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Synthesis of Dimethyl 4-(Alkyliminomethyl)-4-methylheptanedioates

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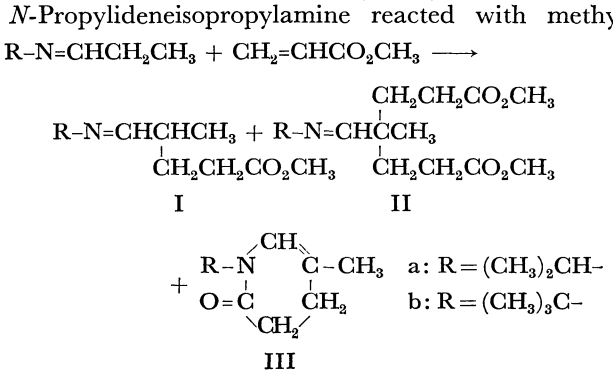
We wish to report the synthesis of dicarboxylic acid esters having an alkylimino group by a Michael type addition of aldimines with methyl acrylate.

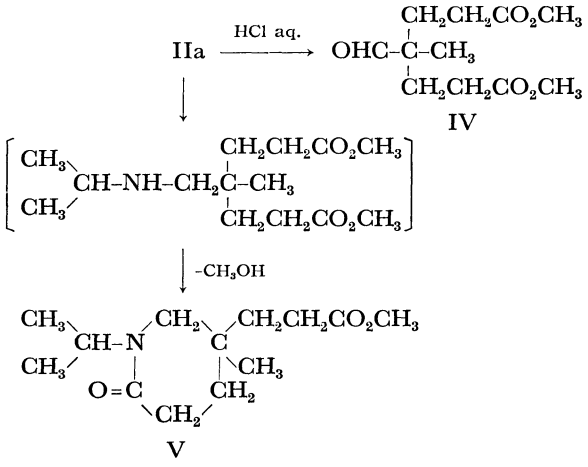
N-Propylideneisopropylamine reacted with methyl



I II

III

a: R = $(CH_3)_2CH$-
b: R = $(CH_3)_3C$-



IV V

Table 1. Physical and analytical data of products

Product	bp °C/mmHg	n_{20}^{D}	C%		H%		N%	
			Found	Calcd	Found	Calcd	Found	Calcd
Ia	57—57.5/2	1.4438	64.83	64.58	10.34	10.26	7.56	7.53
IIa	128—132/3	1.4539	61.97	62.24	9.29	9.29	5.16	5.16
IIIa	62—63/1.5	1.4892	70.55	69.96	9.87	9.85	9.14	9.05
Ib	65/2	1.4357	66.29	65.88	10.62	10.61	7.03	7.09
IIb	130—131/2	1.4540	63.13	63.13	9.54	9.48	4.91	4.82
IV	135—137/2	1.4545	57.37	57.60	7.88	7.84		
V	165—168/2	1.4756	64.70	64.24	9.41	9.44	5.80	5.62

acrylate (a molar ratio 1 : 2) in pyridine at 110—120°C to afford a dicarboxylic acid ester IIa in a 66% yield with small amounts of Ia and IIIa.

Products Ia and IIa are normal Michel addition products. The cyclic product IIIa would be formed through the cyclization of Ia, since heating of Ia in pyridine afforded IIIa.

Product IIa was hydrolyzed by hydrochloric acid to give an aldehyde IV and hydrogenated with PtO_2 to form a saturated cyclic product V.

N-Propylidene-*t*-butylamine reacted in the same way to give IIb and Ib in 74 and 11% yields, respectively.

Experimental

The reaction products were identified by means of elemental analysis, molecular-weight measurement, and IR, NMR spectral measurements. The physical and analytical data of the products, which are all new compounds, are given in Table 1.

Reaction of N-*Propylideneisopropylamine*[1] *with Methyl Acrylate.* A mixture of 20 m*l* of pyridine, 9.9 g (0.1 mol) of *N*-Propylideneisopropylamine, 17.2 g (0.2 mol) of methyl acrylate, and a small amount of hydroquinone was heated at 110—120°C for 16 hr. The reaction mixture was fractionally distilled to afford 0.8 g (4%) of methyl 5-isopropylimino-4-methylvaleate (Ia), 17.9 g (66%) of dimethyl 4-(isopropylimino)methyl-4-methylheptanedioate (IIa) and 1.1 g (7%) of 1-isopropyl-3-methyl-6-oxopyperidine-2-ene (IIIa).

Hydrolysis of IIa. A mixture of 5.4 g (0.02 mol) of IIa and 10 m*l* of 1N HCl aqueous was refluxed for 30 min. The usual work-up of the resultant solution afforded 3.0 g (63%) of dimethyl 4-formyl-4-methylheptanedioate (IV).

Hydrogenation of II. A mixture of 26 g (0.1 mol) of IIa, 0.15 g of PtO_2 and 25 m*l* of absolute ethanol was stirred at a room temperature under a hydrogen pressure of 20 kg/cm^2 for 2 hr in a 100 m*l* autoclave to give 19.3 g (80%) of methyl 3-(1-isopropyl-3-methyl-6-*oxo*-3-piperidyl) propionate (V).

1) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, **66**, 82 (1944).