

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).

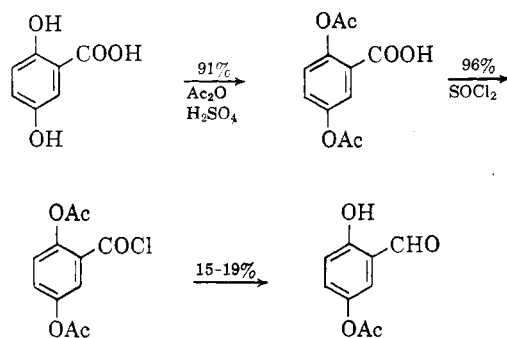
## The Synthesis of 2-Acetoxy-5-hydroxybenzaldehyde

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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

- (1) O. Neubauer and L. Flatow, *Z. physiol. Chem.*, **52**, 380 (1907).
- (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).

procedure of Kloetzel, *et al.*,<sup>9</sup> and the lithium tri-*tert*-butoxy aluminum hydride<sup>10</sup> as described by Brown and Subba Rao.

**Reduction of 2,5-Diacetoxybenzoyl Chloride.**—In a 3-neck flask, fitted with stirrer, dropping funnel, a low temperature thermometer, and a gas outlet tube attached to a drying tube containing anhydrous calcium sulfate, was placed 16.5 g. of acid chloride (0.064 mole) and 50 ml. of anhydrous diglyme (dimethyl ether of diethylene glycol). The flask was immersed in an insulated beaker containing a Dry Ice-trichloroethylene mixture and cooled to  $-70^{\circ}$ . Lithium tri-*tert*-butoxy aluminum hydride (17.0 g.) in 100 ml. of anhydrous diglyme was added slowly over a 1–2 hr. period avoiding any major rise in temperature. The reaction mixture was then allowed to come to room temperature and to stand overnight. After standing, the contents of the flask were poured into an ice-water mixture, and the yellowish, gelatinous hydroxide filtered off. The hydroxide was washed with ethyl alcohol which was added to the filtrate. The filtrate was distilled, adding water if necessary, until 425 ml. of distillate were collected. The remaining solution was filtered and allowed to stand in the refrigerator. About 1.2–1.3 g. of crude aldehyde crystallized extraction of the mother liquors with ether followed by evaporation yielded an additional 0.6–0.9 g. of material. Yield 1.8–2.2 g.; 15–19%. Recrystallization from aqueous ethanol gave material melting at  $79$ – $80^{\circ}$  (uncorr.). The aldehyde was identified by comparison of infrared curves of material synthesized by an independent route.<sup>11</sup> A melting point of an admixture of the aldehydes showed no depression.

**Acknowledgment.**—This work was supported in part by Grant A-5776 from the National Institutes of Health.

(9) M. Kloetzel, R. Dayton, and B. Abadir, *J. Org. Chem.*, **20**, 38 (1955).

(10) Also available from Metal Hydrides Inc., Beverly, Mass.

(11) J. Lambooy, *J. Am. Chem. Soc.*, **76**, 133 (1954).

## The Chlorination of 1-Nitroalkanes

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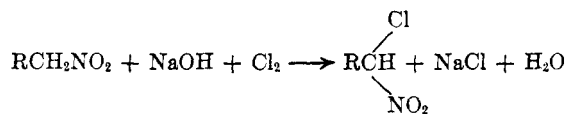
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There has been essentially no work reported in the literature on the chlorination of 1-nitroalkanes to give the 1-chloro-1-nitro derivatives. Henry<sup>1</sup> briefly mentions the preparation of chloronitroethane by the reaction of chlorine and nitroethane in potassium hydroxide. His product was isolated by distillation and could have been the 1,1-dichloro derivative or a mixture of the 1-chloro and the 1,1-dichloro derivatives, since they both boil at essentially the same temperature. More recently some physical studies were made on 1-chloro-1-nitroethane by Hurdes and Smyth,<sup>2</sup> but no mention was made as to the method of preparation of this compound. The preparation of monohalogenitromethanes by aqueous chlorination of the alkali metal salt has been reported by Tindall.<sup>3</sup>

(1) L. Henry, *Chem. Zentr.*, **1**, 192 (1898).

(2) E. C. Hurdes and C. P. Smyth, *J. Am. Chem. Soc.*, **64**, 2829 (1942).

It has now been found in our laboratories that 1-nitroparaffins can be chlorinated to give only the monochloro derivative in very high yield.



Preparation of only the monochloro derivative is particularly important with nitroethane, because 1-chloro- and 1,1-dichloro-1-nitroethane boil at about the same temperatures ( $124$ – $126^{\circ}$ ) and cannot be separated by fractional distillation. Most of the work that will be discussed in this note was done with nitroethane.

1-Chloro-1-nitroethane was prepared in conversions up to 95% by controlled chlorination of nitroethane in aqueous base. The effects of variables on this reaction are discussed below.

**Agitation.**—In a stirred, three-necked flask, conversions to the monochloro compound of 20–40% were obtained. When stirring was eliminated, conversions of 65% were obtained and the product came out of solution as a lower layer. In the apparatus described below, the chlorine was bubbled through a solution of nitroethane in base and the product was removed as it formed. Under these conditions, up to 95% conversions of nitroethane to 1-chloro-1-nitroethane were obtained.

**Temperature.**—The chlorination reaction is very exothermic and, if the heat of reaction is not removed, the only organic products are acetic acid and acetaldehyde. At  $15$ – $20^{\circ}$ , conversions to 1-chloro-1-nitroethane of 60–70% were obtained. At  $0$ – $5^{\circ}$ , 90–95% conversions to the monochloro derivative were obtained.

**Basicity.**—Stoichiometric amounts of base were most satisfactory for high conversions. With 100% excess base, no monochloro derivative was recovered. The monochloro product dissolves in any excess base and undergoes various side reactions. Excess sodium chloride was added to the reaction solution to decrease the solubility of the monochloro derivatives in the aqueous phase.

**Time.**—The reaction is almost instantaneous and is controlled by the rate of chlorine addition which is, in turn, controlled by the efficiency of heat removal. The yield of monochloro derivative decreases markedly with the length of time the product is in contact with the reaction mixture.

**Mechanism.**—The reaction is a noncatalytic ionic chlorination of the *aci*-form of the nitro compound. As shown in Table I, experiment 7, the first product is exclusively 1-chloro-1-nitroethane. As the reaction proceeds, secondary reactions begin to occur. The first of these seems to be the exchange between the sodium salts of nitroethane and chloronitroethane (excess base, if present, reacts similarly),

(3) J. B. Tindall, U.S. Patent 2,309,806 (1943).