

a formula for the oxide of  $\text{Pa}_2\text{O}_5$ , the half-life of the protactinium is calculated, using the relation  $\lambda T = \log_{e_2}$ , where  $\lambda$  is the disintegration constant and  $T$  is the half-life. Since the two samples give the same half-life value within experimental error, the rather more precise value of sample 2 is taken, namely,  $34,300 \pm 300$  years.

The largest uncertainty in the measurements may actually be the structure of the ignited protactinium oxide. We are indebted to Professor W. H. Zachariassen for a study of the X-ray structure of the powder. Although the patterns obtained are complex, there seems to be evidence for a possible  $\text{PaO}_2$  structure. If the composition of the ignited material is actually the dioxide composition, the half-life value given would be low by approximately 3%.

### Discussion

The presently reported value of the  $\text{Pa}^{231}$  half-life, 34,300 years, is higher than any appearing in the literature. The closest correspondence is found with the 1932 value of von Grosse, namely, 32,000 years.<sup>4</sup> This value was obtained from presumed pure macro amounts of the isotope; the values given in the earlier literature are based on growth into purified uranium of the protactinium. These early determinations depend on measuring current intensities in an alpha electroscop, knowing the number of ion pairs produced for both protactinium alphas and  $\text{U}^{238}$  alphas, and knowing precisely the ratio of activity of  $\text{U}^{235}$  and  $\text{U}^{238}$  in natural uranium. The method is beset with corrections and imperfectly known constants, and is inherently inaccurate. Correction of the original data with present values of the constants involved fails to raise the values to the level reported here, although a certain amount of consistency between different determinations by similar techniques can be found. The determination of von Grosse with macro amounts of the isotope eliminated some sources of error, but the determination again was dependent upon knowledge of the number of ion pairs produced per alpha particle, and comparison with alpha emission of uranium as measured in an electroscop. A source of error unknown to von Grosse is the fact that one-eighth the alpha particles emitted by protactinium differ in energy from the rest by some 300 kev.<sup>8</sup> The determination by direct counting of alpha particles, as carried out in our experiments, is therefore the least questionable of the procedures used. The uncertainty of the experimental value is probably well below 1%. A revision of approximately 3% must be made in the value if it is shown that the protactinium oxide obtained under our experimental amounts, so no correction was made. Assuming

(8) F. L. Clark, H. J. Spencer-Palmer and R. N. Woodward, Report Br-522 (1944); T. San-Tsiang, M. Bachelet and G. Bousnieres, *Phys. Rev.*, **69**, 39 (1946).

conditions is  $\text{PaO}_2$  rather than the expected  $\text{Pa}_2\text{O}_5$ .

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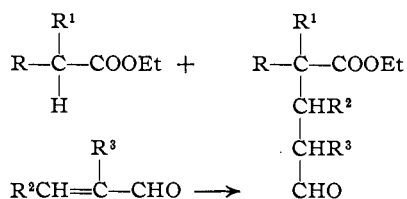
RECEIVED MARCH 7, 1949

### 1,4-Addition Reactions. IV. Addition of Malonate Systems to Alkyl Substituted Acroleins<sup>1</sup>

BY DONALD T. WARNER AND OWEN A. MOE

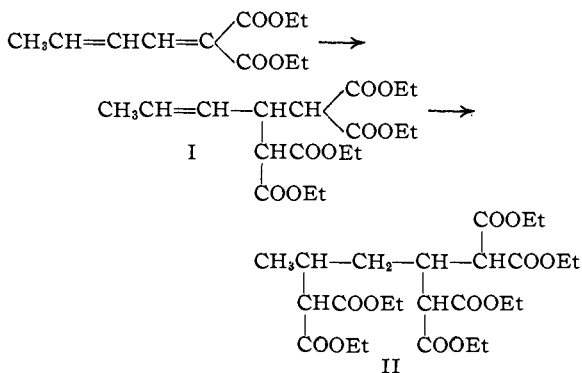
In previous publications<sup>2,3</sup> the 1,4-addition of malonate systems to acrolein has been disclosed. The present report concerns the 1,4-addition of malonate systems to alkyl substituted acroleins such as crotonaldehyde and methacrolein ( $\alpha$ -methylacrolein).

The addition of ethyl malonate, ethyl ethylmalonate, ethyl acetamidomalonate and ethyl acetamidocyanoacetate to methacrolein and crotonaldehyde proceeded to yield the corresponding aldehyde compounds. The aldehyde compounds were characterized either as the phenylhydrazones or as the 2,4-dinitrophenylhydrazones.



The catalytic reduction of  $\gamma$ -acetamido- $\gamma$ , $\gamma$ -dicarboxy- $\alpha$ -methylbutyraldehyde yielded the corresponding carbinol (4-acetamido-4,4-dicarboxy-2-methyl-1-butanol) which may prove to be of interest in the synthesis of  $\delta$ -hydroxyleucine.<sup>4</sup>

Farmer and Mehta<sup>5</sup> reported the reaction between ethyl malonate and crotonaldehyde in the presence of a "fractional molecular proportion" of sodium ethoxide at 0°. By this means, these investigators attempted to show that the formation of the double addition product II from cro-



(1) Paper No. 95, Journal Series, General Mills, Inc., Research Department.

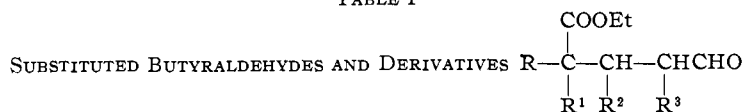
(2) Moe and Warner, *THIS JOURNAL*, **70**, 2763 (1948).

(3) Warner and Moe, *ibid.*, **70**, 3470 (1948).

(4) Dakin, *J. Biol. Chem.*, **154**, 552 (1944).

(5) Farmer and Mehta, *J. Chem. Soc.*, 2561 (1931).

TABLE I



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

<sup>a</sup> Liquid aldehydes, purified by distillation. <sup>b</sup> Crude oil not distilled. <sup>c</sup> This product was the phenylhydrazone <sup>d</sup> Based on crude product, b. p. = 86-110° (0.2-0.4 mm.). <sup>e</sup> Based on crude oil. <sup>f</sup> Based on crude product, m. p. = 89-95°. <sup>g</sup> %N; calcd. 11.66; found, 11.76. <sup>h</sup> %N; calcd. 4.88; found, 4.88. <sup>i</sup> %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 Healy<sup>6</sup> 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 = CH<sub>3</sub>CONH were prepared essentially as described in an earlier publication.<sup>2</sup> The aldehyde compounds in which R = Et or H were prepared according to the general procedure described previously.<sup>3</sup> The physical constants and derivatives of these products are described in Table I.

**Reduction of  $\gamma$ -Acetamido- $\gamma,\gamma$ -dicarboethoxy- $\alpha$ -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 C<sub>20</sub>H<sub>25</sub>O<sub>11</sub>N<sub>3</sub>: 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).

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MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 28, 1949

#### 4,4'-Dibromo- $\alpha,\alpha'$ -dicyanostilbene

By MOSHE WEIZMANN AND SAUL PATAI

Wislicenus and Elvert<sup>1</sup> state that 4,4'-dibromo- $\alpha,\alpha'$ -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.<sup>2</sup>

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).

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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)pyrimidine<sup>1</sup> 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 C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: 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.<sup>2</sup>

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(1) Tchichibabin, *Ber.*, **57**, 1168 (1924).

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