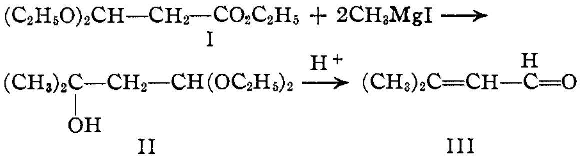
β-Methylcrotonaldehyde

By N. L. Wendler and H. L. Slates

The methods reported for the preparation of β-methylcrotonaldehyde are few in number[1] as well as seriously limited from a preparative standpoint. The present synthesis was developed in connection with work requiring the use of this isoprenoid aldehyde.

The reaction of ethyl β,β-diethoxypropionate (I) with methylmagnesium iodide followed by acid treatment of the intermediate β-hydroxyisovaleraldehyde diethyl acetal (II) afforded β-methylcrotonaldehyde (III) in 40% yield by direct isolation and in 60% yield when isolated as its 2,4-dinitrophenylhydrazone derivative. Since



$$\underset{\text{I}}{(C_2H_5O)_2CH—CH_2—CO_2C_2H_5} + 2CH_3MgI \longrightarrow$$

$$\underset{\text{II}}{(CH_3)_2\underset{\text{OH}}{\underset{|}{C}}—CH_2—CH(OC_2H_5)_2} \xrightarrow{H^+} \underset{\text{III}}{(CH_3)_2C{=}CH—\overset{\text{H}}{C}{=}O}$$

ethyl β,β-diethoxypropionate is now readily available from the reaction of ketene with ethyl orthoformate,[2] a relatively simple synthetic route is thus possible for the preparation of β-methylcrotonaldehyde.

Experimental

β-Methylcrotonaldehyde.—A solution of 76 g. (0.4 mole) of ethyl β,β-diethoxypropionate in 100 cc. of anhydrous ether was added dropwise with stirring at 0–10° to a solution of 1 mole of methylmagnesium iodide prepared from 24 g. of magnesium and 150 g. of methyl iodide in 500 cc. of anhydrous ether. After addition was complete, the reaction mixture, which consisted of two phases, was allowed to stir for one to two hours at room temperature. During this period the reaction mixture became nearly homogeneous. The reaction product was poured onto ice and decomposed with saturated aqueous ammonium chloride solution. The organic material was extracted thoroughly with ether and the ether extracts washed successively with aqueous sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. Evaporation of the ether *in vacuo* afforded crude β-hydroxyisovaleraldehyde diethyl acetal as a lemon-colored oil, wt. 68–70 g.

A solution of 25 g. of (II) in 25 ml. of ethanol was treated with 100 cc. of 3% aqueous sulfuric acid. The homogeneous solution was warmed 4–5 minutes on a steam-bath until turbidity developed and was then allowed to stand at room temperature for fifteen to eighteen hours. The reaction product, possessing an upper oily layer, was diluted with an equal volume of water, saturated with sodium chloride, and thoroughly extracted with ether. The ether extracts were washed with aqueous sodium bicarbonate until neutral to litmus and dried over anhydrous magnesium sulfate. Evaporation of the ether and fractional distillation of the residue in a stream of nitrogen afforded 4.8–5 g. of β-methylcrotonaldehyde, b. p. 130–135° (40%); reported 130–135°[1a]; *semicarbazone*, needles from methanol–m. p. 222–223°; $\lambda_{\max.}^{\text{ethanol}}$ 2700 Å., $E_{1\text{ cm.}}^{1\%}$ 2270 (reported m. p. 221–222°[1c]; $\lambda_{\max.}$ 2730, $E = 33{,}500$[3]).

β-Methylcrotonaldehyde-2,4-dinitrophenylhydrazone.—Obtained from 0.5 g. of the crude β-hydroxyisovaleraldehyde diethyl acetal as glittering red needles from ethanol–ethyl acetate; wt. 0.45–0.47 g. (60%); m. p. 184–185°; $\lambda_{\max.}^{\text{ethanol}}$ 3800 Å., $E_{1\text{ cm.}}^{1\%}$ 1080 in chloroform. (Reported m. p. 182–183°[1c]; $\lambda_{\max.}$ 3820, $E = 29{,}000$ in chloroform.[4])

Anal. Calcd. for $C_{11}H_{12}O_4N_4$: C, 50.00; H, 4.55; N, 21.21. Found: C, 50.17; H, 4.26; N, 21.21.

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[1] (a) Fischer and Löwenberg, *Ann.*, **494**, 263 (1932); *Ber.*, **69**, 30 (1931); (b) Burkhardt, Aldersley and Heilbron, British Patent 512,465; (c) Jones and Weedon, *J. Chem. Soc.*, 937 (1946).

[2] Gresham, U. S. 2,449,471; *C. A.*, **43**, 1055 (1949).

[3] Evans and Gillam, *J. Chem. Soc.*, 5656 (1943).

[4] Braude and Jones, *ibid.*, 498 (1945).

Further Observations on the Preparation and Reactions of Positive Iodine Salts

By Ralph A. Zingaro, Calvin A. VanderWerf and Jacob Kleinberg

In earlier reports[1,2] dealing with the preparation of monopyridine and monopicoline iodine (I) salts of aromatic acids, it was found that certain ortho and para substituted derivatives could not be prepared by the method employed. A number of these compounds have now been prepared by a slight modification of the original procedure. Their yields and decomposition points are reported in Table I. Attempts to prepare the *o*-iodobenzoate, *o*-toluate and *m*-toluate were still unsuccessful.

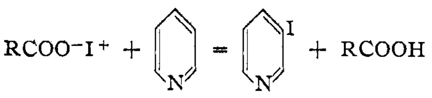
Table I

Some New Positive Iodine Salts

Salt	Decompn. point, °C. (uncor.)	Yield, %	Iodine, %[a] Calcd.	Found
Mono-α-picoline iodine (I) *p*-bromobenzoate	119–121	75	30.2	30.2, 30.1
Monopyridine iodine (I)				
o-Chlorobenzoate	91–95	45	35.1	35.3, 35.1
m-Chlorobenzoate	94–97	51	35.1	35.1, 35.0
o-Bromobenzoate	101–106	68	31.2	31.2, 31.2

[a] For analytical method see ref. 1.

Very small amounts (1–2% of the theoretical) of 3-iodopyridine and 3,5-diiodopyridine were isolated in the reactions of the following representative silver salts with iodine and pyridine in chloroform: *o*-toluate, *o*-chlorobenzoate, *m*-chlorobenzoate and *m*-iodobenzoate. A yield of 1.7% of 5-iodo-2-methylpyridine was obtained in the reaction of silver *m*-chlorobenzoate with iodine in the presence of α-picoline. Thus, the formation of at least some of the free acid noted in the previous communication,[1] can be accounted for by reactions of the type indicated in the equation



Experimental

The solvents, acids and salts were prepared or purified as previously described.

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[1] Zingaro, Goodrich, Kleinberg and VanderWerf, This Journal, **71**, 575 (1949).

[2] Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Jods," Verlag von S. Hirzel, Leipzig, 1932.