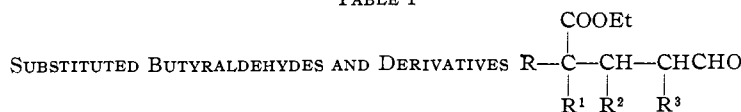


TABLE I



Aldehydes						2,4-Dinitrophenylhydrazones											
R	R'	R ²	R ³	Yield, %	M. p. or b. p. °C. Mm.	Analyses, %		Analyses, %		M. p., °C.	Analyses, %		Analyses, %				
						Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found		Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	
H	COOEt	H	Me	42 ^d	76-77 ^a	0.05	91-92	49.73	49.78	5.40	5.52	13.65	14.04	
Et	COOEt	H	Me	25	77-80 ^a	0.07	60.45	59.90	8.59	8.76	79-81	52.05	52.05	5.98	6.09	12.78	13.11
CH ₃ CONH	COOEt	H	Me	100 ^e	147 ^c	60.46	60.62	7.21	7.50	11.14 ^c	11.48 ^c	
CH ₃ CONH	CN	H	Me	58 ^f	112-113	...	55.00	55.42	6.66	6.83 ^g	193	48.57	48.80	4.76	4.59	20.00	19.88
H	COOEt	Me	H	12	80-83 ^a	.1	57.36	56.96	7.88	7.82	90-91	49.73	49.98	5.40	5.58	13.65	13.83
Et	COOEt	Me	H	38	80-92 ^a	.6-0.7	116	52.05	51.70	5.98	5.94	12.78	12.75	
CH ₃ CONH	COOEt	Me	H	75	88-89	...	54.34	54.07	7.37	7.48 ^h	150	48.82	48.68	5.39	5.34	14.98	15.23
CH ₃ CONH	CN	Me	H	75	175-177	...	55.00	55.03	6.66	6.43 ⁱ	201	48.57	48.85	4.76	4.54	20.00	20.15

^a Liquid aldehydes, purified by distillation. ^b Crude oil not distilled. ^c This product was the phenylhydrazone ^d Based on crude product, b. p. = 86-110° (0.2-0.4 mm.). ^e Based on crude oil. ^f Based on crude product, m. p. = 89-95°. ^g %N; calcd. 11.66; found, 11.76. ^h %N; calcd. 4.88; found, 4.88. ⁱ %N; calcd. 11.66; found, 11.91.

tonylidene malonic ester proceeded through the intermediate crotonylidene dimalonic ester I. However, they reported that the components of the reaction mixture could not be resolved by fractional distillation. Previously, Farmer and Healy⁶ had attempted to prepare this crotonylidene dimalonic ester by the addition of malonic ester to crotonylidene malonic ester without success.

Experimental

Syntheses of the Aldehyde Compounds.—The aldehyde compounds in which R = CH₃CONH were prepared essentially as described in an earlier publication.² The aldehyde compounds in which R = Et or H were prepared according to the general procedure described previously.³ The physical constants and derivatives of these products are described in Table I.

Reduction of γ -Acetamido- γ,γ -dicarboethoxy- α -methylbutyraldehyde.—The crude aldehyde compound (25 g.) was dissolved in 100 cc. of absolute ethanol. Raney nickel (5 g.) was added and the reduction was carried out at 100° with an initial hydrogen pressure of 1500 pounds. After the reduction was complete, the catalyst was removed by filtration and the filtrate was concentrated at reduced pressure to yield a residual oil which resisted crystallization. The carbinol was characterized as its 3,5-dinitrobenzoate which melted at 123-124° after crystallization from absolute ethanol.

Anal. Calcd. for C₂₀H₂₅O₁₁N₃: C, 49.69; H, 5.21; N, 8.69. Found: C, 49.72; H, 5.23; N, 8.66.

(6) Farmer and Healy, *J. Chem. Soc.*, 1065 (1927).

CHEMICAL LABORATORIES
GENERAL MILLS, INC.

MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 28, 1949

4,4'-Dibromo- α,α' -dicyanostilbene

By MOSHE WEIZMANN AND SAUL PATAI

Wislicenus and Elvert¹ state that 4,4'-dibromo- α,α' -dicyanostilbene can be prepared from *p*-bromophenylisonitroacetone trisodium and dilute sulfuric acid at room temperature in almost quantitative yield.

We have tried in vain to duplicate these results using 2.5, 5, 10, 15 and 25% dilute sulfuric acid. In all cases the crude product was either a reddish oil or a sticky mass which, after several recrystalli-

(1) Wislicenus and Elvert, *Ber.*, **41**, 4126 (1908).

zations from benzene, gave yields of 20 to 60%. We have now obtained reproducible good yields of this substance by the action of iodine and sodium ethylate on 4-bromobenzyl cyanide, following the procedure described by Chalanay and Knoevenagel.²

In this way a yield of 38-40 g. (78 to 82%) of a practically pure, light yellow product, m. p. 212°, was obtained from 49 g. of the bromobenzyl cyanide. Recrystallized from benzene, almost colorless crystals were obtained, m. p. 214°, showing no depression of the melting point when mixed with an authentic sample prepared according to reference 1.

(2) Chalanay and Knoevenagel, *ibid.*, **25**, 285 (1892).

DEPARTMENT OF ORGANIC CHEMISTRY
THE HEBREW UNIVERSITY

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NEW COMPOUNDS

2,4-Diketo-octahydro-2-pyrido(1,2-a)pyrimidine

A mixture of 5 g. of 2,4-diketo-3,4-dihydro-2-pyrido(1,2-a)pyrimidine¹ and 0.16 g. of Adams catalyst in 200 ml. of ethanol was shaken at 60° under 3 atm. of hydrogen. After three hours the calculated amount of hydrogen was absorbed. The catalyst and solvent were removed, and the residue, on crystallization from dioxane-ether, yielded 3.5 g. (71%) of light yellow crystals, m. p. 170-173°. A sample prepared for analysis by vacuum sublimation was white and melted at 174.0 to 174.5°.

Anal. Calcd. for C₈H₁₂N₂O₂: C, 57.14; H, 7.14. Found: C, 57.23; H, 7.37.

Although 2,4-diketo-octahydro-2-pyrido(1,2-a)pyrimidine bears a certain formal resemblance to known barbiturate drugs, it was found on intraperitoneal administration of the compound to mice that the only noticeable physiological symptom was hypersensitivity to pain.²

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RECEIVED FEBRUARY 21, 1949

(1) Tchichibabin, *Ber.*, **87**, 1168 (1924).

(2) The physiological tests were conducted by F. M. Berger, M.D., Department of Pediatrics, University of Rochester Medical School.