

monium bromide dissolved in approximately 50 ml. of liquid ammonia in c were titrated with potassium solutions of known concentration delivered from the calibrated buret a. The first appearance of a permanent blue color (characteristic of solutions of metals in ammonia) was taken as the end-point. Data for two such titrations are given in Table I (Expts. 1 and 2).

TABLE I  
REDUCTION OF AMMONIUM BROMIDE AND SILVER(I)  
BROMIDE

Expt. stance	Sub-stance	Reactants, g.		Products		Acctd. for, %
		Meas-ured	Calcd. <sup>a</sup>	Measured	Calcd. <sup>a</sup>	
1	NH <sub>4</sub> Br	1.0061				
	K	0.397 <sup>b</sup>	0.402			99
	H <sub>2</sub>			109 cc.	115 cc.	95
	NH <sub>4</sub> Br	1.0518				
2	K	0.418 <sup>b</sup>	.420			100
	H <sub>2</sub>			119 cc.	120 cc.	99
3	AgBr	.3173				
	K	.0667 <sup>b</sup>	.0660			101
	Ag			0.1818 g.	0.1822 g.	99.8
	AgBr	.2877				
4	K	.0598 <sup>b</sup>	.0599			100
	Ag			0.1646 g.	0.1653 g.	99.6

<sup>a</sup> Calcd. on the basis of the weight of ammonium bromide or silver(I) bromide used. <sup>b</sup> Measured as a portion (15–20 ml.) of a known volume (25–30 ml.) of potassium solution containing a weighed quantity of potassium.

**Reduction of Silver(I) Bromide with Potassium.**—Solutions containing known weights of silver(I) bromide were similarly titrated with potassium solutions. In these cases, however, the end-point could not be detected as indicated above, owing to the presence of the black finely divided precipitate of elemental silver. Consequently, a calculated volume of potassium solution was added, the precipitate allowed to settle, and drops of potassium solution were added to the clear supernatant solution until there was no further evidence of reaction. The combined supernatant solution and washings gave a negative test for silver ion. The resulting data are shown as Expts. 3 and 4, Table I.

### Summary

An improved apparatus for the conduct of reactions in liquid ammonia at its boiling point has been described, and its utility demonstrated. This apparatus provides for titrations employing liquid ammonia solutions of metals and permits one to carry out filtration and purification operations at the boiling point of the solvent.

It has been demonstrated that silver(I) bromide is reduced to elemental silver by reaction with solutions of potassium in liquid ammonia.

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RECEIVED MARCH 25, 1949

## NOTES

### Preparation of Radioactive Cyanide from Carbon Dioxide

BY RICHARD ABRAMS

For synthesis of labeled compounds it is often necessary to convert BaC<sup>14</sup>O<sub>3</sub> to HC<sup>14</sup>N. Available methods treat carbon dioxide with ammonia and potassium metal<sup>1</sup> (yield is a sensitive function of experimental conditions<sup>2</sup>), or treat barium carbonate with sodium azide<sup>3</sup> (yields are low in our experience). A method which has been found to be very satisfactory is based upon the reduction of carbon dioxide to carbon with magnesium powder,<sup>4</sup> and the conversion of amorphous carbon to hydrocyanic acid with ammonia gas at 1000°.<sup>2,5,6</sup> Yields are usually between 60 and 70% and not particularly dependent upon carbon dioxide pressure or magnesium excess.

(1) Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(2) Loftfield, *Nucleonics*, **1**, 54 (1947).

(3) Adamson, *THIS JOURNAL*, **69**, 2564 (1947).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, England, 1925, Vol. 6, p. 71.

(5) Mellor, *ibid.*, 1924, vol. 5, p. 827.

(6) Cramer, Thesis, Harvard, 1941.

In a typical experiment, carbon dioxide was liberated into a vacuum system from 1.1 mmoles. of barium carbonate by mixing with 1.6 g. of lead chloride and heating with a micro-burner.<sup>7</sup> Traces of water were removed by sublimation at –80°. The carbon dioxide was then admitted to a quartz tube containing 2.5 mmoles. of magnesium powder in a thin-walled iron thimble. The tube was heated rapidly with an oxygen flame until the thimble glowed red, and reaction began as noted by the sharp pressure drop. Intermittent heating was continued until the pressure remained constant. The contents of the thimble were washed with 1 *M* hydrochloric acid and with water, transferred as a slurry to a quartz boat, and dried under an infrared lamp. The yield was 0.76 mmole. of carbon which was 89% pure. Based upon the residual pressures of condensable and non-condensable gases and the acetylene liberated upon wetting the reaction mixture, the 30% loss consisted of approximately 5% unreacted carbon dioxide, 10% carbon monoxide, and 15% magnesium carbide.

The boat containing the carbon was placed in a quartz tube surrounded by an electric furnace. Ammonia gas was allowed to flow directly from the tank through the quartz tube and out through a wash bottle containing a 10% excess of 0.1 *M* sodium hydroxide. When all the air had been displaced by ammonia, the furnace was turned on so that the temperature rose to 1000° in thirty minutes, and stayed between 1000° and 1100° for two and one-half hours. All the hydrocyanic acid formed was carried out by the ammonia which flowed through the tube continuously at a

(7) Zwiebel, Turkevich and Miller, *THIS JOURNAL*, **71**, 376 (1949).

rate of 2 to 3 bubbles/second. The cyanide accumulated in the alkaline solution in the wash bottle which was removed at the termination of the heating period. Yields in this step were quantitative.

In a series of four runs, using approximately 1 mmole of barium carbonate, in which the magnesium excess ranged from 14 to 48% over the stoichiometric amount, and the carbon dioxide pressure from 278 to 385 mm., the yields of cyanide obtained were 67, 69, 72 and 59%. The value of 59% was obtained by radioactivity assay, the others by silver nitrate titration.

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RECEIVED JULY 27, 1949

## 2,4-Dinitrophenylhydrazones of Methoxy- and Methylcyclohexanones

BY HOMER ADKINS AND A. G. ROSSOW

Since the literature record of the melting points of these derivatives is confused and contradictory, we have re-examined the behavior of their ketones in the procedure described by Shriner and Fuson.<sup>1</sup>

2-Methoxycyclohexanone gave in our hands not the 2,4-dinitrophenylhydrazone, m. p. 135°, reported by others<sup>2</sup> but slowly and in low yield a red product, m. p. 218–219° uncor., whose analysis corresponded to cyclohexandione-1,2-bis-(2,4-dinitrophenyl)-osazone. *Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>8</sub>O<sub>8</sub>: N, 23.72. Found: N, 23.62. This reaction is analogous to the prior<sup>3</sup> record for 3-methoxy-2-butanone. 3-Methoxycyclohexanone by similar treatment did not yield a 2,4-dinitrophenylhydrazone, m. p. 133.5°,<sup>2</sup> but instead gave rapidly in quantitative yield a product, m. p. 170–170.5° uncor., whose analysis indicated loss of methanol as well as water during the condensation. *Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.30; H, 4.42; N, 20.54. Our product may therefore be either a ring-closed derivative or cyclohexen-2-one 2,4-dinitrophenylhydrazone; the latter has previously been reported as m. p. 163<sup>4</sup> and 117°.<sup>5</sup> From the 4-methoxy ketone we obtained 4-methoxycyclohexanone 2,4-dinitrophenylhydrazone, orange crystals from ethanol, m. p. 142.5–143.5° uncor. *Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub>: N, 18.18. Found: N, 18.20. This accords with the m. p. of 141.5–142.5°<sup>6</sup> but disagrees with the values of 150°<sup>2,7</sup> from the prior literature.

The behavior of 2-methylcyclohexanone was not examined, but its position isomers gave conventional results. 3-Methylcyclohexanone gave an orange-yellow 3-methylcyclohexanone 2,4-dinitrophenylhydrazone, m. p. 153.5–155.0° uncor., which appeared to be a mixture of stereoisomers. *Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: N, 19.17. Found: N, 19.22. The same procedure on 4-methylcyclohexanone gave 4-methylcyclohexanone 2,4-dinitrophenylhydrazone, golden yellow crystals from ethanol, m. p. 134.7–135.1° uncor. *Anal.* Found: N, 19.47.

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RECEIVED NOVEMBER 12, 1948

(1) Shriner and Fuson, "The Systematic Identification of Organic Compounds," p. 148, John Wiley and Sons, Inc., New York, N. Y., 1935; the preparation and properties of the ketones are given in another paper. Adkins, Eloffson, Rossow and Robinson, *THIS JOURNAL*, **71**, 3622 (1949).

(2) Ferrante and Bloom, *Am. J. Pharm.*, **105**, 381 (1933).

(3) Aston, Clarke, Burgess and Greenburg, *THIS JOURNAL*, **64**, 300 (1942).

(4) Bartlett and Woods, *ibid.*, **62**, 2933 (1940).

(5) Whitmore and Pedlow, *ibid.*, **63**, 758 (1941).

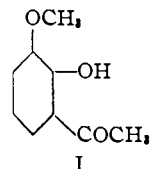
(6) Adamson and Kenner, *J. Chem. Soc.*, 188 (1939).

(7) Marvel and Walton, *J. Org. Chem.*, **7**, 92 (1942).

## The Reaction of *o*-Veratronitrile with Methylmagnesium Iodide

BY E. D. AMSTUTZ

In the course of other work to be reported later relatively large quantities of *o*-acetovanillone (I) were required.



The usual method of synthesis involves the successive conversion of *o*-veratric aldehyde to the methylcarbinol,<sup>1</sup> acetophenone,<sup>2</sup> and demethylation.<sup>3</sup> It has now been found that several of these steps may be obviated with improvement in yield and facility. Although ether splitting is by no means new, the reaction of *o*-veratronitrile with methylmagnesium iodide has previously been reported<sup>4</sup> to yield the dimethoxyketone. Apparently the phenol formed escaped attention.

The present work has shown that the 2,3-dimethoxyacetophenone may be the main product of the reaction but also that conditions may be so arranged that it appears only as a minor product with 2-demethylated ketone assuming major importance. For example, using double the calculated quantity of Grignard reagent over a total reaction time of sixty hours the yield of *o*-acetovanillone rises to about 75% and the yield of non-phenolic ketone drops to about 18%.

Since the methoxyl group ortho to the acetyl is vinylogous with methyl acetate it is not inconceivable that it could have suffered hydrolysis during the acid treatment to destroy the magnesium complex. A sample of the solid magnesium-containing complex was therefore removed from the reaction mixture and rapidly decomposed with cold ammonium chloride solution. Ether extraction removed a yellow material which exhibited (in alc. soln.) a definitely positive test for the phenolic group with ferric chloride. Since it is hardly likely that the hydrolysis could have occurred under these mild conditions and in such a short interval of time, it appears necessary to suppose that the splitting occurred during the reaction of the Grignard reagent. The same conclusion is indicated by the fact that 2,3-dimethoxyacetophenone (in ether soln.) did not yield phenolic bodies on gentle warming and stirring for three hours with dilute hydrochloric acid, although it was obvious other changes were taking place. Also Fuson and Chadwick<sup>5</sup> have

(1) Pauly, *et al.*, *Ann.*, **383**, 317 (1911).

(2) Krannichfeldt, *Ber.*, **46**, 4016 (1913).

(3) Reichstein, *Helv. Chim. Acta*, **10**, 392 (1927).

(4) Richtzenhain and Nippus, *Ber.*, **77B**, 566 (1914); Baker and Smith, *J. Chem. Soc.*, 346 (1936).

(5) Fuson and Chadwick, *J. Org. Chem.*, **13**, 484 (1948).

shown that such hydrolysis is quite liable to remove the acyl group. The production of *o*-acetovanillone therefore appears to be analogous to the formation of isobutyl 3,5-dimethoxy-4-hydroxyphenyl ketone from 3,4,5-trimethoxybenzonitrile and isobutylmagnesium bromide.<sup>6</sup> It differs, however, in the fact that methylmagnesium iodide does not require high temperatures and apparently does not alkylate at the position of attachment of the *o*- or *p*-methoxyl group.

Similar observations have been made on 2-benzyloxy-3-methoxybenzonitrile in which the benzyl ether is split. Since there is no preparative advantage accruing to the use of the benzyl ether rather than the methyl ether, details of these experiments are omitted.

#### Experimental

An ether solution of 16.3 g. (0.1 mole) of *o*-veratronic nitrile was added rapidly to an ether solution of Grignard reagent prepared from 28.4 g. (0.2 mole) of methyl iodide and 4.8 g. (0.2 g.-atom) of magnesium. No refluxing was observed and no precipitate formed for about one hour. The solution was therefore refluxed and stirred for eight hours during a total time of about sixty hours. Although a small amount of Grignard reagent was still present the mixture was then worked up in the usual way with water, ammonium chloride solution and finally dilute hydrochloric acid. Phenolic material, removed from the ethereal solution with dilute alkali, proved to be almost pure *o*-acetovanillone and amounted to 12.36 g. (74.5%), m. p. 50–53.1°, mixed with authentic *o*-acetovanillone, m. p. 51.8–53°. The crude neutral material amounted to 3.25 g. (18%),  $n_{D}^{20}$  1.5282, observed for authentic *o*-acetoveratrone  $n_{D}^{20}$  1.5368. Starting material unaccounted for above was obtained as a water-, ether- and alkali-insoluble resinous gum.

A second run of the same size using a nitrile to Grignard ratio of 1:1.5, refluxing for one hour and standing overnight yielded some tar and 25.6% of *o*-acetovanillone (m. p. 51.8–53°; mixed with authentic, m. p. 51.8–53°) and 32.2% of *o*-acetoveratrone,  $n_{D}^{20}$  1.5368. The neutral fraction yielded iodoform (m. p. 121–123°) and an acid, m. p. 118–120.4° (reported for *o*-veratric acid, m. p. 122°).<sup>7</sup> It also formed a 2,4-dinitrophenylhydrazone, m. p. 150–151.8° which did not depress the melting point of an authentic specimen.

(6) Hurd and Winberg, *This Journal*, **64**, 2085 (1942).

(7) Perkin and Robinson, *J. Chem. Soc.*, **105**, 2383 (1914).

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RECEIVED JULY 1, 1949

### Purification of Xanthopterin<sup>1</sup>

BY A. G. ANDERSON, JR., AND JERRY A. NELSON

In connection with the studies on the physiological properties of xanthopterin in this Laboratory,<sup>2</sup> xanthopterin free of other pterin impurities was desired. A purification procedure satisfactory as a routine method for this purpose was not found in

(1) This investigation was supported in part by a research grant from the Division of Research Grants and Fellowships of the National Institute of Health, U. S. Public Health Service.

(2) Norris and Majnarich, *Amer. J. Physiol.*, **152**, 175, 179, 652 (1948); **153**, 133, 483, 486, 492, 496 (1949); *Science*, **109**, 32, 33 (1949).

the literature. In this investigation xanthopterin has been purified *via* a new crystalline derivative, xanthopterin hydrochloride. Crystalline xanthopterin sulfate has also been prepared. The hydrochloride salt affords a simple, effective means for the purification of synthetic xanthopterin as prepared in this Laboratory. Purification was also effected by sublimation *in vacuo*. This procedure gave poor yields and thus was not practical.

#### Experimental

**Xanthopterin.**—Leucopterin and, from it, xanthopterin were prepared by the procedures of Purmann<sup>3</sup> and Totter,<sup>4</sup> respectively, as modified by Dauben and Goheen,<sup>5</sup> the modified procedure being similar to that recently reported by Hitchings and co-workers.<sup>6</sup> The xanthopterin so obtained was used in the experiments described below.

**Xanthopterin Hydrochloride.**—To 100 mg. of finely powdered xanthopterin was added 20 ml. of concentrated hydrochloric acid and the mixture heated on a steam-bath for ten minutes and filtered by suction while hot. The insoluble material (approximately 20 mg.) was largely xanthopterin hydrochloride and to this was added 5 ml. of hydrochloric acid and the mixture heated and filtered as before. The small quantity (5 mg.) of insoluble material was discarded. The two filtrates were placed in a refrigerator at –5° overnight. The hydrochloride precipitated as tiny, tan hexagonal plates which were separated by filtration, washed with a few ml. of cold alcohol, then with ether and dried. The yield from the first filtrate was 86 mg. (71.5%) and from the second filtrate 10 mg. (8.4%); total yield 96 mg. (79.9%). The salt was recrystallized from hydrochloric acid in corresponding yield. It was soluble in hot water or hot dilute hydrochloric acid but the hydrochloride could not be recovered from these solutions by cooling or concentration. On heating the crystals darkened at 200° and above but no melting point was observed up to 320°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>Cl: N, 32.48. Found: N, 32.41.

Amorphous xanthopterin was recovered quantitatively as a yellow solid on treatment of the hydrochloride with just sufficient 0.1 *N* ammonium hydroxide to effect solution (the xanthopterin began to precipitate a few seconds after the salt had dissolved) and then adjustment of the acidity to pH 5–6 by addition of dilute hydrochloric acid. The mixture was cooled, filtered and the collected precipitate washed with a few ml. of cold water, then acetone and dried.

**Xanthopterin Sulfate.**—Eighty-six mg. of finely powdered xanthopterin was dissolved in 2.3 ml. of sulfuric acid-water (1:1) solution by heating on a steam-bath. As the xanthopterin dissolved the solution became orange in color. On cooling the solution in tap water and scratching the sides of the flask, crystallization occurred and, after standing overnight in a refrigerator, the tiny, tan boat-shaped crystals were separated by filtration, washed with a few ml. of cold alcohol, then with ether and dried; yield 45 mg. (36%). The crystals gradually darkened and decomposed above 200° leaving a black residue at 280°. The sulfate could be recrystallized from the same sulfuric acid solution in corresponding yield. Attempts to obtain a second crop from the filtrate were unsuccessful. Xanthopterin sulfate is quite soluble in dilute or concentrated sulfuric acid and undergoes hydrolysis with water to precipitate amorphous xanthopterin. Recovery of xanthopterin from the sulfate was best effected in the manner described for the hydrochloride.

*Anal.* Calcd. for C<sub>6</sub>H<sub>7</sub>O<sub>6</sub>N<sub>2</sub>S: N, 25.27. Found: N, 25.80.

(3) Purmann, *Ann.*, **544**, 182 (1940).

(4) Totter, *J. Biol. Chem.*, **154**, 105 (1944).

(5) Dauben and Goheen, private communication.

(6) Ellison, Light and Hitchings, *This Journal*, **71**, 741 (1949).

**Chromatographic Analysis of Purified Xanthopterin.**—Paper chromatographs of the xanthopterin purified *via* the hydrochloride and by sublimation *in vacuo* were obtained by the method of Good and Johnson<sup>7</sup> who employed the *n*-butanol-acetic acid-water mixture of Partridge.<sup>8</sup> Under ultraviolet light the chromatographs showed only one fluorescent spot ( $R_f = 0.35-0.38$ ) which was in agreement with the value ( $R_f = 0.38$ ) reported by Good and Johnson.<sup>7</sup> The material was thus free of leucopterin ( $R_f = 0.12$ ), dihydroxanthopterin ( $R_f = 0.26$ ) and other fluorescent pterin impurities. It should be noted that some samples of synthetic xanthopterin prepared as indicated did not contain these impurities and thus required no further purification.

**Absorption Spectra of Purified Xanthopterin.**—Ultraviolet absorption spectra of an aqueous solution ( $pH$  of 11.25) of the xanthopterin purified by sublimation and *via* the hydrochloride showed absorption maxima at 255  $m\mu$ . ( $E_m \times 10^{-3} = 18.2$ ) and 392  $m\mu$ ; ( $E_m \times 10^{-3} = 7.0$ ) in agreement with other reported spectra.<sup>4,9</sup>

(7) Good and Johnson, *Nature*, **168**, 31 (1949).

(8) Partridge, *Biochem. J.*, **42**, 238 (1948).

(9) Rickes, Chalet and Keresztesy, *THIS JOURNAL*, **69**, 2749 (1947).

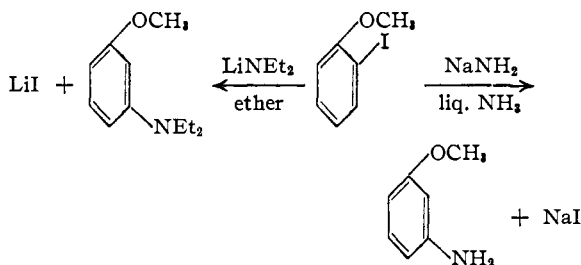
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RECEIVED JUNE 4, 1949

## The Reaction of Sodium Amide with *o*- and *m*-Chlorotrifluoromethylbenzene

BY ROBERT A. BENKESER AND ROLAND G. SEVERSON<sup>1</sup>

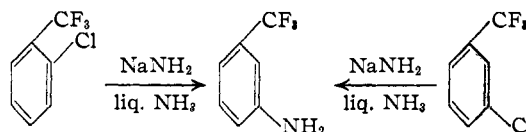
Recently it was reported that certain aryl halides react with a liquid ammonia solution of sodium<sup>2</sup> or potassium amide.<sup>3</sup> It has also been found that ether solutions of aryl halides are attacked by lithium dialkylamides.<sup>4</sup> When the aryl halide has an ether, sulfide or dialkylamino group ortho to the halogen, it was observed that the amino or dialkylamino group does not take up the position which the halogen originally occupied, but rather a meta-substituted product<sup>5,6,7</sup> is formed



The corresponding *p*-haloethers also exhibit this tendency to undergo rearrangement when treated with lithium dialkylamides in ether, but to a somewhat lesser extent.<sup>8</sup>

- (1) Research Corporation Fellow.
- (2) Gilman and Avakian, *THIS JOURNAL*, **67**, 349 (1945).
- (3) Urner and Bergstrom, *ibid.*, **67**, 2108 (1945).
- (4) Horning and Bergstrom, *ibid.*, **67**, 2110 (1945).
- (5) Gilman and Nobis, *ibid.*, **67**, 1479 (1945).
- (6) Gilman, *et al.*, *ibid.*, **67**, 2106 (1945).
- (7) Gilman, Kyle and Benkeser, *ibid.*, **68**, 143 (1946).
- (8) Gilman and Kyle, *ibid.*, **70**, 3945 (1948).

It has now been observed that the same rearrangement occurs even when the halogen is ortho to a strong meta-directing group. Thus, *o*-chlorotrifluoromethylbenzene upon treatment with sodium amide in liquid ammonia for five hours at  $-33^\circ$  gives a 52% yield of pure *m*-aminotrifluoromethylbenzene. Efforts to isolate any of the ortho isomer have been unsuccessful. In contrast, *m*-chlorotrifluoromethylbenzene gives the expected *m*-aminotrifluoromethylbenzene. It is noteworthy that the yield here is only 35%.



### Experimental

***m*-Aminotrifluoromethylbenzene.** (a) From *o*-Chlorotrifluoromethylbenzene.—Sodium amide<sup>9</sup> was prepared from 16.1 g. (0.7 g. atom) of sodium and 750 ml. of liquid ammonia containing 0.4 g. of hydrated ferric nitrate. To this mixture was added 90.3 g. (0.5 mole) of *o*-chlorotrifluoromethylbenzene<sup>10,11</sup> (b. p. 149–150°) during a period of one hour. After stirring for an additional four hours, ammonium chloride was added and the solvent was allowed to evaporate. The residue was dissolved in ether, filtered and treated with anhydrous hydrogen chloride which precipitated 62 g. of a brown hydrochloride. From the ether filtrate 14.4 g. of *o*-chlorotrifluoromethylbenzene (b. p. 149–150°) was recovered. Crystallization of the crude hydrochloride from an ethanol-ether mixture gave 53 g. of white crystals from which the free base was obtained by adding concentrated ammonium hydroxide. After extracting the basic solution with ether, drying the ether extract over Drierite, removing the solvent, and fractionating the product through a small helices-packed column, there was obtained 35.1 g. (52% yield) of *m*-aminotrifluoromethylbenzene boiling at 86° (20 mm.),  $n_D^{20} 1.4801$ ,  $n_D^{25} 1.4775$ .

The acetyl derivative<sup>12</sup> melted at 103–104° and the benzoyl derivative<sup>13</sup> at 110–111°. A mixed melting point between this acetyl derivative and that obtained from an authentic sample of *m*-aminotrifluoromethylbenzene<sup>10</sup> showed no depression.<sup>14</sup>

(b) From *m*-Chlorotrifluoromethylbenzene.—This procedure was identical with that described above. From 90.3 g. (0.5 mole) of *m*-chlorotrifluoromethylbenzene,<sup>10</sup> 47.8 g. of crude hydrochloride was obtained. This gave 36 g. of pure salt when crystallized from an ethanol-ether mixture and 23.9 g. (35% yield) of the free base boiling at 86° (20 mm.),  $n_D^{20} 1.4800$ . The acetyl and benzoyl derivatives melted at 103–104° and 110–111°, respectively.

(9) Vaughn, Vogt and Nieuwland, *ibid.*, **47**, 2002 (1925).

(10) Kindly supplied by the Hooker Electrochemical Company, Niagara Falls, N. Y.

(11) For a description of numerous ortho and para derivatives of benzotrifluoride see Jones, *THIS JOURNAL*, **69**, 2346 (1947).

(12) Swarts, *Bull. acad. roy. Belg.*, 389 (1920); *C. A.*, **16**, 2316 (1922).

(13) *Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>OF<sub>3</sub>N: N, 5.28. Found: N, 5.35.

(14) The literature<sup>11,12</sup> values for the physical constants of *o*-, *m*- and *p*-aminotrifluoromethylbenzene are

	B. p. °C.	Mm.	$n_D$	Acetyl deriv.	Ben- zoyl deriv.
ortho-	72–74	21	1.4785 (25°)	94.5–95°	140–141°
meta-	74–75	10	1.481 (20°) <sup>10</sup>	103°	.....
para-	91	19	1.4815 (25°)	152°	.....

There was recovered 14.3 g. of unreacted *m*-chlorotrifluoromethylbenzene.

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RECEIVED JULY 1, 1949

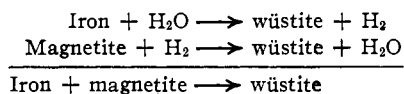
### Preparation of Wüstite

BY R. W. BLUE AND H. H. CLAASSEN

For X-ray diffraction studies of iron oxides it is frequently helpful to have diffraction patterns of the pure oxides for purposes of comparison. Samples of magnetite, ferric oxide and iron are readily obtained but a sample having the ferrous oxide structure is less easily prepared. Fusion of higher oxides with iron often results in samples which do not give clean diffraction patterns.

Previous work<sup>1</sup> indicates that the lower limit for oxygen content of this sodium chloride-type structure is 23.1% oxygen as compared with 22.27% for ferrous oxide. The name wüstite has been given to the material in the composition range, 23.1 to 25.6% oxygen, in which the sodium chloride-type of structure occurs.

A convenient way to prepare a sample of wüstite is to take advantage of the simultaneous reactions



When equimolar amounts of iron and magnetite are placed in an atmosphere of water vapor in the temperature region 750 to 900°, some hydrogen is immediately formed and the water hydrogen ratio is automatically regulated for conversion of both iron and magnetite to wüstite. By keeping the iron and magnetite in separate boats one can use an excess of either reactant; the reactant not in excess is converted to material giving a clean diffraction pattern of the sodium chloride-type of structure but there is a slight difference between the diffraction patterns of the two samples which may be described as follows:

In practice magnetite obtained by burning pure iron at fusion temperatures contains 10 to 50% ferrous oxide.<sup>2</sup> The ferrous oxide diffraction lines obtained with these ferrous oxide-magnetite samples are doublets which become single lines when reduction occurs. When the samples are reduced in a stream of hydrogen the line in each doublet which corresponds to the smaller lattice disappears first. When reduction is carried out by the double-boat method described above, the line corresponding to the larger lattice disappears first; and when wüstite is formed from iron

by the double-boat method the diffraction lines are in the mean position between the doublet positions. The latter differences correspond to only a few thousandths of an ångström but they can be clearly seen by comparing XRD patterns of samples prepared simultaneously by the double-boat method.

Oxides in the composition range 23.2 to 24.3% oxygen have been prepared under various conditions. All samples in this composition range give the same XRD pattern with the exceptions noted above depending on the source material.

In a typical experiment magnetite containing about 40% wüstite was prepared by burning Armco iron in an atmosphere of oxygen. Some of this material, after crushing and screening to 60 to 120 mesh, was reduced with hydrogen at 450° to iron. Thirty-three and one-quarter grams of the magnetite and 3.0 g. of the iron were weighed into separate alundum boats and placed in a quartz tube closed at one end and joined at the other end by a wax seal to a Pyrex tube equipped with a side tube and vacuum connection. A few cc. of water was placed in the side tube and, after the apparatus was assembled, the side tube was cooled in liquid air. The apparatus was then evacuated and the side tube was warmed to room temperature. That part of the tube containing magnetite and iron was then heated to 900°. After seventy-two hours the tube was cooled in a stream of air and the iron oxide samples were removed. (Cooling to room temperature required about five minutes.) Examination by X-ray diffraction revealed that both the wüstite from the iron and that from magnetite contained no other crystalline materials. Reduction in a stream of hydrogen at 450° showed that the wüstite from the oxide contained 23.2% oxygen.

PHILLIPS PETROLEUM COMPANY  
RESEARCH DEPARTMENT  
BARTLESVILLE, OKLAHOMA

RECEIVED JUNE 23, 1949

### N-(Dialkylaminoalkyl)-amides

BY R. O. CLINTON, U. J. SALVADOR AND S. C. LASKOWSKI

Since only a few simple aromatic amide derivatives have been tested as local anesthetics,<sup>1</sup> it seemed desirable to extend these types to include 4-aminobenzamides and related compounds. However, the initially prepared compounds proved relatively inactive in comparison with their ester analogs, and the investigation was terminated after the preparation of only a few compounds.

Attempts were also made to prepare 4-aminobenzamides derived from imino-interrupted side chains, analogous to those derived from sulfur and oxygen-interrupted side chains.<sup>2</sup> Because of the complex mixtures formed, we were unable to prepare pure 4-aminobenzamides of this type.

#### Experimental<sup>3</sup>

**Nitriles.**—The reaction of a primary or secondary amine with acrylonitrile was carried out by the method of Whitmore, *et al.*<sup>4</sup>

(1) Cf. Wenker, *THIS JOURNAL*, **60**, 1081 (1938); Blicke, Parke and Jenner, *ibid.*, **62**, 3316 (1940).

(2) Clinton, Salvador, Laskowski and Suter, *ibid.*, **70**, 950 (1948).



(3) All melting and boiling points are corrected. The authors desire to thank Mr. Morris E. Auerbach and staff for the analyses.

(4) Whitmore, *et al.*, *ibid.*, **66**, 725 (1944).

(1) R. W. G. Wyckoff and E. D. Crittenden, *THIS JOURNAL*, **47**, 2876 (1925); E. R. Jette and F. Foote, *J. Chem. Phys.*, **1**, 29 (1933); *Trans. Am. Inst. Min. and Met. Engrs., Iron and Steel Div.*, **105**, 276 (1933); L. S. Darken and R. W. Gurry, *THIS JOURNAL*, **67**, 1398 (1945).

(2) J. A. Almquist and E. D. Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).

TABLE I  
 4-SUBSTITUTED BENZAMIDES

4-Nitrobenzamides, NO <sub>2</sub>  CONH—X—NR <sub>2</sub>						
X	R <sub>2</sub>	Derivative	M. p., °C.	Formula	Nitrogen analyses, %	
					Calcd.	Found
-(CH <sub>2</sub> ) <sub>3</sub> -	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	Picrate	147.5–148.5	C <sub>20</sub> H <sub>24</sub> N <sub>6</sub> O <sub>10</sub>	16.53	16.30
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>10</sub> <sup>a</sup>	Base	50.5–51.0	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>	14.42	14.34
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>10</sub> <sup>a</sup>	Picrate	206.0–206.5	C <sub>21</sub> H <sub>24</sub> N <sub>6</sub> O <sub>10</sub>	16.15	16.27
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>12</sub> <sup>b</sup>	Base	71.5–72.5	C <sub>16</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub>	13.81	14.15
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>12</sub> <sup>b</sup>	Picrate	174.0–175.0	C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> O <sub>10</sub>	15.76	16.14
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>7</sub> H <sub>14</sub> <sup>c</sup>	Picrate	190.0–191.0	C <sub>23</sub> H <sub>28</sub> N <sub>6</sub> O <sub>10</sub>	10.22 <sup>d</sup>	10.43 <sup>d</sup>
-(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>3</sub> -	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	Dipicrate	161.0–162.0	C <sub>29</sub> H <sub>34</sub> N <sub>10</sub> O <sub>17</sub>	17.63	17.42
-(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>10</sub> <sup>a</sup>	Dipicrate	170.0–171.0	C <sub>30</sub> H <sub>34</sub> N <sub>10</sub> O <sub>17</sub>	17.37	17.00
-(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>12</sub> <sup>b</sup>	Picrate	165.0–166.0	C <sub>26</sub> H <sub>32</sub> N <sub>7</sub> O <sub>10</sub>	9.46 <sup>d</sup>	9.50 <sup>d</sup>
4-Aminobenzamides, NH <sub>2</sub>  CONH—X—NR <sub>2</sub>						
-(CH <sub>2</sub> ) <sub>3</sub> -	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	Dipicrate	149.0–150.5	C <sub>28</sub> H <sub>29</sub> N <sub>9</sub> O <sub>15</sub>	11.88 <sup>d</sup>	11.62 <sup>d</sup>
-(CH <sub>2</sub> ) <sub>3</sub> -	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	Dihydriodide <sup>e</sup>	202.0–203.5	C <sub>14</sub> H <sub>25</sub> I <sub>2</sub> N <sub>3</sub> O	8.31	8.05
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>10</sub> <sup>a</sup>	Base <sup>f</sup>	168.3–169.5	C <sub>15</sub> H <sub>23</sub> N <sub>3</sub> O	16.14	15.96
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>10</sub> <sup>a</sup>	Dipicrate	120.5–122.0	C <sub>27</sub> H <sub>29</sub> N <sub>9</sub> O <sub>15</sub>	11.68 <sup>d</sup>	11.90 <sup>d</sup>
-(CH <sub>2</sub> ) <sub>3</sub> -	C <sub>6</sub> H <sub>12</sub> <sup>b</sup>	Base <sup>g</sup>	121.0–122.8	C <sub>16</sub> H <sub>25</sub> N <sub>3</sub> O	15.26	15.24

<sup>a</sup> 1-Piperidyl. <sup>b</sup> 2-Methyl-1-piperidyl. <sup>c</sup> 2,6-Dimethyl-1-piperidyl. <sup>d</sup> Nitro nitrogen by titration with titanous chloride. <sup>e</sup> Calcd.: HI, 50.65. Found: HI, 50.13. <sup>f</sup> Calcd.: C, 69.19; H, 8.90. Found: C, 69.15; H, 8.73. <sup>g</sup> Calcd.: C, 69.78; H, 9.15. Found: C, 70.01; H, 9.17.

3-(2-Methyl-1-piperidyl)-propionitrile, 87% yield, b. p. 126.4° at 18.0 mm., *n*<sub>D</sub><sup>25</sup> 1.4689.

Anal. Calcd. for C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>: N, 18.41. Found: N, 18.31.

The picrate had m. p. 132.5–133.5°.

Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>5</sub>O<sub>7</sub>: N, 18.37. Found: N, 18.56.

A compound believed to be 3-(2,6-dimethyl-1-piperidyl)-propionitrile (*vide infra*) was obtained in 30% crude yield, b. p. 137–149° at 14 mm. The condensation required prolonged heating; the low yield was probably due to steric effects.<sup>4</sup> The crude compound could not be obtained sufficiently pure for analysis, nor did it yield a crystalline derivative.

3-(3-[1-Piperidyl]-propylamino)-propionitrile, 67% yield, b. p. 116.0° at 0.45 mm., *n*<sub>D</sub><sup>25</sup> 1.4790.

Anal. Calcd. for C<sub>11</sub>H<sub>21</sub>N<sub>3</sub>: N, 21.52. Found: N, 21.28.

The dipicrate had m. p. 177.0–178.3°.

Anal. Calcd. for C<sub>28</sub>H<sub>27</sub>N<sub>9</sub>O<sub>14</sub>: N, 19.28. Found: N, 19.22.

3-(3-[2-Methyl-1-piperidyl]-propylamino)-propionitrile, 86% yield, b. p. 110.0° at 0.15 mm., *n*<sub>D</sub><sup>25</sup> 1.4794.

Anal. Calcd. for C<sub>12</sub>H<sub>23</sub>N<sub>3</sub>: N, 20.08. Found: N, 20.01.

The dipicrate had m. p. 163.5–165.0°.

Anal. Calcd. for C<sub>24</sub>H<sub>29</sub>N<sub>9</sub>O<sub>14</sub>: N, 18.89. Found: N, 19.18.

**Amines.**—The propionitriles were reduced in methanolic ammonia at 100° and 1200 lb. pressure, using Raney nickel catalyst.<sup>4</sup>

3-(2-Methyl-1-piperidyl)-propylamine, 62% yield, b. p. 77.0° at 0.42 mm., *n*<sub>D</sub><sup>25</sup> 1.4742.

Anal. Calcd. for C<sub>9</sub>H<sub>20</sub>N<sub>2</sub>: N, 17.93. Found: N, 18.20.

The dipicrate had m. p. 216.5–218.0°.

Anal. Calcd. for C<sub>21</sub>H<sub>26</sub>N<sub>6</sub>O<sub>14</sub>: N, 4.56. Found: N, 4.54.

(5) Basic amino nitrogen by titration with perchloric acid in glacial acetic acid solution.

The cinnamamide hydrochloride had m. p. 181.0–183.2°.

Anal. Calcd. for C<sub>18</sub>H<sub>27</sub>ClN<sub>2</sub>O: N, 8.67; Cl, 10.98. Found: N, 8.50; Cl, 10.89.

3-(2,6-Dimethyl-1-piperidyl)-propylamine, 58% yield, b. p. 66.3° at 0.20 mm., *n*<sub>D</sub><sup>25</sup> 1.4714.

Anal. Calcd. for C<sub>10</sub>H<sub>22</sub>N<sub>2</sub>: N, 16.46. Found: N, 16.84. A crystalline derivative could not be obtained.

3-(3-[1-Piperidyl]-propylamino)-propylamine, 83% yield, b. p. 111.0° at 0.44 mm., *n*<sub>D</sub><sup>25</sup> 1.4844.

Anal. Calcd. for C<sub>11</sub>H<sub>23</sub>N<sub>3</sub>: N, 21.08. Found: N, 21.15.

The tripicrate had m. p. 208.0–209.0°.

Anal. Calcd. for C<sub>29</sub>H<sub>34</sub>N<sub>12</sub>O<sub>21</sub>: N, 18.96. Found: N, 18.84.

3-(3-[2-Methyl-1-piperidyl]-propylamino)-propylamine, 91% yield, b. p. 104.5° at 0.25 mm., *n*<sub>D</sub><sup>25</sup> 1.4843.

Anal. Calcd. for C<sub>12</sub>H<sub>27</sub>N<sub>3</sub>: N, 19.69. Found: N, 19.57.

The tripicrate melted at 184.5–186.0°.

Anal. Calcd. for C<sub>30</sub>H<sub>36</sub>N<sub>12</sub>O<sub>21</sub>: N, 13.99. Found: N, 13.82.

**4-Nitrobenzamides and 4-Aminobenzamides.**—The 4-nitrobenzamides were prepared from 4-nitrobenzoyl chloride and the amine by the sodium bicarbonate-chloroform-water procedure.<sup>2</sup> The yields were good, but the compounds derived from the tribasic amines proved extremely difficult to purify. The 4-aminobenzamides were obtained by reduction with ferrous sulfate and ammonia. Purification proved difficult in most cases, and with the more complex imino-interrupted side-chain compounds a pure base or characteristic derivative could not be obtained. The 4-nitro- and 4-aminobenzamides are listed in Table I.

STERLING-WINTHROP RESEARCH INSTITUTE  
 RENSSELAER, NEW YORK

RECEIVED JULY 2, 1949

(6) Nitro nitrogen by titration with titanous chloride.



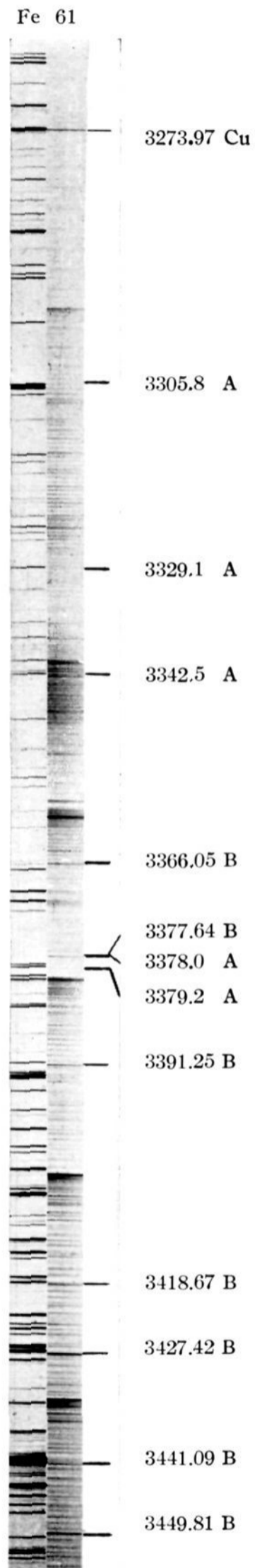


Fig. 1.—Arc emission spectrum of the 3260–3500 Å. region (sample 3). Spectra from the top down: Element 61, Fe. Wave lengths followed by A are those in Table A; wave lengths followed by B are those in Table B. Emission lines are black.



### Note on the Arc Spectrum of Element 61<sup>1</sup>

BY CYRUS FELDMAN

An examination has been made of the arc emission spectra of three samples of the chloride of element 61 prepared by Paul Lantz. This material was separated from a mixture of uranium fission products by fractionation and concentration on a series of Amberlite IR-I and Dowex resin columns.<sup>1a</sup> Detailed accounts of the isolation of milligram amounts of element 61 are to be reported elsewhere by G. W. Parker and P. Lantz of this Laboratory. The amount of element 61 present in these samples was estimated on the basis of published values<sup>1a</sup> of the half-life and energy of the  $\beta$ -radiation of this element. The characterization of material which is radiochemically and spectrographically identical with these samples as element 61 has been confirmed by X-ray emission work.<sup>2</sup>

Once isolated, the material was prepared in the form of approximately 0.05 ml. of a hydrochloric acid solution. A thin layer of Zapon lacquer was deposited on a flat-topped  $\frac{1}{4}$ " diam. high purity graphite electrode; the sample solution was deposited atop this and dried under an infrared lamp. This electrode was made the anode of a 220-volt, 9-ampere d.c. arc. A  $\frac{1}{8}$ " diameter high purity graphite rod served as cathode. The arc gap was 4 mm. The burning took place inside a chamber which permitted light to enter the spectrograph without allowing the vapor containing element 61, which is highly radioactive, to escape into the laboratory.

The light was focused on the slit of a 21-foot (6.5-meter) Jarrel-Ash spectrograph. Further details of dispersion, etc., are given in Table A.

When sample 1 was exposed, spectra of iron, neodymium, element 61, and samarium were obtained in juxtaposition in the order mentioned; in the other two cases, only the spectra of iron, and element 61 were photographed. The placement of the spectra on the plate was effected by means of a Hartmann diaphragm at the slit; the camera was not moved at any time during the exposure. The exposure conditions were essentially the same as those used by Harris, Yntema and Hopkins.<sup>3</sup>

A search was made for the five lines specifically mentioned by them as being common to the spectra of the neodymium and samarium fractions and being somewhat more intense in the

(1) This document is based on work performed under Contract No. 7405 eng. 26 for the Atomic Energy Project, and the information covered therein will appear in the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the Oak Ridge National Laboratory.

(1a) *Chem. Eng. News*, **26**, 205 (1948); J. A. Marinsky, L. E. Glendenin and C. D. Coryell, *THIS JOURNAL*, **69**, 2781 (1947); W. E. Cohn, E. R. Tompkins and J. X. Khym, *ibid.*, **69**, 2769 (1947); B. H. Kettle and G. E. Boyd, *ibid.*, **69**, 2800 (1947).

(2) L. E. Burkhart, W. Peed and E. Spitzer, *Phys. Rev.*, **75**, 86 (1949).

(3) J. A. Harris, L. F. Yntema and B. S. Hopkins, *THIS JOURNAL*, **48**, 1585 (1926).

fractions intermediate between them.<sup>3,4</sup> Wave lengths were located by interpolation between iron lines of known wave length; observations were made on an ARL-Dietert projection comparator, which gives an enlargement of twenty-one-fold.

In all, three samples were tested; the results are summarized in Table A.

TABLE A

Sample no.	1	2	3
Purity	Impure (see text)	Very pure	Very pure
61 content, in $\mu\text{g}$	50	50	100
Dispersion of spectrum in $\text{\AA./mm.}$	5.0	2.5	2.5
Observations in connection with given lines	3305.8 Doubtful 3329.1 Absent 3342.5 Doubtful 3378.0 Absent 3379.2 Absent	Absent Absent Absent Absent Absent	Absent Absent Absent (see text) Absent

Sample 1 was received on February 20, 1948; its spectrum showed the presence of comparatively large amounts of calcium and magnesium, moderate amounts of iron, nickel, sodium and chromium, and small amounts of neodymium. Calcium was easily the major metallic constituent of this sample.

Although no definite line was seen in its spectrum at 3305.8, the proximity of iron 3305.98, which was present, might have masked a weak line at 3305.8. A line was observed at 3342.5, but this line may have been chromium 3342.586.

Two highly purified samples were received from the same source on March 7, 1949. The two samples contained 50 and 100 micrograms, respectively, of element 61. Arc spectra of these samples were taken under the same conditions as used for sample 1, except that higher dispersion was used. The spectrum of sample 3 is shown in Fig. 1.

The results are summarized in Table A. A weak line, not assignable to any known element, was found at  $3377.64 \pm 0.03 \text{ \AA.}$  in the high dispersion spectra, but in view of the fact that Yntema's observations were also made in the second order of a 6.5-meter spectrograph,<sup>4</sup> this line cannot be assumed to be identical with 3378.0. It was the weakest of several lines believed due to element 61 which were observed in the 3000–3450  $\text{\AA.}$  region of spectra 2 and 3. Seven such lines are listed in Table B; although these lines are fairly close to minor lines of various elements listed in the M. I. T. Wavelength Tables, qualitative examination of the spectrum showed that the only impurities present in samples 2 and 3 were faint traces of copper and calcium, and these did not interfere with the lines listed. A detailed study of the arc spectrum of element 61 is being made by W. F. Meggers and B. F. Scribner, Jr., of the National Bureau of Standards.

(4) L. F. Yntema, *ibid.*, **46**, 37 (1924).

TABLE B  
STRONGEST ARC LINES OF ELEMENT 61 IN THE 3000-3450  
Å. REGION

Wave length, Å.	Relative intensity
3366.05 ± 0.03	Weak
3377.64 ± .03	Weak
3391.25 ± .03	Medium
3418.67 ± .03	Weak
3427.42 ± .03	Strong
3441.09 ± .03	Weak
3449.81 ± .03	Medium

Unfortunately, it was impossible to compare these (arc) spectra with the (spark) spectrum observed by Timma.<sup>5</sup> His observations covered the 3630-4400 Å. region; aside from the fact that the methods of excitation used were different, his principal lines could not be looked for in the present arc spectrum with any hope of success because of interference by C<sub>2</sub> and CN bands. However, the spark lines he mentioned as due to element 61 were observed in the spectrum of aliquots of samples 1, 2 and 3 when excited by the copper spark technique.

(5) D. Timma, MonC-166 (U. S. Atomic Energy Commission).

OAK RIDGE NATIONAL LABORATORY  
OAK RIDGE, TENN. RECEIVED JANUARY 26, 1949

## A Convenient Synthesis of Phenaceturic Acid<sup>1</sup>

BY JARED H. FORD

Phenaceturic acid was required as a starting material in numerous experiments directed toward the synthesis of benzylpenicillin.<sup>2</sup> The following method which employs methyl phenylacetate as the starting material was found to be more convenient than the literature method<sup>3</sup> in which phenylacetyl chloride was used.

### Experimental

Glycine (75.1 g.) was added to a solution of 23 g. of sodium in 850 ml. of anhydrous methanol, and the mixture was boiled under reflux a few minutes to obtain a clear solution. One hundred fifty grams of methyl phenylacetate was then added and the solution was boiled under reflux for three days. The methanol was distilled off and the residue was dissolved in 400 ml. of cold water which contained 20 g. of sodium bicarbonate. The resulting solution was twice extracted with ether to remove unchanged methyl phenylacetate, and then acidified to pH 2 with concentrated hydrochloric acid. After standing overnight in a refrigerator, the product was filtered, washed with cold water and dried in a vacuum oven. The resulting white crystals melted at 139-141° (lit.,<sup>3</sup> 143°); yield, 122.6 g. (63.5%). One recrystallization from hot water (400 ml.) gave 114.2 g. of product which melted at 143-144°. From the ether extracts were obtained 42.1 g. (28%) of methyl phenylacetate; b. p. 96-98° (14 mm.).

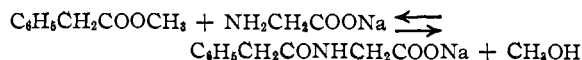
A longer period of heating did not increase the

(1) This work was done under contract between the Office of Scientific Research and Development and The Upjohn Company (Contract OSRD-cmr-399).

(2) Clarke, Johnson and Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949.

(3) Hotter, *J. prakt. Chem.*, [2] **88**, 98 (1888).

yield and it appears likely that an equilibrium is involved



ANTIBIOTICS RESEARCH DEPARTMENT  
THE UPJOHN COMPANY

KALAMAZOO 99, MICHIGAN RECEIVED MAY 5, 1949

## Alkyl Derivatives of Ethylenediamine

BY ALBERT E. FROST, JR., STANLEY CHABEREK, JR., AND  
ARTHUR E. MARTELL

In the course of other work a number of symmetrical dialkyl ethylenediamines have recently been prepared and characterized. A number of other amines, containing a smaller or larger number of alkyl groups, and a few dialkyl piperazines were obtained as by-products. The by-products not previously reported for this method and their properties are listed in Table I. The

TABLE I  
BY-PRODUCTS

Amine	B. p., °C.	Mm.	M. p., °C.	N, % Calcd.	% Found
N,N'-Dioctylpiperazine	187-190	1	53-55	9.02	9.09
N,N,N',N'-Tetraoctyl- ethylenediamine	.....		130-133	5.51	5.29
N,N'-Didodecylpiper- azine	265-275	8	54-56	6.63	6.34
N-Monobenzylethylen- ediamine	155-160	5	.....	18.65	18.72
N,N,N'-Tribenzyl- ethylenediamine	225-235	4	99-100	8.48	8.64
Trioctyldiethylenetri- amine <sup>a</sup>	213-215	2	.....	9.55	9.28

<sup>a</sup> Anal. Calcd. for C<sub>24</sub>H<sub>61</sub>N<sub>3</sub>: C, 76.5; H, 14.0. Found: C, 76.4; H, 14.0.

method of preparation, which involved the reaction of ethylene dichloride with an excess of primary amine, has been described by others.<sup>1,2,3,4,5</sup> The main products were characterized as the picrates and as the phenylureas, which are listed in Table II. Attempts to prepare the phenylurea from tribenzylethylenediamine were unsuccessful, and it was found that picrates could not be formed readily from dioctylpiperazine, tetraoctylethylenediamine, didodecylpiperazine and tribenzylethylenediamine. The picrate obtained with dibenzylethylenediamine was shown by analysis to be the monopicrate. Repeated recrystallization from various solvents did not change the melting point or the analysis.

For this method of preparation, it was found that the separation of the insoluble crystalline monohydrate obtained by treating the reaction product with a dilute aqueous solution of strong base provided the most convenient method of

(1) Sebrell and Clifford, U. S. Patent 1,948,317 (Feb. 20, 1934).  
(2) Kyrides, U. S. Patent 2,126,560 (Aug. 9, 1938); U. S. Patent 2,267,685 (Dec. 23, 1941).

(3) Zienty and Thielke, *THIS JOURNAL*, **67**, 1040 (1945).

(4) Zienty, *ibid.*, **68**, 1388 (1946).

(5) Clifford, U. S. Patent 2,216,620 (Aug. 9, 1938).

TABLE II

Amine	Dipicrate		Derivatives			
	M. p., °C.	Calcd. N, %	Found	M. p., °C.	Calcd. N, %	Found
N,N'-Dibutylethylenediamine	148-149.5 <sup>a,6</sup>	17.78	17.43	174-174.5	13.65	13.31
N,N'-Dioctylethylenediamine	158-159.5 <sup>b,7</sup>	15.09	14.73	129.5-130	10.72	10.30
N,N'-Didodecylethylenediamine	152-154.5 <sup>c,7</sup>	13.11	13.11	235 (subl.)	8.83	8.64
N,N'-Dicyclohexylethylenediamine	210 (dec.)	16.42	16.04	206	12.11	12.45
N,N'-Dibenzylethylenediamine	208-210 <sup>d</sup> (dec.)	14.93	14.71	182 <sup>8</sup>	11.71	11.73
N,N'-Dibutylpiperazine	155-156	17.07	16.89	.....	...	...

<sup>a</sup> King and McMillan reported 188°. <sup>b</sup> Linsker and Evans reported 108°. <sup>c</sup> Linsker and Evans reported 112°. <sup>d</sup> Monopicrate.

isolation. This was not possible in the case of dibenzylethylenediamine, which did not form a solid monohydrate under the conditions employed. The by-products listed in Table I were obtained by fractional distillation of the dialkyl ethylenediamines.

**Acknowledgment.**—The authors are indebted to F. C. Bersworth, of the Bersworth Laboratories, Framingham, Massachusetts, for financial support for this research.

(6) King and McMillan, *THIS JOURNAL*, **68**, 1776 (1946).

(7) Linsker and Evans, *ibid.*, **68**, 1432 (1946).

(8) Van Alphen, *Rec. trav. chim.*, **54**, 93 (1935).

DEPARTMENT OF CHEMISTRY  
CLARK UNIVERSITY

WORCESTER, MASSACHUSETTS RECEIVED JUNE 17, 1949

### Acetyldesoxycellulose Quaternary Salts

BY F. N. HAYES AND CHAO-HAN LIN

A cellulose acetate tosylate was prepared by the method of Malm, Tanghe and Laird.<sup>1</sup> Separate portions of it were heated with pyridine, 3-picoline and isoquinoline to give quaternary salts, resulting from displacement of tosylate ions. Similar reactions of *p*-toluenesulfonate esters with tertiary amines are well known.<sup>2,3</sup> Table I gives analytical data and the calculated values for free hydroxyls, unreacted tosylate ester groups, and quaternary salt groups per glucose unit for each of the three products.

The average over-all percentage conversion of the original hydroxyl groups to quaternary salt

TABLE I

Sample	Percentage N <sup>a</sup>	Percentage S <sup>a</sup>	Amount per g. u.			Tos. re- placed	Percentage Conv. of OH to quat. salt
			Free <sup>b</sup> OH	Tos. <sup>b</sup> ester	Quat. <sup>b</sup> salts		
I	..	6.85	0.96	0.69	..	..	..
II	1.93	5.81	1.02	.14	0.49	71	30
III	1.77	5.96	0.97	.26	.42	61	26
IV	1.72	5.74	0.96	.22	.47	68	29

<sup>a</sup> Analyses by Micro-Tech Laboratories, Skokie, Ill.

<sup>b</sup> Calculated from the analyses, assuming that the acetyl content remains unchanged.

(1) Malm, Tanghe and Laird, *THIS JOURNAL*, **70**, 2740 (1948).

(2) Cary, Vitche and Shriner, *J. Org. Chem.*, **1**, 280 (1936).

(3) King, Dodson and Subluskey, *THIS JOURNAL*, **70**, 1176 (1948).

groups may be used as an estimate of the per cent. primary free hydroxyl in the original cellulose acetate. Our value of 28% compares favorably with a reported value of 25% on a similar sample,<sup>1</sup> determined by the method of tosylation and iodination.

A sample of cellulose acetate, EK-102893,<sup>4</sup> was tosylated<sup>1</sup> and the product (I) was reprecipitated from acetone by alcohol. Pyridine, 3-picoline and isoquinoline were dried and redistilled.

A solution of 6.0 g. of cellulose acetate tosylate in 60 ml. of pyridine was heated on a steam-bath for twenty-four hours, at the end of which time, it was diluted with 40 ml. of acetone and treated with just enough water to obtain a homogeneous solution. This was slowly poured into excess acetone with good stirring. The precipitated product was filtered, washed with acetone and twice reprecipitated from hot alcohol by ether. The yield of the purified product (II) was 5.5 g.

In a similar manner, 3.0 g. of the tosyl ester gave 2.8 g. of a 3-picolinium salt (III) and 8.0 g. yielded 7.8 g. of an isoquinolinium salt (IV).

(4) Kindly supplied for this project by Eastman Kodak Company, with analysis: 1.35 acetyls per glucose unit.

DEPARTMENT OF CHEMISTRY  
ILLINOIS INSTITUTE OF TECHNOLOGY  
CHICAGO, ILLINOIS

RECEIVED JUNE 30, 1949

### Separation of Hafnium and Zirconium by a Fractional Distillational Procedure

BY D. M. GRUEN AND J. J. KATZ

In view of current interest in hafnium-zirconium separations,<sup>1</sup> we have investigated a separation method first reported by van Arkel and De Boer.<sup>2</sup> This method involves fractional distillation at atmospheric pressure of the volatile complex compounds formed by reaction of zirconium and hafnium tetrachlorides with either phosphorus pentachloride or phosphorus oxychloride. Although van Arkel and De Boer showed that distillation resulted in considerable separation of hafnium and zirconium they gave no quantitative data on the relative volatilities of the zirconium and hafnium compounds.

The present work is concerned chiefly with the phosphorus oxychloride complexes, since these have lower boiling points and greater thermal stability than the corresponding phosphorus

(1) K. Street and G. T. Seaborg, *THIS JOURNAL*, **70**, 4268 (1948).

(2) A. E. van Arkel and J. H. De Boer, *Z. anorg. Chem.*, **141**, 289-296 (1924).

pentachloride compounds. van Arkel and De Boer assigned the formula  $2\text{ZrCl}_4\cdot\text{POCl}_3$  on the basis of zirconium and chlorine analyses. However, analyses for phosphorus, a more sensitive criterion of composition, indicate a more probable formula  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  (phosphorus: Calcd. 6.17%; found, 6.27, 6.12, 6.10%).

The vapor pressures of pure  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  and  $3\text{HfCl}_4\cdot 2\text{POCl}_3$  have been determined in the range 0.1–1.0 atmosphere and are represented graphically in Fig. 1. The boiling points are 360 and 355° for the zirconium and hafnium compounds, respectively; the 5° difference in boiling points (which we feel is accurate to  $\pm 1^\circ$ ) leads to a calculated value of  $\alpha_0 = 1.14$  for the ratio of the vapor pressures at the boiling points. The heat of vaporization for both complexes is  $20.5 \pm 0.5$  kcal.

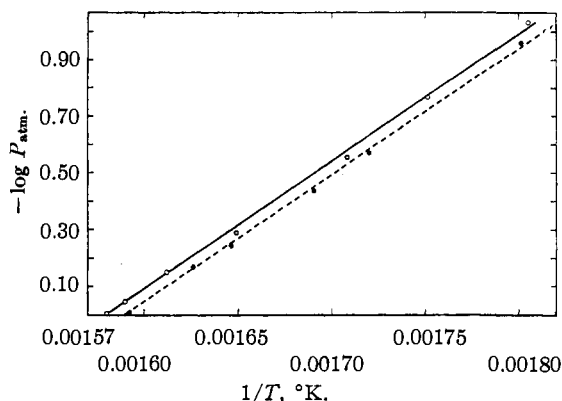


Fig. 1.—Vapor pressure of  $\text{HfCl}_4\text{-POCl}_3$  and  $\text{ZrCl}_4\text{-POCl}_3$  complexes: —, Zr complex; - - -, Hf complex.

A glass perforated plate column<sup>3</sup> with 50 physical plates was used in the distillation. In a typical experiment  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  containing 2.5% hafnium (on the weight of zirconium) yielded a first fraction (5%) containing 16% hafnium. The residue, after distilling 40% away, contained  $<0.2\%$  hafnium.

Calculation shows the column can also be operated to yield essentially pure hafnium. This aspect, as well as further studies of the chemical and physical properties of these interesting compounds, is presently being investigated.

(3) C. F. Oldershaw, *Ind. Eng. Chem., Anal. Ed.*, **13**, 265 (1941).

CHEMISTRY DIVISION  
ARGONNE NATIONAL LABORATORY  
CHICAGO, ILLINOIS

RECEIVED MAY 19, 1949

### Sodium Testosterone Sulfate

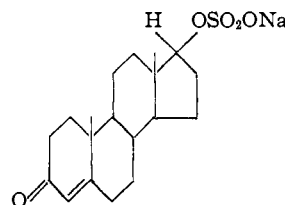
BY G. W. HOLDEN, I. LEVI AND R. BROMLEY

Sodium testosterone sulfate has been prepared with the object of comparing its androgenic activity with that of testosterone and other of its

derivatives. The results of the biological tests will be reported later.

With the exception of the use of charcoal in the purification procedure, the method followed was that described by Butenandt and Hofstetter<sup>1</sup> for the preparation of sodium estrone sulfate.

In alcohol, sodium testosterone sulfate exhibits an absorption maximum at 241  $m\mu$ , characteristic of testosterone. In water the maximum is shifted to 248–249  $m\mu$ .



A solution of chlorosulfonic acid, prepared by dissolving chlorosulfonic acid (1 ml.) in dry chloroform (30 ml.), cooling to 0° and adding pyridine (15 ml.), was added to a solution of testosterone (1.5 g.) in dry pyridine (20 ml.) and dry chloroform (50 ml.). After forty-eight hours at room temperature the solvent was removed *in vacuo* with a water-bath temperature of 40–50°. The solid residue was dissolved in methanol and the acidic solution almost neutralized (litmus) by the addition of methanolic sodium hydroxide. Aqueous sodium bicarbonate was then added to make the solution alkaline and the methanol removed *in vacuo* in the presence of water. The final volume of about 50 ml. was quite clear. This solution was shaken occasionally with Nuchar C (3 g.) at room temperature during one day. The Nuchar was filtered, washed several times with water (negative test for chloride) and eluted by suspending in methanol while still moist. Sodium testosterone sulfate (714.8 mg., 35%) was obtained by concentrating the methanol to small volume, clarifying by filtration using a little Nuchar to remove some yellow color, and precipitating with several volumes of ether. The product, thus obtained, is almost colorless. The m. p. (Fisher-Johns) is quite sharp at 215° with a green color changing to a clear brown at practically the same temperature;  $[\alpha]_D^{25} +74.5^\circ$  (1% in water),  $+68^\circ$  (1% in ethanol);  $\epsilon_{(248-249)} 20,300$  (in water);  $\epsilon_{(240.5-241)} 17,700$  (in ethanol). *Anal.* Calcd. for  $\text{C}_{19}\text{H}_{27}\text{O}_6\text{SNa}$ : C, 58.43; H, 6.97; Na, 5.88. Found: C, 58.54; H, 6.38; Na, 6.03. The semicarbazone precipitated at once on addition of semicarbazide hydrochloride to an aqueous solution of sodium testosterone sulfate. It does not melt up to 300° but starts to darken at 240° becoming slate-gray and finally chocolate-brown. For the determination of testosterone, 53.4 mg. of sodium testosterone sulfate was added to the barium chloride sodium acetate solution described by Talbot<sup>2</sup> for the hydrolysis of sodium dehydroisoandrosterone sulfate. After four hours heating on the steam-bath the solution was extracted with ether. Only 6.5% of the theoretical weight of residue was obtained. Fifty milligrams of sodium testosterone sulfate was then hydrolyzed by refluxing one hour with a mixture of 100 ml. of water and 15 ml. of concd. hydrochloric acid in the presence of 75 ml. of toluene. The toluene was separated, the aqueous solution further extracted with ether and the combined extracts distilled after washing with sodium bicarbonate and water. The yellowish gummy residue weighed 26.8 mg. (68%). It was crystallized by means of aqueous acetone to yield 9.3 mg. (25.3%) of testosterone m. p. 153.5° and mixed m. p. with pure testosterone undepressed.

RESEARCH LABORATORIES  
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RECEIVED JULY 11, 1949

(1) Butenandt and Hofstetter, *Z. physiol. Chem.*, **239**, 222 (1939).  
(2) Talbot, Ryan and Wolfe, *J. Biol. Chem.*, **148**, 598 (1945).

## Mechanism of the Polymerization of Propylene with Aluminum Bromide-Hydrogen Bromide Catalyst<sup>1</sup>

BY FRANK R. MAYO AND CHEVES WALLING

The recent excellent experimental work of Fontana and Kidder<sup>2</sup> on the kinetics of the polymerization of propylene by aluminum bromide-hydrogen bromide at about  $-80^{\circ}$  showed that, after the steady rate is obtained, the rate of polymerization is consistent with the equation

$$\frac{-d[m]}{dt} = \frac{kKc[m]}{1 + K[m]}$$

where  $[m]$  is the monomer concentration,  $c$  is the total concentration of catalyst in all forms,  $K$  is the equilibrium constant for the reversible formation of a postulated complex formed from a catalyst-monomer complex plus additional monomer, and  $k$  is the rate constant for chain lengthening, considered to be rearrangement of the catalyst-polymer-monomer complex into a stable form.

The object of this communication is to present an alternative interpretation of their data. Our scheme assumes (1) that essentially all of the catalyst (or promoter) is bound to the polymer as an un-ionized complex such as

$\text{H}(-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}})_n-\text{Br}\cdot\text{AlBr}_3$ , (2) that the first rate determining step in the propagation reaction is the dissociation of this complex into  $\text{H}(-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}})_n^+$  and

$\text{AlBr}_3^-$ , (3) that actual chain propagation involves addition of the carbonium ion and anion to the propylene before recombination of the original ions occurs. Since, in a solvent of low dielectric constant, the dissociated complex will exist as an *ion pair* surrounded by a cage of solvent and propylene molecules, recombination will be kinetically first order, and the situation parallels that suggested by Matheson<sup>3</sup> for peroxide-initiated polymerizations. Thus, the fraction of the dissociations in which the carbonium ion will add a propylene unit before recombining with the negative ion will be  $K'[m]/(1 + K'[m])$  where  $K'$  is the ratio of the rate constant for the reaction of the ion pair with propylene divided by the rate constant for recombination of the ion pair. The over-all rate of polymerization is then

$$\frac{-d[m]}{dt} = \frac{k'K'c[m]}{1 + k'[m]}$$

where  $k'$  is the rate of dissociation of the catalyst-polymer complex,  $c$ .

The form of the equation shows that an appreciable fraction of the dissociations are accompanied by growth, and also that only one growth step occurs at a time. These requirements are easily met if both ions simultaneously add to the

propylene. Experiments with scale models indicate the probability of this course; they also show that the two mechanisms here considered differ only in details. When this interpretation is applied to isobutylene<sup>4</sup>, styrene<sup>5</sup> and vinyl ethers<sup>6</sup> the integral orders of these polymerizations with respect to monomer suggest that the fraction of ionizations resulting in chain growth is lower, a result to be expected if the respective complexes ionize more readily but give less reactive carbonium ions.

Our proposed interpretation provides a mechanism for carbonium ion polymerizations in solvents of low dielectric constant similar to that proposed for the polymerization of alkenes by sulfuric acid, the solvolyses of alkyl halides, and the Friedel-Crafts reaction. Further, it accounts more readily than the mechanism of Fontana and Kidder for observations<sup>5,6</sup> that the rates of carbonium ion polymerizations increase very rapidly with the dielectric constant of the solvent. However, our interpretation is inconsistent with one conclusion of Fontana and Kidder, that  $\Delta H$  for reversible addition of monomer to complex is 8.9 kcal./mole and that  $K$  decreases with increasing temperature. In our scheme, this corresponds to the anomaly that the activation energy for simple recombination of two ions is 8.9 kcal./mole *larger* than for addition of propylene to a carbonium ion. Since, in the experiments cited, an appreciable but unknown proportion of catalyst precipitated in an inactive form from each reaction mixture, we suggest that experiments at different temperatures have not yielded correct temperature coefficients, a point which is a critical test of our proposal.

(4) Evans and Meadows, *J. Polymer Sci.*, **4**, 359 (1949).

(5) Pepper, *Trans. Faraday Soc.*, **45**, 397, 404 (1949).

(6) Eley and Richards, *ibid.*, 425.

UNITED STATES RUBBER CO.  
PASSAIC, N. J.

RECEIVED AUGUST 25, 1949

## Investigation of Possible Interactions between Thallium(I) and Thallium(III) in Solution and in the Crystalline Thallium Sesqui-halides

BY HARDEN MCCONNELL AND NORMAN DAVIDSON

The discovery<sup>1</sup> that the rate of radioactive exchange between Tl(I) and Tl(III) in aqueous solutions is slow has prompted us to: (1) examine, by a radiochemical method, whether or not the substances  $\text{Tl}_2\text{Cl}_3$  and  $\text{Tl}_2\text{Br}_3$  contain non-equivalent Tl(I) and Tl(III) ions; (2) look for non-additive light absorption<sup>2</sup> in some aqueous solutions containing Tl(I) and Tl(III). Problems (1) and (2) are related because the  $\text{Tl}_2\text{X}_3$  compounds are more colored than the corresponding  $\text{TlX}$  or  $\text{TlX}_3$  compounds.<sup>3</sup>

(1) Harbottle and Dodson, *THIS JOURNAL*, **70**, 880 (1948); Prestwood and Wahl, *ibid.*, **71**, 3137 (1949); see also pp. 226, 205 of "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory, Patchogue, New York, Dec., 1948.

(2) Whitney and Davidson, *THIS JOURNAL*, **69**, 2076 (1947).

(3) Benrath, *Z. anorg. Chem.*, **93**, 161 (1915); **136**, 358 (1924).

(1) Contribution No. 95 from the General Laboratories of the United States Rubber Company.

(2) Fontana and Kidder, *THIS JOURNAL*, **70**, 3745 (1948).

(3) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(1) For the exchange experiment with  $Tl_2Cl_3$ , 4 ml. of dilute HCl solution containing 5.2 mg. of dissolved  $Tl_2Cl_3$  and 1.46 mg. of active  $TlCl_3$  (containing  $Tl^{204}$ ) were evaporated nearly but not quite to dryness by evacuation at room temperature for forty-five minutes. It follows from the data of Benrath that under these conditions essentially all of the  $Tl(I)$  was initially precipitated as  $Tl_2Cl_3$ , and there might be small amounts of  $TlCl_2$  or hydrated  $TlCl_3$  formed subsequently, depending on the completeness of evaporation.<sup>3</sup> (Furthermore by visual inspection of the precipitate one saw only the characteristic hexagonal yellow flakes of  $Tl_2Cl_3$ .)<sup>4</sup> This entire residue, the yellow solid  $Tl_2Cl_3$  and the adhering excess of  $TlCl_2$  or  $TlCl_3$  (solid or solution), was redissolved in water and divided into two 2-ml. samples. Thallous chromate was precipitated from one portion, using the conditions developed by Harbottle and Dodson,<sup>1</sup> washed, and slurried onto a counting plate. The second sample was reduced with sulfur dioxide so that all the thallium could be precipitated as the chromate and the total activity counted. There was no appreciable self absorption in the samples.

A blank experiment was performed which was identical to the above except that the evaporation to give solid  $Tl_2Cl_3$  was omitted, and the sample was allowed to stand for twenty minutes.

For the  $Tl_2Br_3$  experiment, 30 ml. of a solution containing 1.2 g. of  $TlBr_3$  was saturated with inactive  $TlBr$  at room temperature to insure the absence of bromine. The solution was then saturated with active  $TlBr$  at 50°. Two 10-ml. aliquots of this solution were allowed to cool to room temperature, and the red  $Tl_2Br_3$  precipitated out.<sup>5</sup> The thallous activity was determined with one sample and the total activity with the other. For control measurements, the thallous and total activities of 1-ml. aliquots of the solution at 50° were determined.

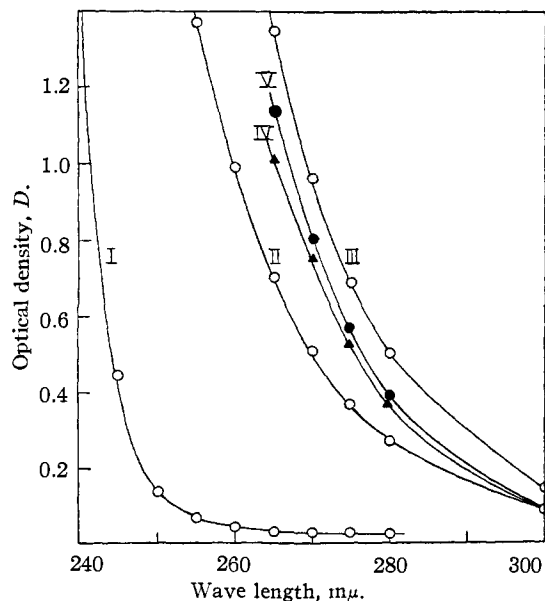


Fig. 1.—The absorption spectra of some thallium(I) and (III) solutions in perchloric acid: I,  $Tl(I)$  0.068  $F$ ; II,  $Tl(I)$  0.034  $F$ ,  $Tl(III)$  0.079  $F$ ; III,  $Tl(III)$  0.157  $F$ , I, II, III in 3.2  $F$   $HClO_4$ ; IV,  $Tl(III)$  0.079  $F$ ; V,  $Tl(I)$  0.113  $F$ ,  $Tl(III)$  0.079  $F$ ; IV, V in 1.6  $F$   $HClO_4$ .

(4) Another sample of  $Tl_2Cl_3$  was further identified by a thallium analysis; for a description of the crystalline form, cf. Meyer. *Z. anorg. Chem.*, **24**, 354 (1900).

(5) The identification of this substance as  $Tl_2Br_3$  is based on its color and crystalline form corresponding to the descriptions given by Benrath<sup>3</sup> and Meyer<sup>4</sup> and on the solubility data determined by Benrath.

TABLE I

## EXCHANGE EXPERIMENTS WITH THALLIUM SESQUI-HALIDES

Experiment	Composition of exchange mixture, mg.		Specific activities, <sup>a</sup> c./min. mg.		Ratio of specific activities of $Tl(III)$ and $Tl(I)$
	$Tl(I)$	$Tl(III)$	$Tl(I)$	$Tl(III)$	
Solid $Tl_2Cl_3$	3.12	2.00 <sup>b</sup>	31.5	321	10 ( $\pm$ 1)
$Tl_2Cl_3$ control	3.12	2.00 <sup>b</sup>	18.6	241	13 ( $\pm$ 1)
Solid $Tl_2Br_3$	32.4 <sup>c</sup>	10.8 <sup>c</sup>	102	27.8	0.27 $\approx$ (0.05)
$Tl_2Br_3$ control	6.1	18.4	87.7	20.2	0.23 $\approx$ (0.05)

<sup>a</sup> For the  $Tl_2Cl_3$  experiment, the specific activities were calculated on the basis of the amounts of  $Tl(I)$  and  $Tl(III)$  added; for the  $Tl_2Br_3$  experiment, see footnote (c). <sup>b</sup> Including 0.96 mg. of active  $Tl(III)$ . <sup>c</sup> These numbers, estimated from the solubility data of Benrath, are included to indicate the probable size of the  $Tl_2Br_3$  precipitate; only the ratio of activities is important for the interpretation of the experiment.

The experimental results (Table I) are that within the uncertainties of the experiments there is no exchange in the solid state. These uncertainties are due to experimental errors and due to the possibilities of differences between the control experiments and the experiments in which solid  $Tl_2X_3$  compounds were separated as to: (a) degree of homogeneous exchange in solution, (b) degree of induced exchange on precipitation of thallous chromate. For the  $Tl_2Cl_3$  experiment, the calculated ratio of specific activities of  $Tl(III)$  and  $Tl(I)$  for complete equivalence in the solid is 2.1 accepting the validity of the control experiment (and assuming no exchange between the solid  $Tl_2Cl_3$  and the excess adhering  $Tl(III)$ ). For the  $Tl_2Br_3$  experiment this ratio is 1.0. Because of the evidence that  $Tl_2Cl_3$  has 64 thallium atoms per unit cell,<sup>6</sup> it is worthwhile to emphasize that our data are not sufficiently accurate to exclude the possibility that a small fraction of the  $Tl(I)$  and  $Tl(III)$  atoms occupy equivalent positions in the  $Tl_2X_3$  lattice.

(2) Figure 1 exhibits the absorption spectra of some thallium (I) perchlorate, thallium (III) perchlorate, and mixed solutions in 3.2 and 1.6  $F$  perchloric acid. Thallium (III) is more colored than  $Tl(I)$  and there is no appreciable non-additive absorption in the mixed solutions. The extinction coefficients of  $Tl(III)$  calculated from these data (Table II) show that  $Tl(III)$  is more colored at lower acidities, suggesting an increased hydrolysis of  $Tl^{+++}$  to  $Tl(OH)^+$  or  $Tl(OH)_2^{++}$ . Har-

TABLE II

EXTINCTION COEFFICIENTS OF  $Tl(III)$  AS A FUNCTION OF ACIDITY

$\lambda$ (m $\mu$ )	290	280	270	265
$\epsilon$ ( $Tl(III)$ )(1.6 $F$ $HClO_4$ )	2.25	4.6	9.5	13.3
$\epsilon$ ( $Tl(III)$ )(3.2 $F$ $HClO_4$ )	1.8	3.25	6.1	8.5

bottle and Dodson<sup>1</sup> and Prestwood and Wahl<sup>1</sup> have previously suggested such a hydrolysis to explain the variation of the rate of exchange between  $Tl(I)$  and  $Tl(III)$  with acidity.

Most of the known cases of interaction absorption in solution are in media containing excess

(6) Jerslev and Hagg, *Experientia*, **2**, 495 (1946).

chloride ions. The insolubility of thallos chloride in water and dilute solutions of thallic chloride, and the presence of free chlorine in concentrated thallic chloride solutions (3.5 *F*) in which thallos chloride has an appreciable solubility<sup>8</sup> prevented an exact spectrophotometric study of solutions having significant concentrations of thallos and thallic chlorides. We can report however that as successive portions of solid thallos chloride were added to a 3.4 *F* thallic chloride solution containing some (*ca.* 0.03 *F*) free chlorine, the optical density of the resulting solutions decreased (as the chlorine was removed) and became constant at the values:  $\lambda = 380 \text{ m}\mu$ ,  $D = 0.065$ ;  $\mu = 360 \text{ m}\mu$ ,  $D = 0.66$ , for a solution that contained 0.04 *F* excess Tl(I). Since the optical densities of the solutions never increased as the TlCl was added, there was probably no significant interaction absorption in the solution.

This work has been supported by the Office of Naval Research. We are grateful to Dr. German Harbottle for communicating to us his excellent method of separating thallos and thallic ions.

CONTRIBUTION NO. 1307 FROM THE  
GATES AND CRELLIN LABORATORIES OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA 4, CALIFORNIA RECEIVED JUNE 8, 1949

### The Lactal Ring Structures of Some Synthetic Pyrimidine Nucleosides<sup>1</sup>

BY MARJORIE ZEIGER NEWMARK, IRVING GOODMAN AND  
KARL DITTMER<sup>2</sup>

The ribosyl, arabinosyl, glucosyl and galactosyl nucleosides of uracil and thymine and the corresponding 5-bromo-uracil derivatives were prepared in our laboratories<sup>3,4</sup> and tested for biological activity<sup>5</sup> on two strains of *Escherichia coli*, two strains of *Neurospora crassa*, a strain of *Lactobacillus casei*, and one of *Streptococcus faecalis* R.

A uracil-requiring mutant of *E. coli* was unaffected by any of the synthetic nucleosides although uracil or natural uridine produced good growth. A uracil-less mutant of *N. crassa* which was shown by Loring to grow well on uracil, uridine or uridylic acid was also unaffected by the synthetic products. Results of studies of *L. casei* and *S. faecalis* R showed a similar lack of biological activity. These studies emphasized the need for complete elucidation of the detailed structure of these synthetic nucleosides.

In order to establish the nature of a possible relationship between structure and activity, a number of naturally occurring and synthetic nucleosides were analyzed by the periodate method as adapted by Davoll, Lythgoe and Todd<sup>6</sup> to determine the ring structures of the sugar component of the nucleosides. In this method glycofuranosyl nucleosides of the pentoses require one mole of periodate per mole of nucleoside for oxidation, whereas glycopyranosides of this type require two moles of periodate. Aldohexoses in the pyranoside form require two moles of periodate for oxidation and liberate one mole of formic acid during the course of the reaction; aldohexoses in the furanoside form also require two moles of periodate for oxidation but liberate no formic acid.

Table I summarizes the results of the periodate oxidation of a number of synthetic pyrimidine nucleosides as well as the naturally occurring pyrimidine nucleosides, uridine and cytidine. All of the synthetic nucleosides here reported possess the pyranoside structure. These results would indicate in part that the known biological activity of uridine and cytidine are dependent upon the furanoside structure.

TABLE I  
PERIODATE OXIDATION OF SOME PYRIMIDINE  
NUCLEOSIDES

N-Glycoside	Moles IO <sub>4</sub> <sup>-</sup> Mole glycoside	Moles HCOOH Mole glycoside
Uridine <sup>a</sup>	1.14	..
Cytidine <sup>a</sup>	1.20	..
1-D-Ribosyl uracil	2.02	.. <sup>b</sup>
1-D-Arabinosyl uracil	2.07	.. <sup>b</sup>
1-D-Xylosyl uracil	1.89	0.86
1-D-Glucosyl uracil	2.01	0.95
1-D-Galactosyl uracil	2.03	.. <sup>b</sup>
1-D-Arabinosylthymine	2.03	.. <sup>b</sup>
1-L-Arabinosylthymine	1.92	.. <sup>b</sup>
1-D-Galactosylthymine	2.04	0.99
1-D-Glucosylcytosine	1.98	0.88

<sup>a</sup> We are indebted to Dr. H. S. Loring of Stanford University for the samples of uridine and cytidine. <sup>b</sup> The theoretical amount of formic acid expected is 1 mole, but due to limited amounts of material the determinations were not made.

(6) J. Davoll, B. Lythgoe and A. R. Todd, *J. Chem. Soc.*, 833 (1946).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF COLORADO  
BOULDER, COLO.

RECEIVED JUNE 16, 1949

### A Complex Praseodymium Fluoride Readily Soluble in Dilute Acids<sup>1</sup>

BY THEODORE P. PERROS AND CHARLES R. NAESER

The insolubility of praseodymium trifluoride in dilute mineral acids is well known. In the course of investigations concerning this compound a complex potassium-praseodymium-fluoride compound, possibly new, which was easily soluble in dilute acids was prepared.

(1) From the thesis for the M.S. degree of T. Perros, The George Washington University.

(1) This work was supported in part by a research grant-in-aid from the National Institutes of Health.

(2) Present address: Dept. of Chemistry, Florida State University, Tallahassee, Florida.

(3) D. Visser, K. Dittmer and I. Goodman, *J. Biol. Chem.*, **171**, 377 (1947).

(4) D. Visser, I. Goodman and K. Dittmer, *THIS JOURNAL*, **70**, 1926 (1948).

(5) K. Dittmer, I. Goodman, D. Visser and H. P. McNulty, *Proc. Soc. Exp. Biol. Med.*, **69**, 40 (1948).

### Experimental

About 10 g. of technical grade potassium hydrogen fluoride was placed in a platinum crucible and heated over a burner until molten. Approximately 0.5 g. of praseodymium trifluoride was placed in the melt and stirred with a platinum rod. Within five minutes the praseodymium fluoride had dissolved completely, giving a pale yellow-green color to the melt. After the melt had cooled and solidified to a hard, brittle mass, it was placed in a beaker and water (containing a few drops of ammonium hydroxide solution) was added to dissolve the excess potassium fluoride and potassium hydrogen fluoride. After several leachings with water, a pale green residue mixed with dark particles of impurities from the potassium hydrogen fluoride remained. The washings, even after concentration, gave no evidence for the presence of praseodymium ions. However, light reflected from the green residue gave the characteristic absorption spectrum of praseodymium ions.

This green residue, but not the black particles, was readily soluble in 3 *N* hydrochloric acid when slightly warmed. This behavior is quite different from that of praseodymium trifluoride.

Purification of potassium hydrogen fluoride by crystallization eliminated the dark impurities. The purified material with praseodymium trifluoride gave a residue completely soluble in the 3 *N* hydrochloric acid. This marked difference in solubility of the two praseodymium-fluoride compounds indicates the formation of a complex ion containing both praseodymium and fluorine.

When  $\text{Pr}_2\text{O}_3$  was added to fused potassium hydrogen fluoride a vigorous reaction took place, and the final green residue showed the same characteristics as that obtained by treatment of the praseodymium trifluoride with potassium hydrogen fluoride.

Investigations to determine whether the composition of this substance is similar to the  $\text{KLaF}_4$  described by W. H. Zachariasen<sup>2</sup> and also to determine the properties of this substance are being continued.

(2) Zachariasen, *THIS JOURNAL*, **70**, 2147 (1948).

DEPARTMENT OF CHEMISTRY  
THE GEORGE WASHINGTON UNIVERSITY  
WASHINGTON, D. C. RECEIVED JULY 11, 1949

### Acid Catalyzed Reaction of Diarylformamidines with Ethyl Orthoformate

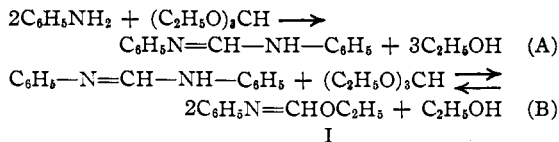
BY ROYSTON M. ROBERTS

Ethyl *N*-phenylformimidate (I) was first prepared by Comstock and Clapp<sup>1</sup> from ethyl iodide and the silver salt of formanilide; the yield was low, and although it has been improved by Smith and Nichols<sup>2</sup> the procedure is expensive and tedious. Claisen<sup>3</sup> prepared this compound from aniline and ethyl orthoformate. He reported that the preparation was accomplished only after numerous unsuccessful attempts and that his directions must be followed exactly; even so, the yield he obtained was only 44% from a reaction mixture heated nine hours. Our attempt to repeat this work resulted in a yield of 11%. Claisen postulated a two-step mechanism for the reaction: first, the formation of *N,N'*-diphenylformamidine (rapid), and second, reaction of this compound with a second mole of ethyl orthoformate (much slower).

(1) Comstock and Clapp, *Am. Chem. J.*, **13**, 527 (1891).

(2) Smith and Nichols, *J. Org. Chem.*, **6**, 489 (1941)

(3) Claisen, *Ann.*, **287**, 363 (1895).



There is no doubt regarding the ease with which the first step (A) takes place, but we have found that the second step (B), is practically completely dependent on acid catalysis. This undoubtedly explains the many unsuccessful experiments mentioned by Claisen and also our first attempt in which we took some care to avoid traces of acid. When we heated pure *N,N'*-diphenylformamidine with ethyl orthoformate containing a little anhydrous potassium carbonate for twenty-four hours, we found practically no alcohol was produced and the *N,N'*-diphenylformamidine was recovered unchanged. Prompted by the observation of acid catalysis in the reaction of ethyl *N*-phenylformimidate with amines (to be published separately) we added a small amount of aniline hydrochloride to the ethyl orthoformate and *N,N'*-diphenylformamidine and found that the calculated amount of ethanol was evolved rapidly and a 96% yield of ethyl *N*-phenylformimidate was produced. Other acids are also effective in catalyzing the reaction; sulfuric and *p*-toluenesulfonic acids gave comparable results and even acetic acid was fairly effective. Ethyl *N-p*-tolylformimidate<sup>4</sup> was produced from *p*-toluidine or *N,N'*-di-*p*-tolylformamidines under similar conditions. The formamidines need not be isolated when the aromatic amine is the starting material. In fact, the acid catalyzed reaction of orthoformate with aromatic amine may not proceed by intermediate formamidine formation but may be more direct. The mechanism of this reaction will be discussed more completely in a subsequent paper. It is interesting to note that reaction (B) is apparently reversible and has previously been described as it occurs in the opposite direction from that reported here! Knott<sup>5</sup> treated ethyl *N*-phenylformimidate in alcoholic solution with carboxylic and sulfonic acids; he obtained *N,N'*-diphenylformamidine salts and was able to identify ethyl orthoformate as the other product in one case.

Recently Hamer, Rathbone and Winton have reported modifying Claisen's procedure obtaining yields of 81–85% by "including aniline hydrochloride to inhibit the formation of carbylamine."<sup>6</sup> Their reason for choosing aniline hydrochloride for this function is not given and there is no mention of acid catalysis.

It is perhaps pertinent to recall attention to the fact that in 1941 Smith and Nichols<sup>2</sup> showed that the reaction of Grignard reagents with ethyl *N*-phenylformimidate was the most satisfactory general method for the synthesis of aromatic

(4) Wheeler and Johnson, *Ber.*, **32**, 35 (1899).

(5) Knott, *J. Chem. Soc.*, 686 (1945).

(6) Hamer, Rathbone and Winton, *J. Chem. Soc.*, 954 (1947).



aldehydes from the corresponding halides except for the difficulty of obtaining the ethyl *N*-phenylformimidate, a reagent which is now easily available.

### Experimental

**Materials.**—Ethyl orthoformate, Eastman Kodak Co., redistilled, b. p. 142–144°; *N,N'*-diphenylformamidine (m. p. 138.5–139.5°, cor.), *N,N'*-di-*p*-tolylformamidine (m. p. 141.4–142.8°, cor.), prepared from the amines and ethyl orthoformate<sup>7</sup>; aniline hydrochloride, *p*-toluidine hydrochloride, prepared from the amines and concentrated hydrochloric acid, dried in a vacuum desiccator.

***N,N'*-Diphenylformamidine and Ethyl Orthoformate.**  
**A. Aniline Hydrochloride as Catalyst.**—In a 200-ml. flask was placed 19.6 g. (0.10 mole) of *N,N'*-diphenylformamidine, 29.6 g. (0.20 mole) of ethyl orthoformate and 1.0 g. (0.008 mole) of dry aniline hydrochloride. An efficient 40-cm. distilling column having a total reflux partial take-off type head was attached and the reaction mixture was heated. Ethanol began to reflux immediately. After one hour of reflux the ethanol was distilled; 6.7 ml. was collected in about fifteen minutes. Anhydrous potassium carbonate (2.0 g.) was added and the mixture was shaken and allowed to stand two hours. The reaction mixture was then distilled through the same column under reduced pressure. Excess ethyl orthoformate was first recovered, 12.3 g., b. p. 83–85° (93 mm.). The pressure was then lowered to 40 mm. and colorless ethyl *N*-phenylformimidate distilled constantly at 117° (40 mm.); 28.7 g. or 96% of the theoretical amount was obtained.

The difference in the conditions under which the two steps of the reaction take place is illustrated by the following experiment. A mixture of 0.40 mole of aniline and 0.60 mole of ethyl orthoformate was heated in a flask to which was attached a 40-cm. distilling column. During one and one-quarter hours 36 ml. of ethanol distilled and then the distillation practically stopped. Aniline hydrochloride (1.30 g., 0.01 mole) was added to the reaction mixture and heating was resumed; distillation of ethanol now took place again at a rapid rate and 11.5 ml. was collected in thirty minutes, then the evolution practically stopped again. Anhydrous potassium carbonate (2.60 g.) was added and the mixture was distilled under reduced pressure. The excess ethyl orthoformate (27.2 g.) was removed first, b. p. 83° (90 mm.), then the product was distilled at 10-mm. pressure; 53.2 g. (89% of the amount calculated from aniline was obtained, b. p. 87–88° (10 mm.), *n*<sub>D</sub><sup>25</sup> 1.5275 (lit., 1.52787<sup>8</sup>).

**B. Sulfuric Acid as Catalyst.**—Aniline (1 mole), ethyl orthoformate (1.5 moles) and sulfuric acid (10 drops, ca. 0.04 mole) were heated under reflux thirty minutes and then 117 ml. of ethanol was distilled through a short column. The catalyst was neutralized with 3.5 g. of dry sodium *t*-butoxide and the mixture was distilled under reduced pressure. After the excess ethyl orthoformate was recovered, 121.6 g. (82% of the theoretical amount) of ethyl *N*-phenylformimidate was obtained, b. p. 117–119° (40 mm.).

**C. Acetic Acid as Catalyst.**—*N,N'*-Diphenylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and glacial acetic acid (0.6 ml., 0.01 mole) were heated under reflux for one hour, then 4.5 g. of distillate, b. p. 76–80°, was collected during forty minutes; the distillation temperature then began to rise sharply. Ethyl orthoformate (ca. 17 g.) was recovered at 82–83° (90 mm.), and 14.6 g. (55% of the theoretical amount calculated from 0.09 mole of *N,N'*-diphenylformamidine) of ethyl *N*-phenylformimidate was obtained, b. p. 117–118° (40 mm.).

***N,N'*-Di-*p*-tolylformamidine and Ethyl Orthoformate; *p*-Toluenesulfonic Acid as Catalyst.**—*N,N'*-Di-*p*-tolylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and *p*-toluenesulfonic acid (0.001 mole) were heated in a 100-ml. flask to which was attached a 15-cm. Vigreux col-

umn with a total reflux partial take-off head. After one hour of reflux 5.8 ml. of ethanol, b. p. 75–79°, was removed. Calcium carbonate was added and the mixture was stirred overnight. Distillation of the filtered reaction mixture gave ca. 12 ml. of ethyl orthoformate, b. p. 83° (93 mm.), and 24.0 g. of ethyl *N*-*p*-tolylformimidate,<sup>4</sup> b. p. 133.5–134° (40 mm.). This was 74% of the calculated amount of product.

Treatment of *p*-toluidine or *N,N'*-di-*p*-tolylformamidine with ethyl orthoformate in the presence of *p*-toluidine hydrochloride or sulfuric acid as described above gave similar results—yields of 74–76% of ethyl *N*-*p*-tolylformimidate.

**Acknowledgment.**—The author gratefully acknowledges the assistance of Mr. Robert H. DeWolfe, who carried out some of the experiments, and a grant from the University of Texas Research Institute which made this assistance possible.

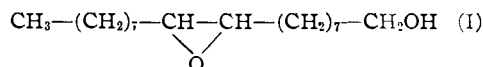
DEPARTMENT OF CHEMISTRY  
 UNIVERSITY OF TEXAS  
 AUSTIN, TEXAS

RECEIVED JUNE 18, 1949

## Chemistry of Epoxy Compounds. X,<sup>1</sup> Polymerization of the Isomeric 9,10-Epoxyoctadecanols

BY DANIEL SWERN AND GERALDINE N. BILLEN

The thermal polymerization of the isomeric 9,10-epoxystearic acids was recently reported.<sup>2</sup> The present note reports the results of the thermal polymerization of the isomeric 9,10-epoxyoctadecanols (I), m. p. 54 and 48°, respectively, in



the presence of naphthalene-2-sulfonic acid as catalyst.

**Starting Materials.**—The isomeric 9,10-epoxyoctadecanols, m. p. 54 and 48°, were prepared from oleyl<sup>3</sup> and elaidyl<sup>4</sup> alcohols, respectively, by epoxidation with peracetic<sup>5</sup> or perbenzoic acid.<sup>6</sup> Calcd. for C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>, oxirane oxygen,<sup>7</sup> 5.62%; found, 5.62%.

**Polymerization Procedures.**—9,10-Epoxyoctadecanol (either isomer) and the required quantity of naphthalene-2-sulfonic acid were mixed and then ground until the catalyst was uniformly distributed. Approximately 5-g. portions of the mixture were then weighed into a series of test-tubes which had been flushed with nitrogen or carbon dioxide. After being filled, the tubes were again flushed with inert gas, stoppered tightly, and then immersed in a constant-temperature oil-bath which maintained the desired temperature to ±0.2°. Fifteen minutes was allowed for the establishment of temperature equilibrium before the polymerization time was counted. During the equilibration period, the tubes were shaken occasionally to ensure homogeneity. At selected time intervals, a tube was removed from the oil-bath, cooled rapidly to room temperature, and then analyzed within twenty-four hours.

(1) For the previous paper in this series, see THIS JOURNAL, **71**, 2219 (1949).

(2) Swern, Billen and Eddy, THIS JOURNAL, **70**, 1228 (1948).

(3) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

(4) Swern, Jordan and Knight, THIS JOURNAL, **68**, 1673 (1946).

(5) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(6) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

(7) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947); Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).

(7) Roberts, *J. Org. Chem.*, **14**, 277 (1949).

(8) Schmidt, *Z. physik. Chem.*, **58**, 523 (1907).

**Analytical Procedures.**—Analyses were carried out as previously reported.<sup>2</sup> Carbonyl oxygen was determined by the procedure reported by Knight and Swern.<sup>3</sup>

### Discussion

Figure 1 shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (ol), m. p. 54°, at 60, 80, 90 and 100°. Figure 2

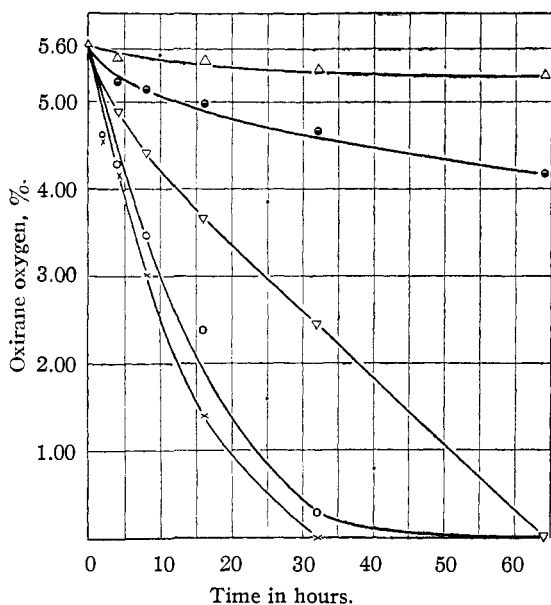


Fig. 1.—Thermal polymerization of 9,10-epoxyoctadecanol(ol), m. p. 54°, with naphthalene-2-sulfonic acid as catalyst: ○, 90°, 2% catalyst; Δ, 60°, 0.75% catalyst; ×, 100°, 2% catalyst; ●, 80°, 0.75% catalyst; ▽, 100°, 0.75% catalyst.

shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (el), m. p. 48°, at 80, 90, 100, 120 and 140°. These data may be briefly summarized as follows: (a) under identical conditions, the high-melting epoxyoctadecanol (ol) polymerizes at a more rapid rate than does the low-melting isomer (el); (b) both isomers can be converted to viscous liquids if the polymerization is permitted to proceed far enough; (c) when the oxirane oxygen value is substantially zero, the molecular weight is about 900, or approximately that of a trimer; (d) in all the polymerizations except the one at 60°, about 20 to 30% of the reduction in oxirane oxygen can be accounted for by isomerization to the carbonyl group; (e)

in two cases in which the comparison has been made, molecular weights determined ebullioscopically in benzene differ from those calculated from the oxirane oxygen analyses by only 7 to 15%; (f) the isomerization of the oxirane group to the carbonyl group is a function of both the temperature and the percentage of catalyst, although there appears to be no simple relationship involved; and (g) the refractive index of the polymers levels off at 1.462 to 1.464 (60°).

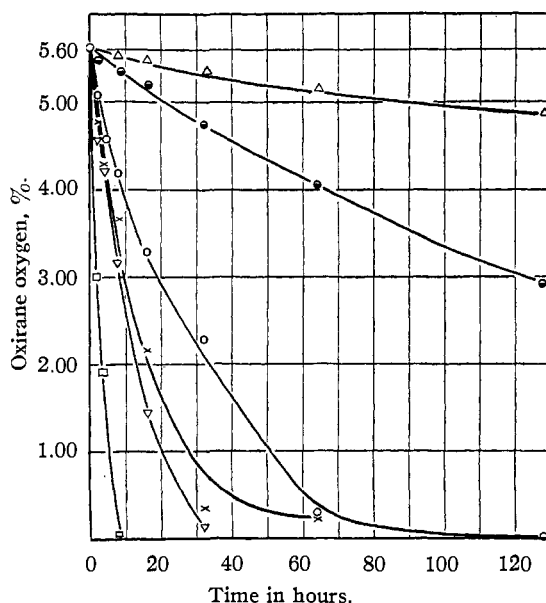
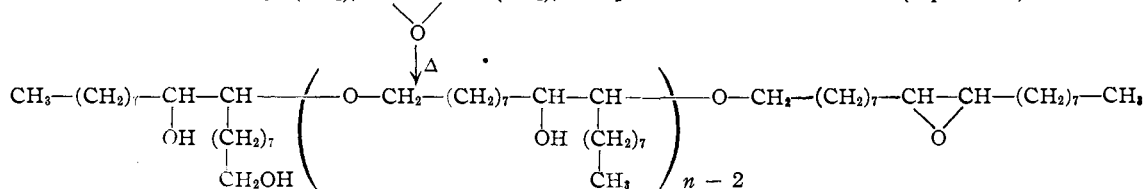


Fig. 2.—Thermal polymerization of 9,10-epoxyoctadecanol(el), m. p. 48°, with naphthalene-2-sulfonic acid as catalyst: ○, 90°, 2% catalyst; Δ, 80°, 0.75% catalyst; ▽, 120°, 0.75% catalyst; ×, 100°, 2% catalyst; ●, 100°, 0.75% catalyst; □, 140°, 0.75% catalyst.

On the basis of the data reported here and the known reactions of oxirane groups, it can be concluded that the main reactions which occur during the thermal polymerization of the 9,10-epoxyoctadecanols are (a) a condensation reaction between the oxirane and primary hydroxyl groups, yielding a polyether, as shown in Equation 1, and (b) isomerization of the oxirane group to the carbonyl group. All the polymers are readily soluble in the common organic solvents, with the exception of petroleum naphtha, thus indicating that cross-linking reactions occur only to a limited extent, if at all.



(8) Knight and Swern, *J. Am. Oil Chem. Soc.*, **26**, 366 (1949).

No information is available on the occurrence

of other possible acid-catalyzed condensation and addition reactions, such as dioxane or polyethylene oxide formation.<sup>2</sup>

EASTERN REGIONAL RESEARCH LABORATORY<sup>3</sup>  
PHILADELPHIA 18, PENNSYLVANIA RECEIVED JUNE 8, 1949

(9) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Note not copyrighted.

## NEW COMPOUNDS

### 2-Methyl-4,6-Dichlorophenoxyacetic Acid

**2-Methyl-4,6-dichlorophenoxyacetic Acid.**—4,6-Dichloro-*o*-cresol<sup>1</sup> (3.82 g.) dissolved in 10 ml. of aq. 20% sodium hydroxide was added hot in 1-ml. portions to a hot solution of 4.75 g. of chloroacetic acid in 10 ml. of 20% sodium hydroxide, and the mixture refluxed for four hours. The solution was then made acid and the precipitate removed by filtration. It was dissolved in dilute sodium carbonate and the excess phenol extracted with ether. The product was precipitated from the carbonate solution with acid and crystallized from alcohol-water; yield 3.3 g., m. p. 187–187.5°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 45.95; H, 3.40. Found: C, 45.87; H, 3.54.

This compound was checked for plant growth activity using the Avena test. The work was done by Dr. Robert Muir, Dept. of Botany, University of Iowa. The compound was found to be inactive. Complete results of these tests will be published elsewhere.

(1) Claus and Riemann, *Ber.*, **16**, 1598 (1883).

DEPARTMENT OF CHEMISTRY  
POMONA COLLEGE  
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CORWIN HANSCH  
DONALD G. CROSBY

RECEIVED JUNE 25, 1949

### Some Derivatives of Benzylvanillin and Benzylvanillic Acid

The benzyl ethers of the monochloro and monobromo derivatives of vanillin and benzyl-2-nitrovanillin were prepared by the alkylation of the appropriate vanillin derivative and benzyl chloride in the presence of sodium hydroxide.<sup>1</sup>

**Benzyl Ethers of Derivatives of Vanillic Acid.**—Five grams of the benzyl ether of the requisite vanillin derivative was dissolved in 50 cc. of pyridine and the solution heated

(1) Späth, Orechhoff and Kufner, *Ber.*, **67B**, 1214–1217 (1934).

to 60–70°. A hot (90–100°), concentrated aqueous solution of 5 g. of potassium permanganate was added in small portions. A vigorous reaction ensued with the immediate precipitation of manganese dioxide. The mixture was cooled and filtered. The residue was washed with a little pyridine and the filtrate and washing were combined. The manganese dioxide in the residue was dissolved in sodium bisulfite solution and dilute hydrochloric acid. A white precipitate remained which was extracted with ethyl ether. The pyridine was removed from the filtrate by steam distillation and the residue was extracted with the ether previously used. The ether layer was repeatedly extracted with sodium hydroxide solution until acidification gave no precipitate. The aqueous extracts were combined, acidified and the resultant precipitate filtered, washed with water and dried. It was then recrystallized from the appropriate solvent (either aqueous ethanol or aqueous acetic acid). The properties of some benzyl ethers of derivatives of vanillin and vanillic acid are listed in the accompanying table. The ethers crystallized as colorless needles except where otherwise noted.

### BENZYL ETHERS OF DERIVATIVES OF VANILLIN AND OF VANILLIC ACID

Substituent	Yield, %	M. p., °C.	Halogen, % Calcd.	% Found
Vanillin Derivatives				
2-Bromo-	48	99–99.5	24.88	24.61
5-Bromo-	52	49–50	24.88	24.80
6-Bromo-	71	96–97	24.88	24.83
2-Chloro-	73	94	12.81	12.79
5-Chloro-	54	43–44	12.81	12.80
6-Chloro-	58	101–102 <sup>a</sup>	12.81	12.92
2-Nitro-	41	106–107 <sup>b</sup>		
Vanillic Acid Derivatives				
2-Bromo-	74	162–163 <sup>c</sup>	23.70	23.73
5-Bromo-	83	157–157.2	23.70	23.77
6-Bromo-	76	173–174	23.70	23.64
2-Chloro-	74	149–150	12.11	11.94
5-Chloro-	81	154	12.11	12.01
6-Chloro-	60	164–165	12.11	12.09
2-Nitro-	78	183–184 <sup>d</sup>	4.62 <sup>e</sup>	5.08 <sup>e</sup>

<sup>a</sup> Pale orange prisms. <sup>b</sup> Brown needles. <sup>c</sup> Light yellow needles. <sup>d</sup> White plates. <sup>e</sup> % Nitrogen.

DEPARTMENT OF CHEMISTRY L. CHARLES RAIFORD<sup>2</sup>  
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RECEIVED APRIL 4, 1949

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