Experimental

The Willgerodt Reactions.—The method of Fieser and Kilmer[3] 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 ± 5°. 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 156–157°.

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
β-Bromostyrene	80
Phenacylpyridinium iodide	53
ω-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°.

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

DEPARTMENT OF CHEMISTRY
FORDHAM UNIVERSITY
NEW YORK 58, N. Y.

The Ternary System $NaVO_3$–Na_2SO_4–H_2O

BY R. TRUJILLO AND E. TEJERA

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Continuing our studies in connection with ternary systems involving alkali vanadates,[1] we here report the solubility relations in the system sodium vanadate–sodium sulfate–water at 25°.

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 $NaVO_3 \cdot 2H_2O$. The sodium sulfate, a Merck product, was used without further purification, after satisfactory tests on the limits of impurities.[2]

The ternary mixtures were placed in test-tubes and rotated in a thermostat at 25.0 ± 0.5° 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 $NaVO_3 \cdot 2H_2O$ and $Na_2SO_4 \cdot 10H_2O$, as determined by the Schreinemakers method.[3] The composition of the hydrates was verified through direct analysis.

TABLE I

SYSTEM $NaVO_3$–Na_2SO_4–H_2O AT 25°

Densities	Liquid solution Wt. % Na_2SO_4	Liquid solution Wt. % $NaVO_3$	Wet residue Wt. % Na_2SO_4	Wet residue Wt. % $NaVO_3$	Solid phase[a]
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

[a] A = $NaVO_3 \cdot 2H_2O$; B = $Na_2SO_4 \cdot 10H_2O$.

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[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.

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

UNIVERSIDAD DE LA LAGUNA
FALCULTAD DE CIENCIAS
LA LAGUNA, CANARY ISLANDS

Unsaturated Lactones. III. Absorption Spectra in a Group of α-Benzal-γ-substituted Crotonolactones[1]

BY CALVIN HANNA AND F. W. SCHUELER

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The effect of substitution of aromatic groups in the α-position on the absorption spectra in a series of γ-phenylcrotonolactones has been previously reported.[2] We have extended this study to include a series of γ-substituted α-benzalcrotonolactones to determine the effect of substituents on the γ-position on the light absorption.

Out of a group of twelve crotonolactones[3] prepared during this investigation four were pre-

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[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).