ventional means, at least) is of considerable importance in relation to the theory that in reactions subject to general acid and/or base catalysis the rate-controlling step is a proton transfer,[4] and also in relation to learning what compounds are *primary* acids and bases in the Lewis sense,[5] it was felt that another check of Orr's work, using his method for separating water from ethanol, would be desirable.[6] However, in order that the final concentration of deuterium in the water should differ more significantly from that used originally, a larger amount of ethanol relative to water, and a higher concentration of heavy water were used in our experiments, of which the following procedure is an example:

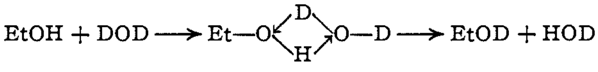
To 3.2 ml. of absolute ethanol at 0° was added 1.0 ml. of water (17.1 atom % deuterium) at about 0.5°. The mixture was shaken until homogeneous (5 seconds), poured onto 10 g. of anhydrous calcium sulfate, shaken for five minutes, and evacuated to 8 mm. pressure for 2.5 hours to remove the ethanol (all at 0°). The water was removed by heating to 197° under 8 mm. pressure, its ethanol content determined by the method of Williams and Reese[7] and its density by the falling drop method of Roseburg and Van Heyningen.[8] From the density and a correction for the 0.0087 g./ml. ethanol (based on the assumption that its partial molal volume is not affected by the deuterium content of the solvent), the water was shown to contain 9.0 atom % deuterium (11.3% would correspond to random distribution).

In another experiment at 0°, 9.4% deuterium (*vs.* 11.3% if random) was found and in a run at room temperature (*ca.* 34°) 10.1% deuterium (*vs.* 11.4% for random distribution) was found.

While we believe we have shown that the prototropic equilibrium between water and the hydroxy group of ethanol is established too rapidly to measure under our conditions, this does not establish any minimum for the rate of reactions such as

$$\mathrm{EtOH} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{EtO^-}, \text{ etc.}$$

which accomplish a net proton transfer, since the unshared electron pairs on oxygen make feasible[9] the establishment of this equilibrium by proton-*exchange* reactions by mechanisms of the type shown below in which ions play no part.



$$\mathrm{EtOH} + \mathrm{DOD} \longrightarrow \mathrm{Et{-}O}\overset{D}{\underset{H}{\langle\rangle}}\mathrm{O{-}D} \longrightarrow \mathrm{EtOD} + \mathrm{HOD}$$

It seems possible that the results of Orr are fortuitous. In no case would an error of more than 0.4 mg. in weighing his pycnometer be necessary to make his results correspond to purely random distribution of deuterium between the hydroxy group of the ethanol and water. From the facts that his weights are given to the nearest 0.1 mg., and that no contrary statement is made, it seems likely that he used an ordinary analytical balance on which the error of weighing (plus all of the other errors in the determination, such as that in filling the pycnometer) might reasonably have this magnitude.

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[4] R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, chap. VII; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 241.

[5] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938); G. N. Lewis, and G. T. Seaborg, This Journal, **61**, 1886 (1939).

[6] Since this problem was begun, we have learned from a private communication that Dr. H. Kwart of the University of Delaware has found the deuterium exchange between methanol and water to be too rapid to measure under similar conditions.

[7] M. B. Williams and H. D. Reese, *Anal. Chem.*, **22**, 1556 (1950).

[8] F. Roseburg and W. E. Van Heyningen, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 363 (1942).

[9] See A. J. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S. S. S. R.*, **74**, 513 (1950).

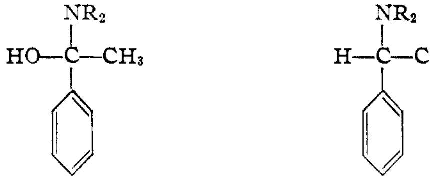
Extension of the Willgerodt Reaction

By Richard T. Gerry and Ellis V. Brown

Received July 2, 1952

Recent papers have shown that the scope of the Willgerodt reaction is considerably broader than had previously been supposed. Several investigators[1,2] have reported successful Willgerodt reactions with olefins, carbinols, thiols and acetylenes.

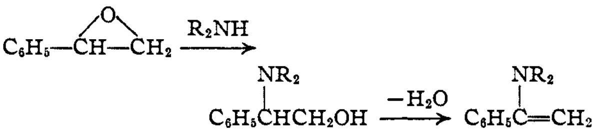
We feel that further extensions of the Willgerodt reaction may be of assistance in elucidating the mechanisms of this reaction as proposed by King and McMillan[1] and Carmack and DeTar.[2] The intermediates proposed by these workers are in many cases too reactive to be isolated by the usual preparative methods. However, the behavior of more stable but closely related compounds may be of interest. For example, Carmack and DeTar postulated a hydramine intermediate (I) in their reaction sequence. We have tested three amines (II) of somewhat related structure.



I II

(R = CH_3, CH_2CH_2OH or H)

Styrene oxide was also investigated since it could conceivably go through the following steps to yield another intermediate of Carmack and DeTar.



$$\mathrm{C_6H_5CH(O)CH_2} \xrightarrow{\mathrm{R_2NH}} \mathrm{C_6H_5\overset{NR_2}{C}HCH_2OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{C_6H_5\overset{NR_2}{C}{=}CH_2}$$

Again, compounds of type III would be expected to follow the sequence of King and McMillan. This is possible since the yields of amides from

$$\underset{\text{III}}{\mathrm{C_6H_5CH_2CH_2X}} \longrightarrow \underset{\text{IV}}{\mathrm{C_6H_5CH_2CH_2SH}} \longrightarrow \mathrm{C_6H_5CH_2C{\overset{O}{\lessgtr}}NH_2}$$

(X = Cl, Br or NH_2)

these compounds are only slightly lower than that reported for 2-phenylethanethiol (IV).

If either mechanism is applied to β-bromostyrene the amides might be formed in fewer steps than from styrene itself. Styrene yielded 71% of phenylacetamide while bromostyrene, under comparable conditions, gave 80% yield of this amide.

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[1] J. A. King and F. H. McMillan, This Journal, **68**, 525, 632 (1946).

[2] M. Carmack and D. F. DeTar, *ibid.*, **68**, 2029 (1946).

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).

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The Ternary System $NaVO_3$–Na_2SO_4–H_2O

BY R. TRUJILLO AND E. TEJERA

RECEIVED SEPTEMBER 12, 1952

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).

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

BY CALVIN HANNA AND F. W. SCHUELER

RECEIVED SEPTEMBER 27, 1952

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).