidone–diacetylene complex provides a convenient tool for the isolation and purification of diacetylene.

A sample of the complex which contained some excess *N*-methylpyrrolidone began to crystallize at 26°, and, as the first few crystals appeared in the mixture, the temperature rose sharply to 27.5°. At 15.5°, the material was almost completely solid. Pure diacetylene melts at –36°, pure *N*-methylpyrrolidone at –24°. When the complex was treated with ether, benzene, ethanol, or water, diacetylene gas was evolved and a homogeneous solution resulted. An infrared spectrum of a satu-

(3) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Co., New York, N. Y., 1947, p. 390.

(1) L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1955).

rated solution of diacetylene in *N*-methylpyrrolidone showed no evidence of a complex in solution. The spectrum exhibited only the normal absorption bands expected for each of the components.

### Experimental

**Determination of the Solubility of Diacetylene and the Amount of Solid Complex Formation in *N*-Methylpyrrolidone at Various Temperatures.**—A 4.85-molal solution of diacetylene in *N*-methylpyrrolidone was prepared at 26°. The diacetylene was synthesized by the treatment of 1,4-dichloro-2-butyne with base.<sup>2</sup> The temperature of the solution was reduced stepwise and the mixture was held at each temperature long enough to establish equilibrium between the solution and the solid complex which separated out. The supernatant liquid was then analyzed for diacetylene<sup>1</sup> and the molality of diacetylene in the liquid phase and the mole % diacetylene precipitated in the complex were calculated. The data are presented in Table I.

TABLE I

SOLUBILITY OF DIACETYLENE AND AMOUNT OF SOLID COMPLEX FORMATION IN *N*-METHYLPYRROLIDONE AT VARIOUS TEMPERATURES

<i>T</i> , °C.	Molality C <sub>4</sub> H <sub>2</sub> in liquid phase	Mole % C <sub>4</sub> H <sub>2</sub> <sup>a</sup> precipitated
26.0	4.85	0.0
19.0	4.61	9.0
15.0	4.00	29.0
9.5	3.51	42.0
2.0	2.84	58.6
-10.0	2.18	70.7

<sup>a</sup> These data were calculated on the basis of a 1:1 molecular complex.

**The Use of the Complex for the Separation of Diacetylene from a Gas Stream Consisting of C<sub>4</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>.**—A stream of acetylene gas was bubbled through a liquid mixture consisting of equal volumes of diacetylene and methylacetylene (a commercial sample containing 70% methylacetylene and 30% allene was employed), and the gas mixture was led into a trap containing *N*-methylpyrrolidone cooled to 0°. When the first crystal of complex appeared in the trap, samples of the gas stream entering (1) and leaving (2) the trap were collected for mass spectrographic analysis. After a considerable amount of precipitate had formed, the trap was removed from the system and warmed to room temperature. A sample of the solid complex was obtained by filtration under nitrogen pressure. The gas evolved on heating both the filtrate (3) and the solid complex (4) was analyzed by means of a mass spectrometer. The composition of the four gas samples is given in Table II.

TABLE II

COMPOSITION OF GAS SAMPLES GIVEN BY MASS SPECTROGRAPHIC ANALYSES

Sample no.	Mole %		
	C <sub>4</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
(1)	45.17	16.43	38.40
(2)	2.09	42.23	55.68
(3)	13.08	51.09	35.83
(4)	96.13	3.71	0.16

(2) E. Keyssner and E. Eichler, German Patent 740,637 (1943).

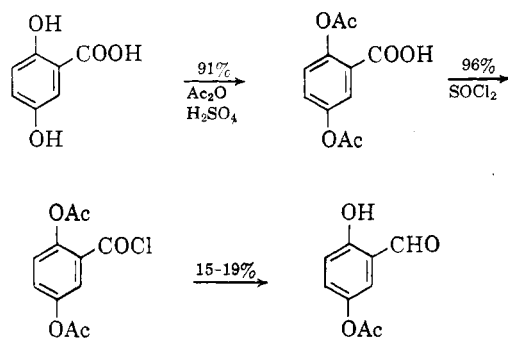
## The Synthesis of 2-Acetoxy-5-hydroxybenzaldehyde

H. YEE AND A. J. BOYLE

Department of Chemistry, Wayne State University, Detroit 2, Michigan

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The original synthesis of 2,5-dihydroxyphenylpyruvic acid from salicylaldehyde<sup>1</sup> has been used since 1907 with but minor modifications. The overall yield has been raised by isolating the intermediate 2,5-diacetoxybenzaldehyde and by utilizing acetyl glycine in place of hippuric acid,<sup>2</sup> but even then it was small because of the low yield (25%) in the initial step of converting salicylaldehyde to 2,5-dihydroxybenzaldehyde.<sup>3-5</sup> As our research concerned 2,5-dihydroxyphenyl pyruvic acid,<sup>6</sup> an effort to raise the yield by the reduction of 2,5-diacetoxybenzoyl chloride as an alternate route was investigated. The Rosenmund reduction of this chloride could not be controlled to give the desired product; however, its reduction with lithium tri-*tert*-butoxy aluminum hydride<sup>7</sup> resulted in a 15-19% yield of 2-acetoxy-5-hydroxybenzaldehyde. The overall yield, 16-17%, of acetoxybenzaldehyde was identical to that actually obtained employing the original methods, although published results indicated a possible 23%. The main advantages of this synthesis are the ease of preparation and high yields of materials prior to the reduction and an end product which is relatively easier to purify. The synthesis is shown by the following diagram.



### Experimental

The 2,5-diacetoxybenzoic acid was prepared from gentisic acid<sup>8</sup>, the 2,5-diacetoxybenzoyl chloride from the acid by the

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- (2) A. Neuberger, *Biochem. J.*, **43**, 599 (1948).
- (3) K. Elbs, *J. prakt. Chem.*, **48**, 179 (1893).
- (4) S. M. Sethna, *Chem. Rev.*, **49**, 91 (1951).
- (5) W. Baker and N. C. Brown, *J. Chem. Soc.*, 2302 (1948).
- (6) H. Yee, D. McCann, M. Keech, C. Denko, and A. Boyle, *A. M. A. Arch. Dermat.*, **84**, 293 (1961).
- (7) H. C. Brown and R. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).
- (8) A. Klemenc, *Monatsh.*, **33**, 1247 (1912).