

## Experimental

**The Willgerodt Reactions.**—The method of Fieser and Kilmer<sup>3</sup> was used throughout this study. Usually several tubes were heated in the same furnace so yields would be directly comparable. Identity of the amide obtained was proved by melting point and mixed melting point with an authentic specimen. The amides were all hydrolyzed and the identity of the acid was also proved by melting point and mixed melting point. The results are given in Table I. A typical example of the procedure is given for the reaction of styrene oxide. Styrene oxide (10 g.), 5 g. of sulfur, 50 ml. of yellow ammonium polysulfide and 40 ml. of dioxane were sealed in a Carius tube and heated in an electric furnace for 7 hr. at  $170 \pm 5^\circ$ . The contents of the cooled tube were evaporated to dryness and the residue extracted several times with boiling water. The product crystallizes on cooling and a second crop of crystals may be obtained by concentration of the mother liquor. Recrystallization from water gave 9.8 g. (87%) of phenylacetamide melting  $156\text{--}157^\circ$ .

TABLE I

PERCENTAGE YIELDS OF PHENYLACETAMIDE FROM WILLGERODT REACTIONS

1-Phenylethylamine	61
1-Phenylethyldimethylamine	31
1-Phenylethyl-(monoethanol)-amine	63
1-Phenylethyl-(diethanol)-amine	66
2-Phenylethylamine	32
1-Phenylethyl bromide	40
2-Phenylethyl bromide	66
Styrene oxide	87
$\beta$ -Bromostyrene	80
Phenacylpyridinium iodide	53
$\omega$ -Morpholinoacetophenone	72

**Hydrolysis of the Amide.**—Three-gram samples of the amides were refluxed for 5 hours with 100 ml. of 10% aqueous potassium hydroxide, acidified and filtered. Phenylacetic acid crystallized in white plates melting at  $76^\circ$ .

(3) L. F. Fieser and G. W. Kilmer, *THIS JOURNAL*, **62**, 1354 (1940).

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The Ternary System  $\text{NaVO}_3\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ 

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Continuing our studies in connection with ternary systems involving alkali vanadates,<sup>1</sup> we here report the solubility relations in the system sodium vanadate-sodium sulfate-water at  $25^\circ$ .

The sodium vanadate was recrystallized from B.D.H. "Laboratory Reagent" material. It was analyzed as follows: vanadium was determined by potentiometric titration with Mohr's salt in presence of sulfuric acid, and sodium was determined as the sulfate after elimination of vanadium by precipitation with mercuric nitrate. The results agreed within several tenths per cent. with the composition  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ . The sodium sulfate, a Merck product, was used without further purification, after satisfactory tests on the limits of impurities.<sup>2</sup>

(1) R. Trujillo and E. Tejera, *An. Soc. Españ. Fis. Quim.*, **XLVII** (B), 495 (1951); R. Trujillo and L. Pastor, *ibid.*, 501 (1951).

(2) Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., Inc., New York, N. Y., 1946.

The ternary mixtures were placed in test-tubes and rotated in a thermostat at  $25.0 \pm 0.5^\circ$  for three days. Samples were taken in the usual way, with a pipet provided with a cotton-waste filter, after one day settling in the thermostat. The remaining solution was poured off and samples of wet residues were also weighed. The concentrations of vanadate and sulfate were determined in each sample, the former by the process already described, and the latter as barium sulfate, by precipitation with a solution of barium chloride slightly acidified with acetic acid to prevent precipitation of the slightly soluble barium vanadate.

The results are listed in Table I. The system is simple, the solid phases being  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , as determined by the Schreinemakers method.<sup>3</sup> The composition of the hydrates was verified through direct analysis.

TABLE I

SYSTEM  $\text{NaVO}_3\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  AT  $25^\circ$

Densities	Liquid solution		Wet residue		Solid phase <sup>a</sup>
	Wt. % $\text{Na}_2\text{SO}_4$	Wt. % $\text{NaVO}_3$	Wt. % $\text{Na}_2\text{SO}_4$	Wt. % $\text{NaVO}_3$	
1.084	...	12.80	...	40.15	A
1.088	3.40	9.62	2.65	30.76	A
1.090	5.30	7.50	3.65	30.22	A
1.091	8.88	5.18	6.49	26.54	A
1.108	10.50	4.60	9.09	15.05	A
1.120	12.00	3.76	8.69	25.21	A
1.129	13.15	3.22	10.56	18.25	A
1.138	14.27	3.15	11.70	17.01	A
1.167	16.05	2.65	13.11	16.87	A
1.179	19.28	1.93	15.65	16.62	A
1.185	19.89	1.53	16.14	15.73	A
1.186	20.86	1.48	29.72	17.63	A + B
1.192	21.54	0.53	41.35	0.12	B
1.194	21.72	0.36	41.10	0.15	B
1.196	21.85	...	42.96	...	B

<sup>a</sup> A =  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ ; B =  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

(3) Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

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Unsaturated Lactones. III. Absorption Spectra in a Group of  $\alpha$ -Benzal- $\gamma$ -substituted Crotonolactones<sup>1</sup>

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The effect of substitution of aromatic groups in the  $\alpha$ -position on the absorption spectra in a series of  $\gamma$ -phenylcrotonolactones has been previously reported.<sup>2</sup> We have extended this study to include a series of  $\gamma$ -substituted  $\alpha$ -benzalcrotonolactones to determine the effect of substituents on the  $\gamma$ -position on the light absorption.

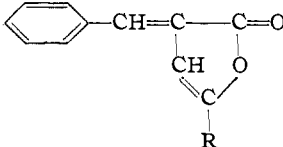
Out of a group of twelve crotonolactones<sup>3</sup> prepared during this investigation four were pre-

(1) This work was aided by a grant from the U. S. Public Health Service.

(2) F. W. Schueler and C. Hanna, *THIS JOURNAL*, **73**, 3528 (1951).

(3) These compounds have been studied for cardiac activity: F. W. Schueler and C. Hanna, *Arch. intern. pharmacodynam.*, **86**, 91 (1951).

TABLE I  
 $\alpha$ -BENZAL- $\gamma$ -SUBSTITUTED CROTONOLACTONE DERIVATIVES

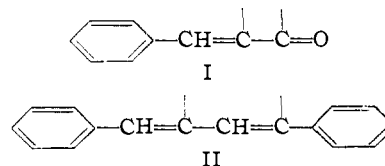


No.	R	M. p., <sup>b</sup> °C.	Formula	Carbon, %		Hydrogen, %		Max. $\epsilon \times 10^4$			
				Calcd.	Found	Calcd.	Found	m $\mu$	m $\mu$		
1	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> - <sup>b</sup>		C <sub>18</sub> H <sub>14</sub> O <sub>2</sub>					256	1.67	395	2.94
2	4-Br-C <sub>6</sub> H <sub>4</sub> - <sup>b</sup>		C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> Br					255	1.48	396	2.39
3	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> - (Y.) or (G.) <sup>a</sup>		C <sub>18</sub> H <sub>14</sub> O <sub>3</sub>					255	1.83	397	3.20
4	4-Cl-C <sub>6</sub> H <sub>4</sub> -		C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> Cl					255	1.47	394	2.38
5	3,4-di-CH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> -	146	C <sub>19</sub> H <sub>16</sub> O <sub>2</sub>	82.59	82.52	5.84	5.79	256	1.98	397	3.04
6	2-Tetraaryl-	150	C <sub>21</sub> H <sub>18</sub> O <sub>2</sub>	83.41	83.55	6.00	6.10	256	1.78	397	3.50
7	4-C <sub>6</sub> H <sub>5</sub> -O-C <sub>6</sub> H <sub>4</sub> -	143	C <sub>23</sub> H <sub>16</sub> O <sub>3</sub>	81.15	81.32	4.74	4.81	250	1.95	397	1.71
8	4-C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> -	201	C <sub>23</sub> H <sub>16</sub> O <sub>2</sub>	85.16	85.27	4.97	4.85	288	0.34	400	3.08
9	4-CH <sub>3</sub> CONH-C <sub>6</sub> H <sub>4</sub> -	232	C <sub>19</sub> H <sub>16</sub> O <sub>3</sub> N	74.74	74.69	4.94	4.98	288	1.61	409	2.92
10	2-Thienyl- (O.) <sup>a</sup>	131	C <sub>15</sub> H <sub>10</sub> O <sub>2</sub> S	70.85	71.10	3.96	3.87	278	1.49	400	3.44
11	3-Acenaphthyl- (O.) <sup>a</sup>	131	C <sub>23</sub> H <sub>16</sub> O <sub>2</sub>	85.16	85.21	4.97	5.02	246	1.47	410	2.22
12	2-Fluorenyl- (O.) <sup>a</sup>	207	C <sub>24</sub> H <sub>16</sub> O <sub>2</sub>	85.69	85.78	4.80	4.83	298	1.75	410	3.52

<sup>a</sup> All compounds had a yellow color except as otherwise noted, thus O. orange, G. green. <sup>b</sup> Melting points corrected.

viously reported and no spectroscopic data appear to have been reported on any of these materials in which the aromatic group at the  $\alpha$ -position is now substituted. The crotonolactones synthesized in this study are detailed in Table I together with their absorption maxima, melting points and analysis.

In regard to the conjugated system in the  $\alpha$ -benzal- $\gamma$ -phenylcrotonolactone molecule, which may be involved in the absorption of light, there appear to be three possibilities



and (III) some cross conjugation of the above two systems. The K-bands of a large number of  $\alpha,\beta$ -unsaturated ketones with a conjugated system of type (I) have maxima which fall within the range of 218 to 241 m $\mu$ . It would appear that the first possibility (I) in the crotonolactones studied is not the dominant system. An open chain analog of system (II) would be 1,1,3,4-tetraphenylbutadiene but no spectrographic data have been reported on this compound. However, a number of tetraphenylbutadienes have been studied<sup>4</sup> and of these only 1,1,4,4-tetraphenylbutadiene which cannot exist as *cis-trans* isomers is comparable with the  $\alpha,\gamma$ -substituted crotonolactones.

Of the tetraphenylbutadienes studied, only 1,1,4,4-tetraphenylbutadiene exhibits two band spectra with no fine structure as do the crotonolactones. The relationships involved are illustrated in Fig. 1. The positions of the maxima of this butadiene are very similar with respect to shape, position and magnitude, to that of  $\alpha$ -benzal- $\gamma$ -phenylcrotonolactone, indicating that the conjugated system (II) is probably dominant in the crotonolactones.

#### Experimental

**Absorption Spectra.**—All spectra were determined with a model DU Beckman quartz spectrophotometer.

Measurements of the optical densities were made regularly at 2-m $\mu$  intervals within the range 220 to 300 m $\mu$ , at 5-m $\mu$  intervals between 300 and 400 m $\mu$ , and at 10-m $\mu$  intervals above 400 m $\mu$ ; except in the neighborhood of maxima and minima where the interval was reduced to 1 m $\mu$ . Silica cells of a path length of 1 cm. were employed in the

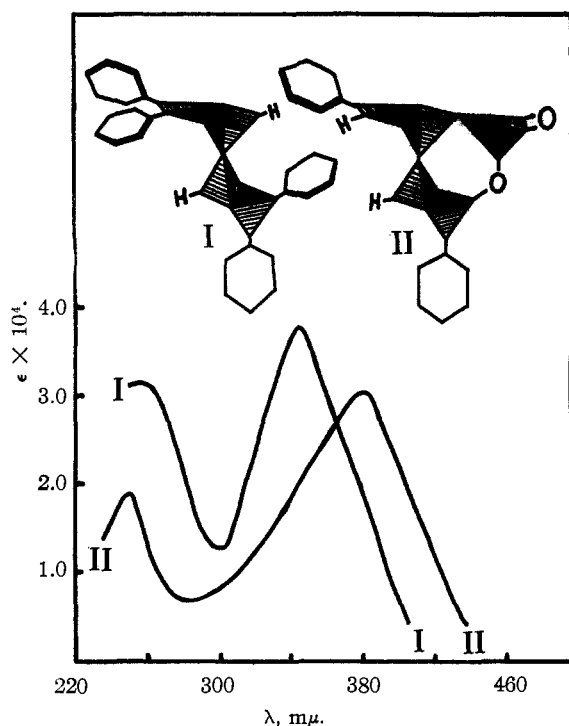


Fig. 1.—I, 1,1,4,4-Tetraphenylbutadiene redrawn from reference 4 in dioxane; II,  $\alpha$ -benzal- $\gamma$ -phenyl crotonolactone in 95% ethanol, absolute ethanol or glacial acetic acid.

(4) Y. Hirshberg, E. Bergmann and F. Bergmann, *THIS JOURNAL*, **72**, 5120 (1950).

(5) W. Borsche, *Ber.*, **47**, 1108 (1914).

(6) E. P. Kohler, G. A. Hill and L. A. Bigelow, *THIS JOURNAL*, **39**, 2417 (1917).

determinations in the ultraviolet region and corex cells of the same thickness were used in the visible region. The solvent used for the samples and blank was 95% ethanol. All samples were dissolved in the solvent to a concentration of 10 mg. per l. at 20 to 25°. The results in the measurement of the absorption spectra of the azlactones are expressed as the molar extinction  $\epsilon$  which was obtained from the optical density readings  $D$  and the molecular weights  $m$  by the relations  $k = D/cl$  and  $\epsilon = km$ , where  $c$  is the concentration of the solution in mg. per ml. and  $l$  is the length of the cell.

**Preparation of Materials.**—The crotonolactones were prepared by the following general procedure: A mixture of 0.05 mole of benzaldehyde, 0.05 mole of the corresponding  $\beta$ -aroylpropionic acid, 0.05 mole of freshly fused sodium acetate and 16 ml. of acetic anhydride was heated in a beaker on a hot-plate until a complete solution was obtained. The beaker was then transferred to a steam-bath and heating was continued until crystals separated. The reaction was next poured into water, the solid product filtered with suction, washed with water and finally recrystallized repeatedly from 95% ethanol until a constant melting point was obtained. The yield, in general, ranged from 50–70%. The crotonolactones No. 6–12 of Table I are relatively insoluble in 95% ethanol (10 mg./100 ml.) and were recrystallized from chloroform.

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### 1-Nitrofluorenone

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Recently the first synthesis of 1-nitrofluorenone has been described by Chase and Hey<sup>2</sup> who used the sequence: chloride of 2-methyl hydrogen 3-nitrophthalate  $\rightarrow$  peroxide of this acid  $\rightarrow$  methyl 3-nitrobiphenyl-2-carboxylate  $\rightarrow$  3-nitrobiphenyl-2-carboxylic acid  $\rightarrow$  1-nitrofluorenone (m.p. 188.5–189.5°). The substance was obtained later in very small amounts by the action of heat on diazotized 2-amino-6-nitrobenzophenone.<sup>3</sup> The structure of the substance was proved<sup>2</sup> by reduction to the known 1-aminofluorenone.<sup>4</sup>

The purpose of this Note is to describe our synthesis of 1-nitrofluorenone by three routes, two of which involve an intermediate used by Chase and Hey. These syntheses are of interest as practical preparative methods and involve several compounds described here for the first time.

(A).<sup>5</sup>—1-Aminofluorenone was diazotized and converted to the nitro compound by the action of sodium nitrite and mixed copper sulfites.<sup>6</sup>

(B).<sup>5</sup>—2-Aminobiphenyl  $\rightarrow$  2-acetaminobiphenyl  $\rightarrow$  3-nitro-2-acetaminobiphenyl  $\rightarrow$  3-nitro-2-aminobiphenyl  $\rightarrow$  3-nitro-2-cyanobiphenyl  $\rightarrow$  3-nitrobiphenyl-2-carboxylic acid  $\rightarrow$  1-nitrofluorenone.

(C).<sup>7</sup>—3-Nitrophthalimide  $\rightarrow$  6-nitrophthalamic acid  $\rightarrow$  6-nitro-2-aminobenzoic acid  $\rightarrow$  methyl 6-

nitro-2-aminobenzoate  $\rightarrow$  methyl 3-nitrobiphenyl-2-carboxylate  $\rightarrow$  1-nitrofluorenone. The last step in this synthesis was carried out directly and avoided the isolation of 3-nitrobiphenyl-2-carboxylic acid.<sup>2</sup>

#### Experimental Part

All melting points are uncorrected.

**1-Nitrofluorenone.**—1-Aminofluorenone<sup>4</sup> was diazotized and treated with sodium nitrite and mixed copper sulfites.<sup>6</sup> There was obtained a 34% yield of bright yellow needles, m.p. 190.5–191.5° after recrystallization from glacial acetic acid. Mixed melting points of this product with those from our other syntheses were not depressed.

*Anal.* Calcd. for  $C_{13}H_9O_2N$ : C, 69.3; H, 3.14; N, 6.22. Found: C, 69.4; H, 3.37; N, 6.28.

Attempts to replace the diazo group by the cobaltinitrite method<sup>8</sup> or by the action of sodium nitrite on the diazonium fluoroborate<sup>9</sup> were unsuccessful.

**1-Nitrofluorenone Oxime.**—0.91 g. of 1-nitrofluorenone and 1 g. of hydroxylamine hydrochloride were heated at 100° for five hours in 10 cc. of pyridine and 10 cc. of absolute alcohol. The reaction mixture was diluted with 200 cc. of ice-water and the oxime obtained in 97% yield, m.p. 198–199° dec.

*Anal.* Calcd. for  $C_{13}H_9O_2N_2$ : C, 65.0; H, 3.36; N, 11.7. Found: C, 65.0; H, 3.48; N, 11.4.

The infrared absorption spectrum of this compound is available.<sup>5</sup> The oxime was soluble in 2 *N* sodium hydroxide. It was hydrolyzed to the parent ketone by heating in 65% sulfuric acid at 125° for two hours.

**3-Nitro-2-cyanobiphenyl.**—This was prepared from 3-nitro-2-aminobiphenyl<sup>10</sup> by a procedure similar to that used for the isomeric 5-nitro compound.<sup>11</sup> We obtained a 32% yield of crude material, m.p. 124–130°, which was sublimed to give colorless needles, m.p. 131.5–132.0°.

*Anal.* Calcd. for  $C_{13}H_8O_2N_2$ : C, 69.6; H, 3.60; N, 12.5. Found: C, 69.4; H, 3.78; N, 12.6.

**3-Nitrobiphenyl-2-carboxylic Acid.**—Hydrolysis of the hindered nitrile by the procedure used for the 5-nitro isomer<sup>11</sup> was difficult. The procedure of Sudborough<sup>12</sup> was used to obtain 35% yields of colorless needles, m.p. 200–205°; Chase and Hey<sup>2</sup> record m.p. 200.5–201.5°. The acid was cyclized by heating in concentrated sulfuric acid for ten minutes at 115° and a 93% yield of 1-nitrofluorenone obtained.

**Methyl 6-Nitro-2-aminobenzoate.**—6-Nitro-2-aminobenzoic acid was prepared from Eastman Kodak Co. 3-nitrophthalimide by way of 6-nitrophthalamic acid.<sup>13,14</sup> 2.4 g. (0.0134 mole) of the acid was dissolved in the minimum amount of dry ether and esterified with diazomethane in ether by the conventional procedure. 2.45 g. (95% yield) of crude product was washed with dilute bicarbonate solution and then recrystallized from methyl alcohol-water to give orange crystals, m.p. 105–108°.

*Anal.* Calcd. for  $C_8H_8O_4N_2$ : N, 14.3. Found: N, 14.5, 14.6.

Satisfactory values for the saponification equivalent in aqueous solution were not obtained but the acid was recovered from the partially hydrolyzed samples. We were unable to prepare the methyl ester by the conventional procedure used with isomeric nitroaminobenzoic acids,<sup>15</sup> by the use of methyl alcohol and ethylene dichloride,<sup>16</sup> by the method of Newman<sup>17</sup> or by the use of boron trifluoride.<sup>18</sup> The latter method resulted in decarboxylation.

(8) H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 22 (1944); H. H. Hodgson and E. R. Ward, *ibid.*, 127 (1947).

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(1) Address communications to E. R. Atkinson, Dewey & Almy Chemical Co., 62 Whittemore Avenue, Cambridge 40, Mass.

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(5) E. A. Ham, Ph.D. Thesis, Massachusetts Institute of Technology, 1951.

(6) H. H. Hodgson, A. P. Mahadevan and E. R. Ward, *J. Chem. Soc.*, 1392 (1947); *Org. Syntheses*, 28, 52 (1948).

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