NOTES

Condensation Products from Acetaldehyde

BY A. H. ANDERSEN, R. M. KITCHEN AND C. H. NEUFELD

Nord, *et al.*,[1] condensed acetaldehyde with magnesium aluminum alkoxide catalysts and isolated from the reaction product the monoacetate of 1,3-butanediol. No mention is made in their papers of the ethyl ester of β-hydroxybutyric acid which we have found to be present in the reaction mixture in approximately equimolecular proportion to the monoacetate of 1,3-butanediol. Similar proportions of the diol and the hydroxy acid have also been found in an oily by-product obtained in the commercial preparation of ethyl acetate from acetaldehyde.[2]

Experimental.—The procedure adopted for separating the constituents of the high-boiling oils was as follows:

(1) Acid hydrolysis with excess water and butanol: the mixture was heated in a flask provided with a packed distillation column. The overhead temperature was kept at the boiling point of the butyl acetate–butanol–water ternary azeotrope by adjusting the reflux ratio. The ester-containing top layer of the distillate was drawn off while the water layer was decanted back to the flask. This was continued until the temperature could no longer be kept below 90° by refluxing. The excess butanol was then removed in the same manner at a temperature of 92°.

(2) Neutralization and saponification: the saponification equivalent of the aqueous residue was determined, and just sufficient sodium hydroxide was added in 10% solution to neutralize the free acid and saponify the remaining esters. The mixture was boiled for an hour and cooled.

(3) Filtration to remove any resinous by-products.

(4) Vacuum distillation of filtrate: the excess water and the butanediol are removed leaving a fused residue of crude sodium β-hydroxybutyrate.

The glycol was purified by fractionation, b. p. 207°, $n^{20}\text{D}$ 1.441.

The sodium β-hydroxybutyrate was purified by recrystallization from butanol, m. p. 157–158°. It was identified by comparison with an authentic sample prepared through crotonic acid,[3] m. p. 157–158°; mixed m. p. 157–158°.

The butyl ester of β-hydroxybutyric acid was prepared from the sodium salt, hydrochloric acid and butanol, b. p. 103–104° (14 mm.).

The separation has also been carried out using potassium hydroxide. The potassium β-hydroxybutyrate melts at 148–149°. Care must be exercised since all the derivatives of β-hydroxybutyric acid so far examined by us are heat labile, dehydrating rather readily to the crotonates.

From our observations we conclude that termolecular condensation of acetaldehyde occurs under the influence of the coördination catalyst of Nord[1] and also to a much smaller extent under the influence of aluminum alkoxides. We believe that this reaction results from an initial aldolization followed by a condensation between the aldol and aldehyde molecules. This condensation can occur in either of two ways

$$CH_3CHO + CH_3CHOHCH_2CHO \longrightarrow CH_3CHOHCH_2CH_2OCOCH_3$$

Monoacetate of 1,3-butanediol (1)

$$CH_3CHO + CH_3CHOHCH_2CHO \longrightarrow CH_3CH_2OCOCH_2CHOHCH_3$$

Ethyl ester of β-hydroxybutyric acid (2)

Tischtschenko[4] mentions the formation of the ethyl ester of β-hydroxybutyric acid from acetaldehyde, and our observations confirm this and indicate that the ethyl ester is formed in similar quantities to the glycol ester.

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[1] (a) Kulpinski and Nord, *J. Org. Chem.*, **8**, 256–270 (1943); (b) Villani and Nord, THIS JOURNAL, **68**, 1674 (1946); (c) F. F. Nord, U. S. Patent 2,403,876.

[2] Benson and Cadenhead, *J. Soc. Chem. Ind.*, **53**, 40–3T (1934).

[3] Billman, *Ber.*, **43**, 579 (1910).

[4] Tischtschenko, *Chem. Centr.*, **77**, II, 1309 (1906).

SHAWINIGAN CHEMICALS LIMITED
SHAWINIGAN FALLS
QUEBEC, CANADA

RECEIVED SEPTEMBER 15, 1947

The Addition of Dimethylamine to Benzoquinone

BY RICHARD BALTZLY AND EMIL LORZ

In the usual procedure for the preparation of *bis*-(dialkylamino)-quinones from benzoquinone two-thirds of the quinone is employed as an oxidizing agent so that, at best, only around 30% of the starting quinone can be isolated as the product.[1]

It has been found that re-oxidation of the intermediates can be accomplished by a stoichiometric amount of cupric salt or by a smaller quantity when the reaction mixture is stirred with oxygen. The latter procedure is preferable since the product crystallizes in virtually pure form from solution, uncontaminated by cuprous salts. The method was unsuccessful with methylamine, aniline and ammonia.

Procedure

A one-liter three-necked flask equipped with mercury-seal and stirrer was connected to a two-liter graduated cylinder having a levelling bulb and a stopcock for admission of oxygen. The system was flushed out with oxygen and a solution containing 20 g. (0.1 mole) of cupric acetate monohydrate and 27 g. (0.6 mole) of dimethylamine in 300 cc. of methanol was introduced. One-tenth mole (10.8 g.) of benzoquinone in 200 cc. of methanol was then added and the system was closed. The stirrer was started and the reaction was followed by the oxygen absorption which was initially about 120 cc. per minute. Considerable heat was evolved at the start of the reaction and the temperature was held near 25° by ice-water cooling. About five minutes after the beginning of the reaction, crimson platelets of *bis*-(dimethylamino)-benzoquinone became visible on the sides of the flask. After oxygen-absorption had ceased the flask was refrigerated overnight and the product was collected. This material melted at 171° (lit., 173°). A further crop of 2.5 g. was obtained by concentration of the filtrate (total yield, 93%).

bis-(Dimethylaminobenzoquinone is not itself oxidized

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[1] (a) Mylius, *Ber.*, **18**, 463 (1885); (b) Kehrmann, *Ber.*, **23**, 897 (1890); (c) Anslow and Raistrick, *J. Chem. Soc.*, 1449 (1939).

under the above conditions but benzoquinone (and perhaps the intermediate quinones) can be. If the concentration of cupric ion is significantly diminished such oxidations take place and the yield is less. In the presence of 0.01 mole of cupric acetate the oxygen-absorption was about the same but the bisaminoquinone was then obtained in 72–76% yield.

THE WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK RECEIVED OCTOBER 14, 1947

Isolation of a Saponin from the Leaves of *Solidago canadensis* L.

BY R. C. BURRELL AND FORREST G. HOUSTON

In the course of the investigation of the chemical composition of several common weeds, leaves of *Solidago canadensis* L. were examined for the possible presence of a saponin. There are several reports of the recognition of both acid and neutral saponins in various other species of goldenrod,[1,2,3] but none of actual isolation.

Experimental

Method of Isolation.—Leaves of *Solidago canadensis* L. were gathered in late July, 1946, dried at room temperature, and ground to a fine powder. A 230-g. sample of this powder in a small cloth bag was exhaustively extracted, first with acetone, then with ether and finally twice with 95% ethyl alcohol. The combined alcoholic extracts were concentrated to a small volume (about 100 cc.) and 5 volumes of ether added with shaking. This produced a gummy, white precipitate. After decanting the ether, this precipitate was dissolved in the least possible amount of hot methanol. This solution, which had a light yellow color, was treated with acetone added from a large pipet while shaking the mixture vigorously. A flocculent white precipitate formed from which the liquid was decanted. The precipitate was once more dissolved in hot methanol and the acetone precipitation repeated. The final white flocculent precipitate was amorphous and very hygroscopic. It produced a stable creamy foam with water and stabilized an emulsion of kerosene in water. Fehling solution showed no reduction.

Preparation of the Sapogenin.—The moist saponin preparation was brought into solution in 50 cc. of 10% hydrochloric acid, 25 cc. of 95% ethyl alcohol added to reduce foaming and this solution refluxed for three hours. A grainy precipitate formed which consisted of microscopic, colorless needles. The supernatant liquid gave a positive Fehling reaction. The crystals were filtered off and brought into solution by refluxing with methanol. This solution was concentrated to about 50 cc. and on cooling some 500 mg. of colorless needles were isolated, representing a yield of 0.22% of the dried leaves.

Properties of the Sapogenin.—The crystals, which melted at 310–315° with decomposition, were slightly soluble in ethanol methanol, acetone, ether and ethyl acetate, insoluble in water, but dissolved easily in cold concentrated sulfuric acid, giving a faintly yellow colored solution which became deep red on warming or on the addition of a few drops of acetic anhydride, suggesting the behavior of a triterpene. The Rast method indicated a molecular weight of approximately 500.

Anal. Calcd. for $C_{30}H_{50}O_5$ (490.4): C, 73.41; H, 10.28. Found: C, 72.97; H, 10.02.

Insolubility in hot alkali and a neutral reaction in alcoholic solution indicates the absence of a carboxyl group. The acetate was prepared as flat rectangular crystals which melt at 182–183°. A search of the literature failed to reveal a compound approximating $C_{30}H_{50}O_5$ which possesses the above properties.

CONTRIBUTION FROM THE
DEPARTMENT OF AGRICULTURAL CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO RECEIVED SEPTEMBER 27, 1947

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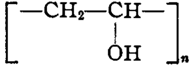
[1] L. Krober, *Heil-gewurz Pflanzen*, **12**, 131 (1930).

[2] F. P. Rey, *Rev. farm.* (*Buenos Aires*), **74**, 93 and 131 (1932).

[3] E. Wagner, *Seifensieder-Ztg.*, **68**, 35 (1941).

The Infrared Spectrum of Polyvinyl Alcohol

BY ELKAN R. BLOUT AND ROBERT KARPLUS

Despite two previously reported measurements on the infrared spectrum of polyvinyl alcohol[1,2] we should like to record some of our data, using carefully purified samples, because of their possible bearing on the details of the molecular structure of this material. The presence of chemical groups and arrangements other than those of the poly-1,3-glycol  $\left[\begin{array}{c}\text{—CH}_2\text{—CH—}\\ \qquad | \\ \qquad \text{OH}\end{array}\right]_n$ has been shown by chemical investigation. For example, terminal acetal,[3] keto or ketal[4] and 1,2-glycol groups[5] have been shown to be present in low percentage in the material known as polyvinyl alcohol.

The infrared spectra for the region 700–4000 cm.$^{-1}$ of carefully purified and dried films of polyvinyl alcohols of various degrees of polymerization are shown in Fig. 1. These spectra correspond in most salient features to those reported by Thompson and Torkington[2] except that there is no evidence of a band at 1650 cm.$^{-1}$. Other samples prepared so that water was not rigidly excluded at the time of measurement show a characteristic absorption band in this region. Another band typical of incompletely hydrolyzed polyvinyl alcohol is seen at 1710 cm.$^{-1}$ in Fig. 2, curve A. This figure also shows the effect of careful acid hydrolysis (removal of residual acetate groups) and drying on the spectrum in the region 1400–1800 cm.$^{-1}$.

It is difficult to correlate absorption bands definitely with molecular structure except through mathematical analysis. In the spectra shown in Fig. 1 the assignments of the bands above 1400 cm.$^{-1}$, *viz.*, 3350 cm.$^{-1}$ (O—H stretching), 2940 cm.$^{-1}$ (C—H stretching) and 1435 cm.$^{-1}$ (C—H bending) seem reasonable, based on analogy with the spectra of simple molecules and on the calculated characteristic frequency of various molecular groups.[6] In the region 1000 cm.$^{-1}$ to 1400 cm.$^{-1}$ five bands are observed at 1380, 1330, 1240 1135 and 1085 cm.$^{-1}$ which are probably associ-

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[1] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

[2] Thompson and Torkington, *Trans. Far. Soc.*, **41**, 246 (1945).

[3] Marvel and Inskeep, THIS JOURNAL, **65**, 1710 (1943).

[4] Clarke and Blout, *J. Pol. Sci.*, **1**, 419 (1946).

[5] Flory and Leutner, "The Occurrence of Head-to-Head Arrangements of the Structural Units in Polyvinyl Alcohol and Acetate," paper presented at the New York meeting of the American Chemical Society, September 15, 1947.

[6] Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945.

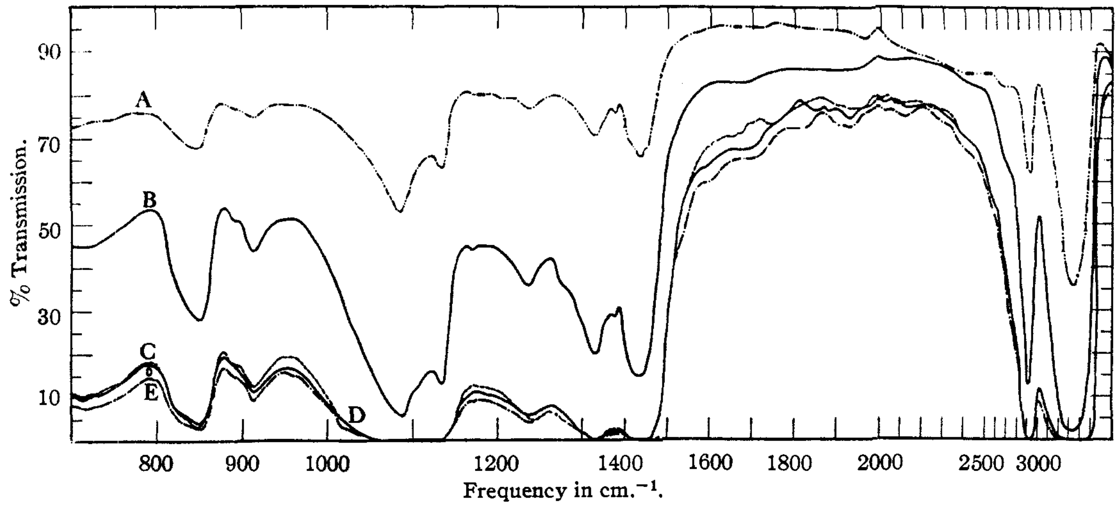

Fig. 1.—Polyvinyl alcohols after acid hydrolysis and drying: curve A, ··—··—··—, JRG-8200 (0.0002″ film); curve B, ————————, RH-391 (0.0003″ film); curve C, — — — — — — — —. RH-393 (0.001″ film); curve D, ——-——-——, RH-391 (0.001″ film); curve E, ·—·—·—·, RH-349 (0.001″ film).

ated with the motions of the substituent groups in the material, the last band arising from stretching of the C—O bond.[7] The absorption bands below 1000 cm.$^{-1}$ cannot be identified except as due to motions of the carbon skeleton. We find that the band at 1240 cm.$^{-1}$ is not removed by acid hydrolysis although a band at 1265 cm.$^{-1}$ in unpurified samples is removed simultaneously with the 1710 cm.$^{-1}$ band. This fact suggests that the 1240 cm.$^{-1}$ band is not associated with the acetate groups of polyvinyl alcohol, as has been previously pointed out.[2]

It is interesting to note that the band at 1380 cm.$^{-1}$, which is present even after repeated acid hydrolysis, is located in the region characteristic of the symmetrical deformation frequency of the C—CH_3 group.[6,8,9] This suggests the possibility that either the polymer contains methyl groups branching off the chain, or the chain ends are methyl groups or perhaps both.

Experimental

Materials.—The various polyvinyl alcohols were obtained as white powders.[7,10] Since they are prepared by the hydrolysis of polyvinyl acetate, further purification was undertaken to assure complete absence of residual acetate groups. This was accomplished by hydrolyzing 5% aqueous solutions with 0.02 N hydrochloric acid for twenty-four hours at 90° followed by precipitation and thorough washing with ethanol. The material so obtained was air-dried, then dissolved in water (approximately 15% solution) and cast into thin films (0.0002″–0.001″ thick) on glass plates at room temperature. To remove the

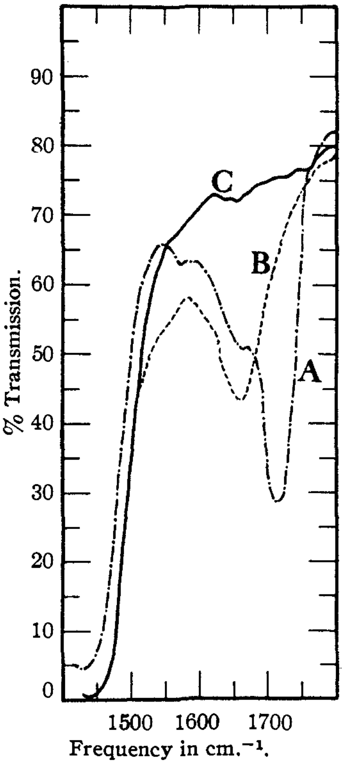

Fig. 2.—Polyvinyl alcohol (JRG-8200): curve A, ·——·——·, cast as received (0.0006″ film); curve B, — — — — — —, cast after acid hydrolysis (0.001″ film); curve C, ————, dried film cast after acid hydrolysis (0.001″ film).

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(7) *Cf.* analogous compounds in refs. 1 and 6.

(8) Thompson and Torkington, *Proc. Roy. Soc.* (*London*), **184**, 3 (1945).

(9) Fox and Martin, *ibid.*, **175**, 208 (1940).

(10) All polyvinyl alcohols referred to in this paper were obtained from E. I. du Pont de Nemours and Co. The designations used are those of the du Pont Co.

Grade	Viscosity	Approximate viscosity centipoises of 4% in aqueous solutions at 20°C.	%Residual[a] acetate
RH-393	Low	5	1
RH-349	Medium	24	1
RH-391	High	55	1
JRG-8200[b]	High	115	4

[a] After acid hydrolysis as described below there were no acetate groups detectable by saponification. [b] Experimental sample obtained through the courtesy of Dr. R. E. Burk, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

5–10% of retained water the films were heated at 160° for one hour immediately before spectral analysis. Determinations showed that during the time it took to measure the spectra no appreciable absorption of moisture occurred.

Instrument.—The spectral measurements[11] were made on a Perkin–Elmer infrared spectrometer Model 12-A using a 40-cycle chopper, a Strong nickel-strip bolometer, an a. c. amplifier and a Brown Instrument Company potentiometer. The data were obtained on a point-to-point basis, the points being taken from 5 to 10 cm.$^{-1}$ apart at frequencies up to 1900 cm.$^{-1}$ and at larger intervals at higher frequencies.

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[11] We are indebted to Mr. Dwight Merrill for some of the spectral measurements.

CHEMICAL RESEARCH LABORATORY
POLAROID CORPORATION
CAMBRIDGE 39, MASSACHUSETTS RECEIVED JULY 18, 1947

A Convenient Synthesis of Octahydropyrrocoline and 2-(γ-Hydroxypropyl)-piperidine

BY V. BOEKELHEIDE AND S. ROTHCHILD[1]

It has been found that octahydropyrrocoline, which has previously been prepared in poor yield by procedures involving three or more steps,[2] can be obtained readily in excellent yield by the direct hydrogenation of 2-(γ-hydroxypropyl)-pyridine[3] at 200° and 2500 lb. pressure with Raney nickel catalyst.

When the reduction was carried out at 125° instead of 200°, the product was not octahydropyrrocoline but rather 2-(γ-hydroxypropyl)-piperidine. The yield of 2-(γ-hydroxypropyl)-piperidine is practically quantitative and this is undoubtedly the best method for its preparation.[4] At temperatures intermediate between 125 and 200° the reduction gave mixtures of octahydropyrrocoline and 2-(γ-hydroxypropyl)-piperidine. Although it is probable that 2-(γ-hydroxypropyl)-piperidine is an intermediate in the formation of octahydropyrrocoline, 2-(γ-hydroxypropyl)-piperidine is not readily affected by heat and can be distilled repeatedly without change.

Experimental[5]

Octahydropyrrocoline.—A mixture of freshly distilled 2-(γ-hydroxypropyl)-pyridine (9.0 g., 0.066 mole), Raney nickel (2 g.), and absolute alcohol (10 cc.) was heated at 200° with shaking under an initial pressure of 2540 p. s. i. of hydrogen. At the end of one hour the drop in hydrogen pressure corresponded to that calculated. After removal of the catalyst by filtration, the oily product was distilled yielding 6.4 g. (78%) of a colorless oil; b. p. 71–72° at 32 mm.; $n^{21.2}$D 1.4702.

For purposes of identification, there were prepared the following derivatives: picrate, m. p. 228–9° (lit.,[2] m. p. 226°, 231–232°); gold chloride double salt, m. p. 188–192° (lit.,[2] m. p. 191–193°).

The methiodide of octahydropyrrocoline was formed in benzene and proved to be unstable in the presence of air. The amorphous solid, obtained from benzene, decomposed at 280–283° and was analyzed directly without further purification.

Anal. Calcd. for $C_9H_{18}NI$: C, 40.46; H, 6.79. Found: C, 40.00; H, 7.10.

2-(γ-Hydroxypropyl)-piperidine.—A mixture of freshly distilled 2-(γ-hydroxypropyl)-pyridine (14.0 g., 0.102 mole), Raney nickel (2 g.), and absolute alcohol (4 cc.) was heated at 125° with shaking under an initial pressure of 2500 p. s. i. of hydrogen. At the end of four hours the pressure drop corresponded to that calculated. After removal of the catalyst and solvent, the product was distilled yielding 12.5 g. (85%) of a colorless oil; b. p. 101–102° at 3 mm.; $n^{21.5}$D 1.4882.

For identification there was prepared the hydrochloride, m.p. 128–129° (lit.,[2b] m. p. 127–128°), and the mercuric chloride complex, m. p. 180–182° (lit.,[2a] m. p. 182–183°).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK RECEIVED NOVEMBER 14, 1947

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[1] Aided by a Grant from the National Foundation for Infantile Paralysis.

[2] (a) Loeffler and Kaim, *Ber.*, **42**, 94 (1909); Loeffler and Flugel *ibid.*, **42**, 3423 (1909), and Tullock and McElvain, THIS JOURNAL, **61**, 961 (1939); (b) Clemo and Ramage, *J. Chem. Soc.*, 2969 (1932); (c) Wibaut and Beets, *Rec. trav. chim.*, **60**, 905 (1940); (d) Diels and Alder, *Ann.*, **498**, 16 (1932).

[3] 2-(γ-Hydroxypropyl)-pyridine is available from Reilly Tar and Chemical Co., Indianapolis, Indiana.

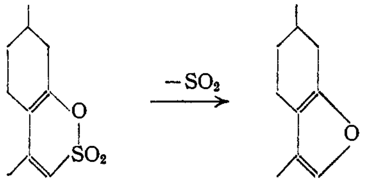
[4] Previous methods for preparing 2-(γ-hydroxypropyl)-piperidine are given in ref. (2a).

[5] Analysis by Mrs. G. L. Sauvage. All melting points are corrected.

The Sulfonation of Mesityl Oxide

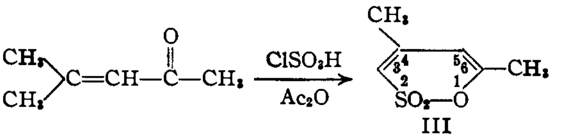
BY RICHARD H. EASTMAN AND DON GALLUP[1]

In seeking a convenient method for the synthesis of alkylated furans we have sought to extend to simple α,β-unsaturated ketones and aldehydes the observation of Treibs[2] that pulegone on treatment in acetic anhydride at ice temperature with concentrated sulfuric acid yields cyclopulegenol-sulfonic ester (I) from which menthofuran (II) is obtained in excellent yield on pyrolysis with zinc oxide at atmospheric pressure.



I II

We have attempted the sulfonation under varied conditions of concentration and temperature, using both sulfuric acid and chlorosulfonic acid, of crotonaldehyde, cyclohexylidenecyclohexanone, 3,4-dimethylhexene-3-on-2 and mesityl oxide. A clean-cut reaction was obtained only in the case of the sulfonation of mesityl oxide which on sulfonation with chlorosulfonic acid in acetic anhydride gave the cyclic sulfonic ester III in good yield. Pyrolysis of the cyclic sulfonic ester of mesityl oxide (III) at atmospheric pressure,



III

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[1] The work reported here is taken from a thesis presented by Don Gallup to Stanford University in partial fulfillment of the requirements for the degree of Master of Science.

[2] W. Treibs, *Ber.*, **70B**, 85 (1937).

under reduced pressure and in an atmosphere of nitrogen did not effect the transformation analogous to I→II, but led rather to intractable tars.

Bromination of III with one mole of bromine resulted in a substitution product, formulated tentatively as the 5-bromo derivative of III. Treatment of III with an excess of bromine led to an unstable compound $C_6H_7O_3SBr_3$, formulated tentatively as the 5-bromo-3,4-dibromide of III.

Experimental

Mesityl Oxide Cyclic Sulfonic Ester (III).—Mesityl oxide (19.6 g.) was added to 41 g. acetic anhydride and the mixture was cooled to 0°. Chlorosulfonic acid (22.3 g.) was added dropwise while the temperature was kept at 0° with an ice-salt-bath. The mixture was stirred for one-half hour after the addition of the acid was complete, and then placed in the cold-room overnight. The reaction mixture was decomposed by pouring it into an equal volume of ice-water with vigorous stirring. The light-yellow precipitate which formed was separated and purified by crystallization from methanol to yield 13 g. (41%) of stout, colorless prisms of m. p.[3] 65–67°.

Anal. Calcd. for $C_6H_8O_3S$: C, 45.0; H, 5.03. Found: C, 45.1; H, 5.19.

After several weeks a sample of the compound suddenly decomposed with violence, the production of sulfur dioxide and a black tar.

Bromination of the Cyclic Sulfonic Ester of Mesityl Oxide.—A 5.0-g. sample of the ester (III) was dissolved in carbon tetrachloride (25 ml.) and bromine was added dropwise during ten minutes until the decolorization of it became slow. A precipitate formed rapidly and hydrogen bromide was evolved. A slight excess of bromine was removed with sodium thiosulfate solution and the solvent was removed by distillation. The crude product was crystallized from alcohol to give 3.0 g. of white, crystalline material of m. p. 75–76° (mixed with III, m. p. 46–47°).

Anal. Calcd. for $C_6H_7O_3SBr$: C, 30.1; H, 2.95. Found: C, 30.4; H, 3.36.

The substance is a powerful skin irritant and is formulated as the 5-bromo derivative of the cyclic sulfonic ester of mesityl oxide (III).

A 5.0-g. sample of the cyclic sulfonic ester (III) was dissolved in 25 ml. of carbon tetrachloride and 10 g. of bromine was added rapidly. The mixture was allowed to stand for a day and the precipitate that formed was separated and washed thoroughly with methanol-water (1:1). The white crystalline product turned dark near its melting point and then melted with decomposition at 156–60°.

Anal. Calcd. for $C_6H_7O_3SBr_3$: C, 18.2; H, 1.88. Found: C, 18.3; H, 1.77.

This substance is formulated as the 5-bromo-3,4-dibromide of the cyclic sulfonic ester (III).

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[3] Melting points are not corrected.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED AUGUST 28, 1947

The Reaction of *t*-Butylmagnesium Chloride with Ethyl Oxalate

BY G. F. HENNION AND CHARLES F. RALEY

In connection with another problem we have recently had occasion to re-examine the reaction of *t*-butylmagnesium chloride with ethyl oxalate.[1] Our observations are not entirely in accord with the previous report which states that the reaction gives a mixture of products containing *t*-butylglycolic acid, ethyl *t*-butylglycolate, α-ethoxy-β,β-dimethylbutyric acid and smaller amounts of substances thought to be *t*-butyl neopentyl ketone and *sym*-di-*t*-butylglycol. *t*-Butylglycolic acid and its ethyl ester were obtained in the present study but the other products could not be found; instead, several other compounds were isolated.

We have carried out the reaction in three ways: addition of ethyl oxalate to the Grignard reagent (1:4); addition of the Grignard reagent to the ester (2:1); and simultaneous reaction of magnesium (2.5), *t*-butyl chloride (2.0), and ethyl oxalate (1.0). In each case there was considerable evolution of gas, evidently isobutylene, and after working up the products in the usual way complex mixtures were encountered. In view of the latter fact the reaction seems to have little preparative value.

Experimental

A. **Direct Addition.**—When 0.385 mole of ethyl oxalate was added dropwise to 1.54 moles of *t*-butylmagnesium chloride in anhydrous ether (previously filtered through glass wool), 0.7 mole of isobutylene was recovered by absorption in sulfuric acid. After hydrolysis of the reaction mixture with ice and hydrochloric acid in the usual way, extraction of the ether layer with sodium bicarbonate solution removed 18 g. of impure *t*-butylglycolic acid. The neutral components, after removal of the ether, were saponified and thus yielded an additional 10 g. of the acid. It was best purified by vacuum distillation (b. p. 110–117° at 4 mm.), followed by crystallization from water; m. p. 85–86°. Smaller amounts of other products were formed also; of these only hexamethylethane and diisobutylene were recognized.

B. **Reverse Addition.**—In this experiment, when 1.35 moles of filtered Grignard reagent was added to 0.676 mole of ester, the only acidic substance recovered was 2.5 g. of impure oxalic acid. There was obtained by distillation of the ether layer after hydrolysis, etc., 27 g. of ethyl *t*-butylglycolate and 30 g. of a substance whose analysis corresponds to $C_{12}H_{24}O_3$. There was good evidence that the latter compound is the previously unknown ethyl di-*t*-butylglycolate, $(t\text{-}C_4H_9)_2C(OH)COOC_2H_5$. In addition to these two compounds there was 26 g. of higher boiling material.

C. **Barbier Reaction.**—When this method was employed with 2.5 gram atoms of magnesium, 2.0 moles of *t*-butyl chloride and 1.0 mole of ethyl oxalate (the latter mixed and added slowly to the magnesium under ether), hydrolysis and removal of the ether left 137 g. of pale yellow oil. Distillation *in vacuo* through a helix-packed column yielded 38 g. of impure ethyl *t*-butylglycolate and 40 g. of ethyl di-*t*-butylglycolate. The remainder of the product was distilled at 2.5–3.0 mm. without the column and appeared to decompose somewhat in the process. The distillate (39 g.) deposited a crystalline solid; after removal and crystallization from aqueous alcohol it melted at 113–113.5°. The analytical data corresponded with the formula $C_{14}H_{28}O_2$. Despite the oxygen content this substance gave none of the tests specific for alcohols, carbonyl compounds, etc. It was tentatively decided that the compound is di-*t*-butylpivaloycarbinol, $(t\text{-}C_4H_9)_2C(OH)COC(CH_3)_3$. Decomposition by strong heating and the failure to respond to functional group reactions are consistent with this structure.

The physical properties and the analytical data for purified samples of the various products are summarized below.

***t*-Butylglycolic acid**: b. p. 118° at 9 mm.; m. p. 85–86°. Calcd. for $C_6H_{12}O_3$: C, 54.52; H, 9.15; neutral equiv.,

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[1] Egorova, *J. Russ. Phys.-Chem. Soc.*, **41**, 1454 (1909); *Chem. Zentr.*, **81**, 1003 (1910).

132.2. Found: C, 54.50; H, 9.06; neutral equiv., 133.6.

Ethyl *t*-butylglycolate: b. p. 53° at 5 mm.; $n^{25}D$ 1.4210; d^{25} 0.9661. Calcd. for $C_8H_{16}O_3$: C, 59.97; H, 10.07. Found: C, 59.26; H, 10.03.

Ethyl di-*t*-butylglycolate: b. p. 70° at 3.5 mm.; $n^{25}D$ 1.4431; d^{25} 0.9525. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; -OC_2H_5, 20.84. Found: C, 66.51; H, 11.05; -OC_2H_5, 18.73.

Di-*t*-butylpivaloylcarbinol (?): m. p. 113–113.5°. Calcd. for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.48; H, 12.56.

Ethyl *t*-butylglycolate failed to react with semicarbazide, as expected, but did yield a derivative, m. p. 166°, with 2,4-dinitrophenylhydrazine, probably due to oxidation at the *alpha* carbon atom.

The analyses for carbon and hydrogen were carried out by Mr. Charles W. Beazley, Micro-Tech Laboratories, Skokie, Ill.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
RECEIVED AUGUST 20, 1947

Some New 1,1,1-Trichloro-2,2-bis-(*p*-alkylphenyl)-ethanes

BY G. F. HENNION AND JOSEPH G. WALSH

The condensations of chloral hydrate with toluene,[1] two of the xylenes,[2] *t*-butylbenzene[3] and benzene itself[4] are known to yield crystalline derivatives structurally analogous to DDT. We have recently extended the reaction to several other alkylbenzenes to determine whether it may be used to prepare solid derivatives useful for identification purposes. Furthermore, an assortment of 1,1,1-trichloro-2,2-bis-(*p*-alkylphenyl)-ethanes (I) was desired to explore the possibility of preparing 4,4′-dialkyldiphenylacetylenes (III) from them by elimination of hydrogen chloride and chlorine.

$$\underset{\text{I}}{(R-C_6H_4)_2CH-CCl_3} \xrightarrow{\text{KOH}} \underset{\text{II}}{(R-C_6H_4)_2C{=}CCl_2} \xrightarrow{\text{2Na}} \underset{\text{III}}{R-C_6H_4-C{\equiv}C-C_6H_4-R}$$

The reactions of the alkylbenzenes with chloral hydrate were carried out in concentrated sulfuric acid (96.9%) in the ordinary manner. Toluene and *t*-butylbenzene gave solid products identical with those previously described.[1,3] Ethylbenzene, isopropylbenzene, *n*-butylbenzene, *s*-butylbenzene and 2-*s*-amylbenzene, however, yielded viscous oils which could not be induced to crystallize. The isolation and purification of these products proved somewhat troublesome because dilution of the crude reaction products with water gave emulsions, probably due to appreciable sulfonation as a side reaction. The emulsions were broken with ether and salt and the ethereal extracts finally distilled three times *in vacuo*. The physical constants, yields after the first distillation, and analyses for these compounds are given in Table I.

Each of the seven products (I) was treated with alcoholic potassium hydroxide to prepare the corresponding dichloroethylenes (II). Again the toluene and *t*-butylbenzene derivatives gave solids, as previously reported, while all the other yielded oils. In all cases the dichloroethylenes were insoluble in liquid ammonia and failed to react well with sodium in this medium. An ethereal solution of the di-*p*-tolyl compound, for example, decolorized only a fraction of the theoretical amount of sodium in liquid ammonia and yielded an insoluble, infusible, polymeric substance containing chlorine. All attempts to prepare acetylenes (III) in this manner failed.

TABLE I

1,1,1-TRICHLORO-2,2-*bis*-(*p*-ALKYLPHENYL)-ETHANES

Alkyl group	B. p., °C.	Press., mm.	Yield, %	$n^{25}D$	Chlorine, % Calcd.	Chlorine, % Found
Ethyl[a]	183	0.8	51	1.5780	31.2	31.1
Isopropyl	199	1.4	40	1.5672	28.8	28.5
n-Butyl	203	0.4	42	1.5611	26.8	25.6
s-Butyl	204	0.4	36	1.5597	26.8	25.7
2-*s*-Amyl	210	0.4	27	1.5515	25.0	24.2

[a] Wild, *Helv. Chim. Acta*, **29**, 497(1946), reported the boiling point to be 180° at 0.2 mm. The refractive index was not given.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
RECEIVED AUGUST 20, 1947

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[1] Fischer, *Ber.*, **7**, 1190 (1874).

[2] Elbs, *J. prakt. Chem.*, [2] **39**, 300 (1889).

[3] Cristol, Hayes and Haller, THIS JOURNAL, **68**, 913 (1946).

[4] Baeyer, *Ber.*, **5**, 25 (1872).

Nitration of (*p*-Bromophenyl)-cyclopentane

BY RICHARD D. KLEENE

It was desired to prepare an acetamino derivative of (*p*-bromophenyl)-cyclopentane by the method of Ipatieff and Schmerling[1] for alkyl benzenes. The product obtained was free of halogen as described below.

(3,5-Diacetaminophenyl)-cyclopentane.—One gram of the bromo compound[2] was nitrated with 5 ml. of a mixture of one part of 70% nitric acid and one part of 98% sulfuric acid by volume. The red oil so obtained was dissolved in alcohol and reduced with tin and 36% hydrochloric acid. The amine was then acetylated with acetic anhydride and the resulting solid was recrystallized three times from dilute alcohol. Very fine hair-like needles were formed which melted at 233–234° (uncor.); yield 50%. Analysis showed the complete absence of bromine.

Anal. Calcd. for $C_{15}H_{20}O_2N_2$: C, 69.2; H, 7.70; N, 10.8. Found: C, 68.4; H, 7.57; N, 10.4.

A mixture of this new compound with (2,4-diacetaminophenyl)-cyclopentane[1] (m. p. 228°) melted at 220–225°. The two compounds also appeared dissimilar under the microscope. The removal of the bromine atom indicates that it is probably activated by both nitro groups. This reduces the possibility that the new compound is the 2,5- or the 2,6-diacetamino isomer.

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[1] V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **59**, 1056 (1937); **60**, 1476 (1938).

[2] R. D. Kleene, *ibid.*, **62**, 2883 (1940).

The removal of halogens from aromatic compounds during the reduction of two activating nitro groups is a well-known phenomenon. Thus the reduction of 2,4-dibromo-3,5-dinitrotoluene with tin and hydrochloric acid gives 3,5-diaminotoluene.[3]

In contrast to the nitration with mixed acid as described above, nitration with 70% nitric acid alone according to the method of Mayes and Turner[4] led to a mixture of products from which a considerable amount of 1-nitro-4-bromobenzene was isolated. The other products were not identified.

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(3) W. A. Davis, *J. Chem. Soc.*, **81**, 873 (1902).

(4) H. A. Mayes and E. E. Turner, *ibid.*, 500 (1929).

CHICAGO, ILLINOIS RECEIVED MAY 29, 1947

The Acylation of Thiophene and Furan by Means of Boron Trifluoride[1]

BY HOWARD D. HARTOUGH AND ALVIN I. KOSAK[2]

The acetylation of thiophene and furan to form the respective 2-acyl derivatives has been effected previously by means of several catalysts.[3] This reaction has now been effected by means of catalytic amounts of boron trifluoride complexes in ether, methanol, and acetic acid. The yields were satisfactory (70%) with 0.03–0.075 mole of the catalyst per mole of acetic anhydride. When acetyl chloride was used instead of acetic anhydride the yield was poor. The analogous reaction with benzoyl chloride was effected in 22% yield.

Although the nucleus of 2-acetylthiophene is acetylated in the presence of zinc chloride, orthophosphoric acid and phosphorus pentoxide,[3] acetylation at the side chain of this ketone occurred in the presence of a molecular equivalent of boron trifluoride to form a triacetylthiophene in 17% yield; however, the product has not been identified. Acetylation at the side chain might have been anticipated from the work of Meerwein, Pannwitz and Vossen[4] and Hauser and Adams.[5]

With furan, acetic anhydride and a catalytic amount of boron trifluoride in methanol, 2-acetylfuran was obtained in 46% yield.

Boron Trifluoride Complexes.—The boron trifluoride etherate was used as received from the Eastman Kodak Co. The boron trifluoride methanol complex and the boron trifluoride acetic acid complex were prepared by saturating methanol and acetic acid with boron trifluoride gas at 100 p. s. i. pressure in a stirring autoclave.

2-Acetylthiophene.—To a mixture of 252 g. (3 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride cooled to 10° by means of an ice-bath was added 4 g. of boron trifluoride-methanol complex (60% boron trifluoride). The temperature rose to 13° and when it finally subsided after five minutes to 5° the ice-bath was removed and the flask warmed to 50° for two hours. Two hundred milliliters of water was added, the mixture agitated for fifteen minutes, the lower organic layer drawn off, washed with 10% sodium carbonate solution until neutral, and distilled. Thiophene, 180 g., was recovered and 84 g. (70%) of 2-acetylthiophene, b. p. 87–88° (8 mm.),[6] n^{20}D 1.5666, was obtained.

2-Benzoylthiophene.—To 126 g. (1.5 moles) of thiophene and 141 g. (1 mole) of benzoyl chloride was added 4 g. of boron trifluoride–acetic acid complex. No heat of reaction was noted and the mixture was heated at 90–95° for six hours. After cooling, the reaction mixture was washed with 10% sodium hydroxide solution until neutral. Distillation yielded thiophene, 42 g. (22%) of 2-benzoylthiophene, b. p. 146–147° (5 mm.), m. p. 56.5–57°,[7] after recrystallization from ASTM naphtha, and 21 g. of tarry residue.

"2-Triacetylthiophene."—To 42 g. (0.33 mole) of 2-acetylthiophene was added 107 g. (1 mole) of 95% acetic anhydride and 110 g. (0.84 mole) of boron trifluoride etherate. The temperature rose to 38° and after fifteen minutes the mixture was warmed on a steam-bath at 55° for thirty minutes. The hot mixture was poured slowly into one liter of water containing 120 g. of sodium acetate and shaken until the oily liquid crystallized. The crystals were filtered, washed with cold benzene, and purified by vacuum sublimation, yielding 12 g. (17%) of bright yellow crystals, m. p. 176–177°.[8]

Anal. Calcd. for $C_{10}H_{10}O_3S$: S, 15.31, Found: S, 14.92.

Oxidation with alkaline permanganate gave 2-thiophenecarboxylic acid, m. p. and mixed m. p. 127–128.5°.

2-Acetylfuran.—A procedure, analogous to that employed for to 2-acetylthiophene, was used but the temperature of the reaction mixture was maintained at 25° instead of 50° for two hours. Distillation yielded 53 g. (48%) of 2-acetylfuran, b. p. 89–90° (43 mm.),[9] m. p. 30–32°,[9] n^{30}D 1.5015.

Acknowledgments.—The authors wish to thank Dr. D. E. Baderscher for advice and interest in this problem and Miss Loretta G. Conley who helped with a number of the laboratory experiments.

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(1) Paper VII of this series.

(2) Present address: Ohio State University, Columbus, Ohio.

(3) (a) Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946); (b) **69**, 1012 (1947); (c) **69**, 3093 (1947); (d) **69**, 3098 (1947); (e) Hartough, Kosak and Sardella, *ibid.*, **69**, 1014 (1947); (f) Hartough and Conley, *ibid.*, **69**, 3096 (1947).

(4) Meerwein, *Ber.*, **66B**, 411 (1933); Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934); Meerwein and Vossen, *ibid.*, **141**, 149 (1934).

(5) Hauser and Adams, THIS JOURNAL, **66**, 345 (1944).

(6) Reported data (ref. 3a): b. p. 77–78° (4 mm.) and n^{20}D 1.5666.

(7) Reported data (ref. 3b); b. p. 143–144 (4 mm.) and m. p. 56.5–57°.

(8) Alternate purification procedures involved numerous recrystallizations from benzene or precipitation of the material from ethyl acetate by addition of petroleum ether yielding brown crystals, m. p. 173–175°.

(9) Reported data (ref. 3c): m. p. 30–32° and b. p. 45–50° (5 mm.).

SOCONY-VACUUM LABORATORIES
RESEARCH AND DEVELOPMENT DEPARTMENT
PAULSBORO, N. J.
RECEIVED SEPTEMBER 23, 1947

Derivatives of Diethylamino Compounds

BY NELSON J. LEONARD, FELICE MARY KRAFT AND VIVIAN WOLFMAN

In connection with studies in progress on reactions of aminoalcohols and aminoketones involving possible rearrangement, it was desirable to obtain readily identifiable derivatives of certain diethylamino compounds. The compounds of interest included amines, aminoethers, aminoalcohols and aminoketones, in all of which the amine function was tertiary. Derivatives have been formed with picric acid, picrolonic acid and ethyl iodide. Diethyl-*n*-propylamine has been obtained pure, as have β-ethoxyethyldiethylamine and γ-ethoxypropyldiethylamine. 2-Diethylamino-2-methyl-1-propanol has been prepared by a method similar to the previously unsuccessful diethylation of 2-amino-2-methyl-1-propanol[1] and the successful ethylation of 2-ethylamino-2-methyl-1-propanol.[2]

Experimental[3]

Diethyl-*n*-propylamine.—A mixture of 70 g. of *n*-propyl bromide, 32 g. of ethylene glycol and 61 g. of diethylamine was refluxed for forty hours. The amine was liberated with alkali and extracted with ether. After the ether solution was dried over potassium hydroxide the ether was removed, and 19 g. (27%) of diethyl-*n*-propylamine was distilled at 111.5–112.5° (750 mm.); n^{20}_D 1.4064; d^{20}_4 0.742.

Anal. Calcd. for $C_7H_{17}N$: C, 72.97; H, 14.88; N, 12.16; MR_D, 38.35. Found: C, 73.10; H, 15.01; N, 12.14; MR_D, 38.18.

The **ethiodide** melted at 262–263° (cor.) with decomposition (von Auwers and Mauss reported 255–256°[4]).

The **picrate** was prepared in and recrystallized from ether as long yellow needles, m. p. 82–84° (cor.).

Anal. Calcd. for $C_{13}H_{20}N_4O_7$: C, 45.34; H, 5.86; N, 16.27. Found: C, 45.41; H, 5.91; N, 16.14.

The **picrolonate** was prepared in ether and recrystallized from ethanol–ether as orange-yellow elongated prisms, m. p. 140–141° (cor.).

Anal. Calcd. for $C_{17}H_{25}N_5O_5$: C, 53.81; H, 6.64; N, 18.46. Found: C, 53.92; H, 6.69; N, 18.41.

Diethylisopropylamine Picrolonate.—Prepared from diethylisopropylamine[5] in ether, the picrolonate was recrystallized from absolute ethanol in leafy clusters of yellow prisms, m. p. 164–165.5° (cor.).

Diethylisopropylamine Ethiodide.—Formed by refluxing diethylisopropylamine in benzene with excess ethyl iodide, the microcrystalline ethiodide melted at 264–266° (cor.) with decomposition.

β-Ethoxyethyldiethylamine.—A mixture of a six to one molar proportion of diethylamine (50 g.) and β-ethoxyethyl bromide (16.7 g.) was heated under reflux for twenty-four hours. The product was isolated as in the method for diethyl-*n*-propylamine; b. p. 63–64° (25 mm.); n^{20}_D 1.4179.

Anal. Calcd. for $C_8H_{19}NO$: C, 66.15; H, 13.18; N, 9.64. Found: C, 65.81; H, 12.96; N, 9.64.

No picrate, picrylsulfonate, picrolonate, methiodide or mineral acid salt could be formed.

γ-Ethoxypropyldiethylamine.—Fifty grams of diethylamine and 19 g. of γ-ethoxypropyl bromide were heated under reflux and the product was isolated in the usual manner; b. p. 78–81° (25 mm.); n^{20}_D 1.4223.

Anal. Calcd. for $C_9H_{21}NO$: C, 67.87; H, 13.29; N, 8.80. Found: C, 68.01; H, 13.01; N, 8.84.

Prepared in and recrystallized from ethanol, the **picrolonate** melted with decomposition at 213–215° (uncor.).

Anal. Calcd. for $C_{19}H_{29}N_5O_6$: C, 53.89; H, 6.93. Found: C, 53.75; H, 6.92.

2-Diethylamino-2-methyl-1-propanol.—2-Diethylamino-2-methyl-1-propanol was prepared by a method similar to that of Olson and Whitacre and Bachman and Mayhew[2]; b. p. 82–83° (22 mm.); n^{20}_D 1.4421.

Anal. Calcd. for $C_8H_{19}NO$: N, 9.64. Found: N, 9.61.

The **picrolonate** was recrystallized from benzene containing a small amount of ethanol as elongated yellow prisms; m. p. 185.5–187° (uncor.) with decomposition.

Anal. Calcd. for $C_{18}H_{27}N_5O_6$: C, 52.80; H, 6.65. Found; C, 52.73; H, 6.67.

The **picrate** was recrystallized from ethanol–petroleum ether solution as yellow prisms; m. p. 156° (uncor.).

Anal. Calcd. for $C_{14}H_{22}N_4O_8$: C, 44.92; H, 5.92. Found: C, 45.00; H, 5.89.

Diethylaminoacetone Picrolonate.—Formed from diethylaminoacetone[6] in ether and recrystallized from ethanol, the picrolonate formed clusters of yellow prisms, m. p. 143–144° (cor.).

Anal. Calcd. for $C_{17}H_{23}N_5O_6$: C, 51.90; H, 5.89; N, 17.80. Found: C, 51.74; H, 6.11; N, 17.81.

5-Diethylamino-2-pentanone Picrolonate.—Prepared from Noval ketone in ether and recrystallized from ethanol–ether, the picrolonate formed stout yellow prisms, m. p. 105–107° (cor.).

Anal. Calcd. for $C_{19}H_{27}N_5O_6$: C, 54.14; H, 6.46; N, 16.62. Found: C, 54.32; H, 6.67; N, 16.67.

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[1] Olson and Whitacre, THIS JOURNAL, **65**, 1019 (1943).

[2] Bachman and Mayhew, *J. Org. Chem.*, **10**, 243 (1945).

[3] The microanalyses were performed by Miss Theta Spoor. Boiling points are uncorrected for emergent stem error.

[4] von Auwers and Mauss, *Ber.*, **61**, 2411 (1928).

[5] Caspe, THIS JOURNAL, **54**, 4457 (1932).

[6] Stoermer and Dzimiski, *Ber.*, **28B**, 2220 (1895).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MAY 7, 1947

Conversion of Benzylamine to N-Substituted Thiobenzamides

BY FREEMAN H. MCMILLAN[1]

In a previous publication[2] the modified Willgerodt reaction[3] was applied to styrene in the presence of a series of amines and the yield of phenylacetic acid obtained by hydrolyzing the crude reaction mixture was measured. In some instances there was isolated from the crude reaction mixture a little of the pure thioamide for characterization and analysis. It has been found that the compound isolated and called N-benzylphenylthioacetamide was in reality N-benzylthiobenzamide. Since there was no doubt that it was phenylacetic acid which was obtained from the hydrolysis of the crude reaction mixture, the hydrolysis of pure N-benzylthiobenzamide was investigated. It was found that this thioamide was very slowly attacked by refluxing 50% (by weight) sulfuric acid (the conditions used for hydrolyzing the crude thioamides), thus explaining the absence of benzoic acid in the hydrolysate from the crude reaction mixture of styrene, sulfur and benzylamine. The identity of N-benzylthiobenzamide was established by hydrolysis with refluxing 65% (by weight) sulfuric acid followed by isolation of benzoic acid and benzylamine in the form of its picrate.

Since none of the other amines used to prepare thioamides reported in ref. 2 had the possibility of undergoing a reaction analogous to that which benzylamine underwent, there is no reasonable doubt as to their identity.

Although it is possible that the N-benzylthiobenzamide could have arisen through cleavage[4]

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[1] Present address: Warner Institute for Therapeutic Research, 113 West 18th St., New York, N. Y.

[2] King and McMillan, THIS JOURNAL, **68**, 2335 (1946).

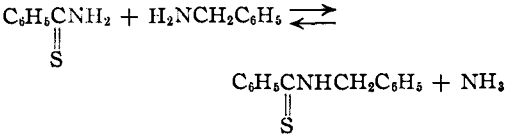
[3] Schwenk and Bloch, *ibid.*, **64**, 3051 (1942).

[4] For discussion of cleavage in Willgerodt reaction *cf.* McMillan and King, *ibid.*, **69**, 1207 (1947).

of styrene, such cleavage has not been observed with other amines, *e. g.*, morpholine, where the yield of phenylthioacetmorpholide is very good, and consequently this mode of formation is not considered probable. An alternative mode of formation is by oxidation (replacement of two hydrogens by sulfur) of part of the benzylamine used.[5]

It was found that by heating equimolecular portions of benzylamine and sulfur a 91% yield of N-benzylthiobenzamide was obtained. Wallach[6] reported that the reaction of benzylamine with sulfur in a sealed tube at 180° gave thiobenzamide. The discrepancy between our results and those of Wallach may be explained by the fact that ammonia was given off copiously from our reaction. Any reaction in which ammonia is one of the products would be favored in an open reaction vessel where the ammonia could escape and would be suppressed in a sealed tube where it would remain at the site of the reaction. Two such possible reactions which would lead to our product would be

$$C_6H_5CH_2NH_2 + H_2NCH_2C_6H_5 \rightleftarrows C_6H_5CH_2NHCH_2C_6H_5 + NH_3 \quad (1)$$



$$C_6H_5\underset{\substack{\| \\ S}}{C}NH_2 + H_2NCH_2C_6H_5 \rightleftarrows C_6H_5\underset{\substack{\| \\ S}}{C}NHCH_2C_6H_5 + NH_3 \quad (2)$$

It was also found that heating an equimolecular mixture of benzylamine and morpholine with sulfur gives thiobenzmorpholide, presumably by the same route as the benzylamine–sulfur reaction.

Acknowledgment.—The author wishes to acknowledge the helpful criticisms of Dr. John A. King in the preparation of this manuscript.

Experimental[7,8]

Reaction of Benzylamine with Sulfur.—A mixture of benzylamine (21.4 g., 0.20 mole) and sulfur (8.0 g., 0.25 mole) was heated at reflux for forty-five minutes. Evolution of ammonia was noticed almost immediately after heating was begun. The cooled reaction mixture was treated with Skellysolve "C" (100 ml.) and then filtered. The solid material weighed 19.5 g. (91%) and melted at 81–83°. After crystallization from Skellysolve "C" (250 ml.) it melted at 84–85°.

Anal. Calcd. for $C_{14}H_{13}NS$: N, 6.16; S, 14.10. Found: N, 5.85; S, 14.10.

There was no depression in melting point when this compound was mixed with the material reported to be N-benzylphenylthioacetamide[2] but now known to be N-benzylthiobenzamide.

Hydrolysis of above Reaction Product.—The compound melting at 84–85° (2.0 g.) was refluxed for one hour with 65% (by weight) sulfuric acid (30 ml.). The hydrolysis mixture was cooled and extracted with two 30-ml. portions of ether. The combined ether extracts were extracted with 25 ml. of 10% sodium hydroxide solution and the caustic extract was acidified with dilute hydrochloric acid. The acidified solution was extracted with two 30-ml. portions of ether; the ether solution was dried over anhydrous sodium sulfate and the ether was removed under vacuum. The residue was crystallized from water giving white crystals (0.4 g.) melting at 120–121°, undepressed when mixed with an authentic sample of benzoic acid.

The hydrolysis mixture was made alkaline with 10% sodium hydroxide solution and then extracted with three 100-ml. portions of ether. The ether was dried over anhydrous potassium carbonate and the ether was removed under vacuum. The residue was treated with saturated alcoholic picric acid solution and gave a picrate which after crystallization from alcohol melted at 193–195°, undepressed when mixed with an authentic sample of benzylamine picrate.[9]

Reaction of Benzylamine, Morpholine and Sulfur.—A mixture of benzylamine (10.7 g., 0.10 mole), morpholine (8.7 g., 0.10 mole) and sulfur (6.4 g., 0.20 mole) was heated at 160° for one hour. The cooled reaction mixture was taken up in 150 ml. of boiling alcohol and then chilled. The solid that formed weighed 8.4 g. (40.6%) and melted at 137–138°, undepressed when mixed with an authentic sample of thiobenzmorpholide.[5]

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(5) For discussion of this type of oxidation see McMillan and King, submitted for publication in THIS JOURNAL.

(6) Wallach, *Ann.*, **259**, 300 (1890).

(7) Melting points uncorrected.

(8) Analyses performed under the direction of Mr. M. E. Auerbach.

(9) Moureu and Lazennec, *Bull. soc. chim.*, [3] **35**, 1183 (1906).

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK
RECEIVED APRIL 16, 1947

Diffusion Coefficient of Nitroglycerin in Rocket Powder and in Cellulose Acetate[1]

BY S. S. PENNER[2] AND S. SHERMAN[3]

Double base rocket powders, consisting of approximately 60% nitrocellulose, 40% nitroglycerin and some minor components, constitute one type of widely used rocket propellant. These powders burn easily over their entire exposed surface. In order to restrict burning to a preferred direction and thereby lengthen the total burning time it is necessary to cover a portion of the powder surface with a strongly bonded inert material such as cellulose acetate. These wrappings of cellulose acetate, though initially almost noncombustible, lose their protective action in the course of time because of the diffusion of nitroglycerin into the cellulose acetate. By determining the nitroglycerin concentration as a function of the distance from the cellulose acetate–powder interface at a given time, it is possible to ascertain the average diffusion coefficient of nitroglycerin in cellulose acetate and in powder. Knowledge of the maximum allowable nitroglycerin concentration in the cellulose acetate permits calculation of maximum safe storage times at all temperatures for which diffusion coefficients are available.

A complete experimental study was not carried through. In view of the limited experimental

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(1) This paper is based on OSRD report No. 4963 (PB report No. 50864) on the "Diffusion of Nitroglycerin in Wrapped Powder Grains." The diffusion study was carried out at the Allegany Ballistics Laboratory, Cumberland, Maryland, operated by the George Washington University under OSRD contract OEMsr-273. Analytical work was performed by J. J. Donovan and N. Marans.

(2) Present address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

(3) Present address: 413 Eckart Hall, University of Chicago, Chicago, Ill.

data available for calculation of the diffusion coefficient, an approximate treatment was employed which is strictly applicable only if the cellulose acetate and the powder have identical physical properties as regards the diffusion of nitroglycerin. The theoretical treatment of diffusion through a composite cylinder for the boundary values of interest in connection with the present study has been reported elsewhere.[4]

More extensive experimental investigations along the lines discussed in this report were carried out independently by B. H. Sage[5] and, at a later date, by J. J. Donovan.[5]

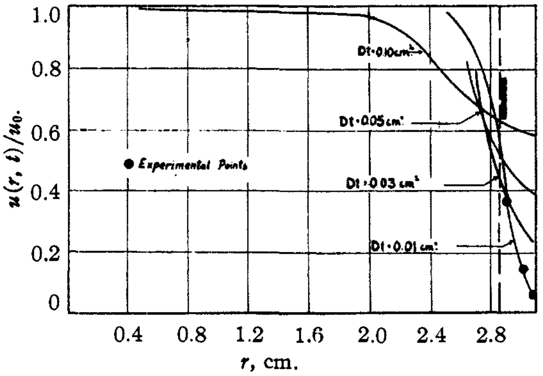

Fig. 1.—Comparison between experimental and calculated data.

Theoretical Treatment.—Consider an infinite cylinder of radius b surrounded by a cylindrical shell of thickness $c - b$. The initial concentration of diffusing material is U_0 in the cylinder and zero in the shell. From these data the boundary value problem may be formulated as follows[6]

$$\partial u/\partial t = D[\partial^2 u/\partial r^2 + (1/r)(\partial u/\partial r)],\ 0 \leqslant r < c,\ t > 0 \tag{1}$$

$$u(r,0) = U_0,\ 0 \leqslant r < b \tag{2}$$

$$u(r,0) = 0,\ b < r < c \tag{3}$$

$$\partial u(c - 0,t)/\partial r = 0 \tag{4}$$

Here $u(r,t)$ represents the concentration of diffusing material at any point at any time, D is the coefficient of diffusion, r is the radial distance from the axis of the cylinder, and t represents the time. Condition (4) arises from the assumption that no nitroglycerin is lost through the outer boundary of the cellulose acetate wrapping. The general solution of the problem specified by equations (1) to (4) may be written as[7]

$$u(r,t)/U_0 = b^2/c^2 + (2b/c^2) \sum_{j=1}^{\infty} J_1(\lambda_j b) J_0(\lambda_j r) e^{-D\lambda_j^2 t}/\lambda_j[J_0(\lambda_j c)]^2 \tag{5}$$

where the positive eigen values λ_j satisfy the condition

$$J_1(\lambda_j c) = 0$$

and J_0 and J_1 represent, respectively, Bessel functions of order zero and order one of the first kind.

Calculation of Diffusion Coefficient.—The particular grain of wrapped powder for which analyses for nitroglycerin were available consisted of a long cylindrical powder stick 2.858 cm. in radius, wrapped with cellulose acetate 0.228 cm. thick. The powder grain was stored for a period of two months at an average temperature close to room temperature. At the end of this time it was sectioned and nitroglycerin analyses were carried out according to U. S. Army Specification R11B. The material to be analyzed is extracted with ether. The ether in the extract is then replaced by glacial acetic acid. Finally, the nitroglycerin is reduced with ferrous chloride and the concentration of ferric ion determined with titanous chloride.

By use of equation (5) it is possible to calculate the ratio $u(r,t)/U_0$ as a function of r for various values of the parameter Dt. The results of this calculation are represented in Fig. 1. Since the storage time was two months or 1440 hours, D in sq. cm. per hour is 1/1440 of the value of Dt for which theoretical and experimental results agree. Reference to Fig. 1 indicates that a satisfactory value for Dt is 0.01 sq. cm. so that D is 7×10^{-6} sq. cm. per hour.

The theoretical curve for $Dt = 0.01$ sq. cm. lies considerably below the experimental points closest to the cellulose acetate–powder interface. This discrepancy may probably be ascribed to contamination during sectioning of the sample closest to the interface with some powder, thereby causing abnormally large values of the nitroglycerin concentration and also impairing the reproducibility of the results.

The curves for different values of Dt show that the theoretical curve is quite sensitive to the value chosen for Dt. In view of the close agreement between experimental and calculated curves for $Dt = 0.01$ sq. cm., it follows that the calculated value for the average diffusion coefficient in powder and cellulose acetate is of the correct order of magnitude.

The boundary value problem specified by equations (1) to (4) may be simplified for the particular powder grain used for the present study. Thus, the composite cylinder may be approximated by a powder slab of thickness b in contact with a slab of cellulose acetate of thickness $c - b$. The composite slab treatment leads to the same value for Dt as the cylindrical treatment given here. Equally good results are obtained if the powder is considered to be a semi-infinite solid. However, it is not permissible to represent the relatively thin cellulose acetate coating by a semi-infinite solid.

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RECEIVED JUNE 21, 1947

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(4) Penner and Sherman, *J. Chem. Phys.*, **15**, 569 (1947).

(5) Unpublished data in classified OSRD reports.

(6) For application of the Laplacian in cylindrical coördinates see Churchill, "Fourier Series and Boundary Value Problems," McGraw-Hill Book Co., New York, N. Y., 1941.

(7) For methods of solution of boundary value problems see ref. 1; also Byerly, "Fourier Series and Spherical Harmonics," Ginn and Co., London, 1893.

N-β-Bromoethylaniline Hydrobromide

BY WILLIAM M. PEARLMAN

Although a product designated[1,2] as N-β-bromoethylaniline hydrobromide has been reported to be formed by converting N-phenylethanolamine into its hydrobromide at 100° with gaseous hydrobromic acid and then heating to 150–160°, no identification was made and no yields were given. In addition, the indicated procedures are cumbersome. It was found that the desired product could be obtained in 85% yield from β-hydroxyethylaniline and hydrobromic acid by a slight modification of the procedure of Cortese.[3]

Experimental

β-Hydroxyethylaniline (100 g.) was precooled to 0° and 310 ml. of precooled (0°) 48% hydrobromic acid was added dropwise with stirring and cooling. When all of the hydrobromic acid had been added the mixture was distilled with an efficient fractionating column until a constant boiling distillate was reached. The residue was cooled slightly, placed in a large, open dish in a vacuum desiccator and evacuated with a water jet overnight. The resulting slurry was filtered and the solid recrystallized from absolute ethanol. The yield of nearly colorless needles was 180 g. (85.5%), m. p. 136–139°. A sample recrystallized from benzene was colorless, m. p. 137–138°.

Anal. Calcd. for $C_8H_{11}Br_2N$: C, 34.19; H, 3.95; N, 4.99. Found: C, 33.87; H, 4.16; N, 4.97.

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(1) French Patent 800,369; abstracted in *C. A.*, **30**, 8241^5 (1936).

(2) Julius v. Braun, *Ber.*, **70**, 979 (1937).

(3) "Organic Syntheses," Coll. Vol. II, 91, ed. by Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943.

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Oxidation–Reduction Potentials and Ionization Constants of the Reversible Series: Hexahydroxybenzene – Tetrahydroxyquinone – Rhodizonic Acid

BY PAUL W. PREISLER, LOUIS BERGER AND EDGAR S. HILL

Professor G. Schwarzenbach of the Universität at Zürich has recently called our attention to omission of reference in our publication[7] to the prior work and publication by Schwarzenbach and Suter[6] with the same substances. The oxidation–reduction potentials and ionization constants of this series of related compounds has been reported on several occasions.[1–7] It is regretted that there was no discussion of the work of Schwarzenbach and Suter[4,6] in our publications,[5,7] which oversight resulted from their being no abstract of the thesis of Suter[4] in *Chemical Abstracts* and no indication in the abstract[6a] of their joint publication[6] that they had worked with any compound of the rhodizonic acid series oxidation–reduction systems.

The two reports[6,7] differ mainly in the estimation of the ionization constants of rhodizonic acid. Our constants of $pK_1 = 4.1$ and $pK_2 = 4.5$ should be rejected in favor of those of Schwarzenbach and Suter, who found $pK_1 = 3.15$ and $pK_2 = 4.9$, since our values were estimated from the E_0'–pH curve of the rhodizonic acid–tetrahydroxyquinone system in a range where the curve is quite flat, while their values were determined by colorimetric and photometric methods.

Accepting their constants, 3.15 and 4.9, curves of $E_0' - p$H may be drawn which fit our experimentally determined points reasonably well. These changes do not affect the tetrahydroxyquinone–hexahydroxybenzene curve; the estimated ionization constant of tetrahydroxyquinone being unchanged at $pK_1 = 4.8$. Our E_0' values at $p\text{H} = 0$ become altered: for rhodizonic acid–tetrahydroxyquinone to $E_0' = +0.426$ volt (increase of $+0.016$) and for tetrahydroxyquinone–hexahydroxybenzene to $E_0' = +0.388$ volt (increase of $+0.008$).

These extrapolated values for $p\text{H} = 0$ and our measured potentials agree as well as may be expected for systems of this type with the potentials of Schwarzenbach and Suter. However, we experienced no difficulties in obtaining rapidly adjusting stable potentials in the entire pH range studied from 3.5 to 9.9. Therefore, where the slopes of our E_0'–pH curves are sufficiently well established, as for the tetrahydroxyquinone–hexahydroxybenzene system, we consider the ionization constants reported,[7] for tetrahydroxyquinone $pK_2 = 6.8$ and for hexahydroxybenzene $pK_1 = 9.0$, to be reliably estimated.

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(1) P. W. Preisler, E. S. Hill, E. Ronzoni and L. Young, *J. Biol. Chem.*, **123**, XCV (1938).

(2) G. E. Carpeni, Thesis, Paris, 1938.

(3) P. W. Preisler, *Cold Spring Harbor Symposia on Quantitative Biology*, **7**, 94 (1939).

(4) H. Suter, Thesis, Zürich, 1940.

(5) P. W. Preisler and L. Berger, paper presented at the meeting of the American Chemical Society, April, 1941; THIS JOURNAL, **64**, 67 (1942).

(6) G. Schwarzenbach and H. Suter, *Helv. Chim. Acta*, **24**, 617 (1941).

(6a) *Chemical Abstracts*, **35**, 7806 (1941).

(7) P. W. Preisler, L. Berger and E. S. Hill, THIS JOURNAL, **69**, 326 (1947).

DEPARTMENT OF BIOLOGICAL CHEMISTRY
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RECEIVED SEPTEMBER 15, 1947

Freezing Point Depression of Sulfuric Acid by Siloxanes

BY FRASER P. PRICE

Since sulfuric acid is used as an equilibrating agent in the preparation of silicones,[1] it is of interest to investigate the kinds of particles produced when siloxanes are dissolved in this acid. It was hoped that such an investigation would shed some light on the mechanism of siloxane rearrangement.

The molal freezing point depressions and the van't Hoff "*i*" factors in approximately 100% sulfuric acid were determined by the method of Hammett and Deyrup.[2] The only departure from their method was that the weight of solvent

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(1) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(2) Hammett and Deyrup, *ibid.*, **55**, 1900 (1933).

was determined by weighing the freezing point tube containing the solute and acid at the end of the run and subtracting the weight of solute and tube.

The nomenclature used in this paper is a modification of that developed in this Laboratory for the simplified representation of polymethylpolysiloxane structures[3]: M = $(CH_3)_3Si$, D = $(CH_3)_2Si$, T = CH_3Si, Q = Si. The results of the study are given in Table I.

TABLE I

VAN'T HOFF "*i*" FACTORS FOR SEVERAL SILOXANES IN 100% SULFURIC ACID

Solute	[Solute]	$[H_2O]$	ϑ(°C.)	*i*	*i* (av.)
MOM	0.0368	0.066	0.947	4.29	
	.0802	.066	2.053	4.27	4.28
$(DO)_4$	$.148 \times 10^{-3}$	.134	0.277	11.88[a]	
	$.487 \times 10^{-3}$	.134	0.965	12.60	
	1.01×10^{-3}	.134	1.951	12.58	12.59
$(MO)_3T$	8.59×10^{-3}	.092	0.425	8.20	
	21.0×10^{-3}	.092	1.035	8.25	
	39.0×10^{-3}	.092	1.874	8.23	8.23
$(MO)_4Q$	7.84×10^{-3}	.092	0.449	9.48	
	15.66×10^{-3}	.092	0.889	9.46	
	$26.6 \quad 10^{-3}$	.092	1.507	9.57	9.50

[a] This figure rejected as it is too far out of line.

Previous work with silyl sulfates[4] shows that only the normal sulfate is isolated when hexamethyldisiloxane is treated with sulfuric acid. However, the freezing point data for this siloxane indicate that the major reaction is

$$\text{MOM} + 3H_2SO_4 \longrightarrow 2MHSO_4 + H_3O^+ + HSO_4^- \quad (1)$$

which gives an "*i*" of 4. The slightly higher value observed is presumably due to the partial ionization of the $MHSO_4$. If the formation of the normal sulfate were the major reaction, then an "*i*" of only 3 would be observed or it would be necessary to assume that the reaction

$$M_2SO_4 \longrightarrow M^+ + MSO_4^-$$

went to completion in order to explain the observed value. Furthermore, it seems highly improbable that in this acid medium anything other than the acid sulfate could exist in appreciable quantity. It is more likely that the previous workers' results are due to the normal sulfate having a much higher solubility than the bisulfate in the extracting solvents. Hence, any small amount of sulfate that was formed would be removed and the equilibrium would shift to make up the deficiency.

The result obtained with the cyclic tetramer $(DO)_4$ is explained by the reaction

$$(DO)_4 + 12H_2SO_4 \longrightarrow 4D(HSO_4)_2 + 4H_3O^+ + 4HSO_4^- \quad (2)$$

The deviation from the integral value of 12 is probably due to ionization of the $D(HSO_4)_2$.

The deviations of the "*i*" factors from integers for both MOM and $(DO)_4$ are 0.28 and 0.59, respectively. However, when these deviations are made comparable by dividing by the number of silicon atoms, practically identical values are obtained. It then appears that the ionizations of $MHSO_4$ and $D(HSO_4)_2$ both proceed to about the same extent and that the replacement of methyl by bisulfate has little effect.

The two remaining siloxanes contain units capable of producing a three dimensional network Furthermore, these networks, if they form, will be quite insoluble in the acid. If these siloxanes reacted in a manner analogous to the two discussed above, the "*i*" factors should be 10 and 13 for $(MO)_3T$ and $(MO)_4Q$, respectively. Since the observed values are much lower, it is obvious that some type of polymerization must have occurred to remove T or Q units.

For the $(MO)_3T$ case the equations which most closely approximate the observed "*i*" value are

$$(MO)_3T + 6H_2SO_4 \longrightarrow 3MHSO_4 + \frac{1}{x}[T(HSO_4)O]_x + 2H_3O^+ + 2HSO_4^- \quad (3)$$

$$(MO)_3T + 7.5H_2SO_4 \longrightarrow 3MHSO_4 + 0.5[T(HSO_4)_2]_2O + 2.5H_3O^+ + 2.5HSO_4^- \quad (4)$$

Assuming that x in Equation 3 is large, these equations give values of "*i*" of 7 and 8.5 for Equations 3 and 4, respectively. It is, therefore, probable that both these reactions take place.

Consideration of the possible reactions for the $(MO)_4Q$ system leads to

$$(MO)_4Q + 7.5H_2SO_4 \longrightarrow 4MHSO_4 + \frac{.5}{x}[Q_2(HSO_4)_2O_3]x + \frac{5}{2}H_3O^+ + \frac{5}{2}HSO_4^- \quad (5)$$

$$(MO_4)Q + 9H_2SO_4 \longrightarrow 4MHSO_4 + \frac{1}{x}[Q(HSO_4)_2O]_x + 3H_3O^+ + 3HSO_4^- \quad (6)$$

with "*i*" factors of 9 and 10 for Equations 5 and 6, respectively. Whereas in the case of the $(MO)_3T$ the reaction lay between the cyclic polymer, $[T(HSO_4)O]_x$ and the dimer, $[T(HSO_4)_2]_2O$, here it lies between the three-dimensional gel and the cyclic polymer. In no case, however, does the number of HSO_4 radicals attached to silicon exceed two.

When freshly prepared polysiloxane hydrolysates are equilibrated with sulfuric acid, catalytic amounts, *ca.* 5%, of 95% acid are used. Hence, the conditions observed in the freezing point experiments are not exactly those prevailing during equilibration. In spite of these differences, in view of the non-integral values of "*i*" for MOM and $(DO)_4$ a probable active intermediate in the rearrangement is a positive siliconium ion which attacks the oxygen of the unreacted siloxane, forming a new Si–O bond and ejecting a new siliconium ion which repeats the process.

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RECEIVED JULY 21, 1947

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[3] Sauer, THIS JOURNAL, **68**, 954 (1946).

[4] Sommer, Pietrusza, Kerr and Whitmore, *ibid.*, **68**, 156 (1946).

A Side Reaction of Acid Hydrazides in Qualitative Organic Analysis

BY LOUIS SATTLER AND F. W. ZERBAN

In the course of the identification of small amounts of carbonyl derivatives obtained from heated fructose solutions which had been subsequently fermented with baker's yeast, *p*-nitrobenzhydrazide[1] and diphenylacethydrazide[2] were used.

With the *p*-nitrobenzhydrazide in 50% acetic acid, we obtained a small amount of a by-product of *s*-bis-(*p*-nitrobenzoyl)-hydrazine which crystallized in the form of yellow needles, and which on recrystallization from nitrobenzene melted at 288°.[3a] Previously reported melting points are 291°[3b] and 283°[3c].

Anal. Calcd. for $C_{14}H_{10}O_6N_4$: C, 50.91; H, 3.05. Found: C, 50.52; H, 3.21.

Similarly, diphenylacethydrazide in 60% ethanol plus 2 drops of glacial acetic acid[2b] yielded a white crystalline by-product of *s*-bis-(diphenylacetyl)-hydrazine. It was purified by recrystallization from a mixture of equal volumes of dioxane and 99% isopropyl alcohol. The pure crystals melted at 307°.

Anal. Calcd. for $C_{28}H_{24}O_2N_2$: C, 79.97; H, 5.75; N, 6.67. Found: C, 79.65; H, 5.60; N, 6.70.

Strain[4] has pointed out that while aqueous solutions of *m*-nitrobenzhydrazide are stable over long periods of time, strong acid solutions and elevated temperatures cause the formation of the symmetrical *bis*-hydrazine. It is evident that in addition to the normal reaction of acid hydrazides, a side reaction can also take place even in the absence of prolonged heating or strong acids. The ease with which these by-products are formed and isolated complicates the identification of expected derivatives. Consequently, due caution should be exercised in using hydrazides as derivatives of carbonyl compounds.

The authors express their thanks to Dr. Francine Schwartzkopf for the micro analyses.

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[1] Eastman Kodak Co., #3341.

[2a] Aspelund, *Ber.*, **63B**, 1197 (1930), has described this compound but we found it more convenient to prepare it from ethyl diphenylacetate according to the general procedure (b) Sah and Ma, *J. Chinese Chem. Soc.*, **2**, 40 (1934).

[3a] The melting points are uncorrected.

[3b] Dann and Davies, *J. Chem. Soc.*, 1050 (1929).

[3c] Heller and Ebeling, *J. prakt. Chem.*, **142**, 274 (1935).

[4] Strain, THIS JOURNAL, **57**, 758 (1935).

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RECEIVED NOVEMBER 6, 1947

4-Phenyl-*m*-dioxane

BY ROBERT W. SHORTRIDGE

4-Phenyl-*m*-dioxane is produced in small amounts when styrene and formaldehyde react in acetic acid solution in the presence of a mineral acid catalyst such as sulfuric acid. The major product is 1-phenyl-1,3-diacetoxypropane, formed by the participation of the acetic acid in the reaction.

Prins,[1] in his original study of this reaction, erroneously formulated the products as derivatives of 2-phenyl-1,3-propanediol. Later, Fourneau, Benoit and Firmenich[2] proved their correct structure as derivatives of 1-phenyl-1,3-propanediol. Recently the structure of these compounds has been discussed by Emerson[3] on the basis of the results of the earlier workers.

It became necessary in the course of some research in this Laboratory to prepare moderate amounts of 4-phenyl-*m*-dioxane. To this end it was decided to study the reaction of Prins with a view to increasing the yield of the desired compound and the convenience of obtaining it.

An obvious change in the Prins procedure was to employ an inert mutual solvent in place of the acetic acid; such a change, of course, would eliminate entirely the formation of the undesired 1-phenyl-1,3-diacetoxypropane. It might be expected that the corresponding glycol would be formed under these changed conditions; this, however, proved not to be the case. When styrene and formaldehyde (in the form of trioxane) in a molar ratio of 1:2 were allowed to stand at room temperature in dioxane solution in the presence of sulfuric acid, a 78% yield of 4-phenyl-*m*-dioxane was obtained. There was no evidence of glycol formation and the remainder of the yield was accounted for by the production of polymers of styrene and of formaldehyde.

In a further step toward simplification the mutual solvent was eliminated completely and the reaction was run as a heterogeneous system, containing styrene, 37% aqueous formaldehyde and sulfuric acid. It was found necessary in this instance to work at reflux temperature. Carried out under these conditions the reaction yielded a maximum of 88% of 4-phenyl-*m*-dioxane. The sole identifiable by-products were polymers of styrene and of formaldehyde.

Since the completion of these studies, a patent[4] has issued claiming the preparation of a phenyl-*m*-dioxane in undisclosed yield by the reaction of styrene and 37% aqueous formaldehyde in the presence of hydrochloric acid and an inert hydrocarbon diluent. It is stated that only resinous products are obtained in the absence of the diluent. It appears, however, that under the conditions specified in the present paper the use of such a diluent is unnecessary.

Experimental

Reaction in Dioxane Solution.—A mixture of 220 g. of dioxane, 32 g. of 96% sulfuric acid, 30 g. of trioxane (du Pont) and 52 g. of styrene (Dow N-99) was allowed to stand at room temperature over a week-end. At the end of this time the reaction mixture was poured into 600 ml. of water and the organic layer was separated. The aqueous layer was extracted with three 50-ml. portions of benzene and the combined organic layer and extracts were washed with three portions of water and distilled. After removal of the benzene 64 g. (78%) of 4-phenyl-*m*-dioxane was obtained, b. p. 94–104° at 3 mm.

Reaction as a Heterogeneous System.—A mixture of 104 g. of styrene, 300 ml. of 37% aqueous formaldehyde and 16 g. of 96% sulfuric acid was refluxed and stirred overnight. The organic layer was washed successively

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[1] Prins, *Proc. Acad. Sci. Amsterdam*, **22**, 51 (1919).

[2] Fourneau, Benoit and Firmenich, *Bull. soc. chim.*, **47**, 894 (1930).

[3] Emerson, *J. Org. Chem.*, **10**, 464 (1945).

[4] Engel, U. S. Patent 2,417,548 (March 18, 1947).

with dilute sodium carbonate solution, dilute sodium bisulfite solution and water. It was then dried by azeotropic distillation with 100 ml. of benzene. Further distillation yielded 144 g. (88%) of 4-phenyl-*m*-dioxane, b. p. 121–123° at 11 mm.

In several repetitions of the preceding preparation, the yields varied from 84 to 88%. The combined products were fractionated through a Vigreux column. A center cut from this distillation had these physical properties: b. p. 95° at 2 mm., n^{25}D 1.5288, d^{25} 1.101. Prins[1] reported b. p. 128–30° at 13 mm., n^{18}D 1.53063, d^{18}_4 1.1111.

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The Vapor Pressures of Solutions of Sodium and Potassium Bisulfates at 25°

BY R. H. STOKES

As part of a general study of the vapor pressure–concentration curves of a number of mono-sodium and mono-potassium salts of dibasic acids which is in progress in this Laboratory, isopiestic vapor pressure measurements have been made on sodium and potassium bisulfates. Owing to the relatively large second dissociation constant[1] of sulfuric acid ($K_2 = 0.012$ at 25°) these two salts have little in common with the others being investigated and are therefore reported separately.

Stock solutions of the two bisulfates were prepared by dissolving the calculated amount of the anhydrous normal sulfate in sulfuric acid which was previously analyzed by weight-titration against sodium carbonate. The resulting solutions were equilibrated (in platinum dishes) against sodium chloride as reference substance by the usual technique,[2] the molalities of pairs of solutions of equal vapor pressure being given in Table I. From these results and the standard values[3] for sodium chloride the vapor pressures at round concentrations were computed and are given in Table II in the form of $(p_0 - p)/mp_0$. A graph of this relative molal vapor pressure lowering against m shows a rapid rise below 1M as is to be expected in consequence of the increasing dissociation of the bisulfate ion with dilution. There seems, however, to be little justification for attempting a quantitative estimate of the amounts of the various ionic species present. The calculation of activity coefficients is also complicated by this dissociation which makes extrapolation to infinite dilution difficult. Consequently, though the data are of good accuracy (0.1–0.2%) no solute activity data derived from them are included in Table II.

TABLE I

(a) Isopiestic solutions of sodium bisulfate and sodium chloride at 25°

m_{NaHSO_4}	0.1041	0.1237	0.1482	0.1529	0.2039	
m_{NaCl}	0.1190	0.1400	0.1664	0.1713	0.2255	
m_{NaHSO_4}	0.2823	0.4272	0.6425	0.7774	1.084	1.174
m_{NaCl}	0.3078	0.4573	0.6763	0.8119	1.119	1.210
m_{NaHSO_4}	1.340	1.382	1.632	2.398	3.065	4.067
m_{NaCl}	1.376	1.420	1.671	2.456	3.138	4.140
m_{NaHSO_4}	4.191	5.112	5.240	5.610	6.320	
m_{NaCl}	4.265	5.122	5.228	5.555	6.147	

(b) Isopiestic solutions of potassium bisulfate and sodium chloride at 25°

m_{KHSO_4}	0.1068	0.1277	0.1361	0.1445	0.2423	0.4216
m_{NaCl}	0.1199	0.1425	0.1505	0.1595	0.2584	0.4311
m_{KHSO_4}	0.5287	0.7233	0.7538	1.002	1.156	1.502
m_{NaCl}	0.5300	0.7038	0.7307	0.9471	1.074	1.359
m_{KHSO_4}	1.664	1.827	2.259	2.653		
m_{NaCl}	1.485	1.614	1.943	2.235		

TABLE II

RELATIVE MOLAL VAPOR PRESSURE LOWERINGS $(p_0 - p)/mp_0$ OF SODIUM AND POTASSIUM BISULFATES AT 25° (CALCULATED RELATIVE TO p_1 = 23.756 MM.)

m	$NaHSO_4$	$KHSO_4$	m	$NaHSO_4$	$KHSO_4$
0.1	0.03838	0.03775	1.2	0.03425	0.03074
.125	.03778	.03722	1.4	.03435	.03035
.15	.03737	.03669	1.6	.03456	.03000
.2	.03671	.03589	1.8	.03482	.02977
.3	.03590	.03469	2.0	.03508	.02957
.4	.03537	.03384	2.5	.03582	.02916
.5	.03502	.03316	3.0	.03658	
.6	.03477	.03266	3.5	.03731	
.7	.03460	.03223	4.0	.03795	
.8	.03445	.03188	4.5	.03847	
.9	.03436	.03156	5.0	.03882	
1.0	.03432	.03129	6.0	.03912	

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RECEIVED SEPTEMBER 5, 1947

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[1] W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

[2] R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

[3] R. A. Robinson, *Trans. Roy. Soc. New Zealand*, **75** (II), 203 (1946); see also appendix to R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946).

Quinazolines. IV. Synthesis and Hydrolysis of 3-(4'-Quinazoyl)-4-quinazolone[1]

BY ARTHUR J. TOMISEK AND BERT E. CHRISTENSEN

In the attempts to prepare 4-cyanoquinazoline by fusion of 4-chloroquinazoline with either silver or cuprous cyanide[2] only small amounts of a fibrous material were isolated. This product appeared to be pure, and analysis suggested that it might be a diquinazolyl ether. Since 4-chloroquinazoline is easily hydrolyzed by traces of water, it is possible to account for diquinazolyl ether as resulting from the condensation of the 4-chloroquinazoline with small amounts of hydroxyquinazoline impurity.

There is no record in the literature of a diquinazolyl ether. Bogert and May attempted the syn-

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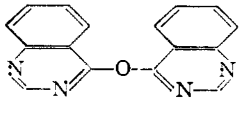
[1] Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 115, School of Science.

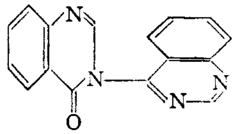
[2] Tomisek and Christensen, THIS JOURNAL, **67**, 2114 (1945).

thesis by refluxing sodium 4-quinazolonate with 4-chloroquinazoline in a benzene medium.[3] Attributing their failure to the insolubility of sodium 4-quinazolonate in benzene, the work was repeated in this laboratory using a dry dioxane solvent. This modified procedure gave a product which was found to be identical with that resulting from the cyanide fusions.

A diquinazolyl ether synthesized as above could have either of two possible structures: di-4-quinazolyl ether (I) or 3-(4'-quinazolyl)-4-quinazolone (II). Among the alkylquinazolyl ethers, O-ethers (I) or N-ethers[4] (II) are synthesized depending on which radical contains the halide and which the —ONa group (Fig. 1). When both radicals are quinazolyl, analogy to the alkylquinazolyl ethers fails to distinguish between the two possible isomers.



I



II

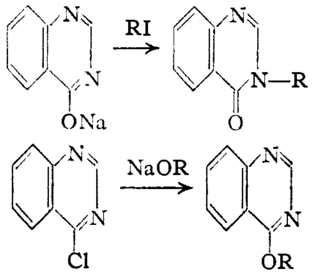


Fig. 1.

O-Ethers are very easily cleaved by acid in contrast to N-ethers which are stable.[3] The diquinazolyl ether prepared above reacted very readily with dilute hydrochloric acid to yield almost quantitatively a product ($C_{15}H_{13}N_3O$) which contained a quinazoline unit bound apparently to a degraded quinazoline nucleus. The failure to obtain 4-hydroxyquinazoline as the hydrolysis product, together with the fact that the two nuclei remain attached after hydrolysis, suggests an N-ether type of linkage. The stability of the ether toward boiling alcohol or water and to dry heat (m. p. 232° without decomposition or rearrangement) lends additional support to this point of view. The O-ethers are generally unstable under these conditions.[5]

Experimental[6]

3-(4'-Quinazolyl)-4-quinazolone.—Twelve and seventenths grams of 4-hydroxyquinazoline was added to a solution containing 4.5 g. of potassium hydroxide (0.08 mole) in 75 ml. of absolute alcohol. The solvent was then removed on a steam-bath and the quinazolinate throughly dried under high vacuum. One hundred milliliters of dry dioxane and 14.6 g. of 4-chloroquinazoline (0.088 mole) were added to the pulverized residue and the mixture was refluxed for three days. Potassium chloride was removed by filtration while the reaction mixture was still hot. 3-(4'-Quinazolyl)-4-quinazolone separated from the liquors on cooling. Additional product was obtained by evaporating the mother liquors to dryness. The combined fractions were then triturated with dilute sodium hydroxide solution. The crude product (16.1 g., 74%), purified by charcoal treatment of a hot alcohol solution, yielded 14.1 g. (64%) of pure 3-(4'-quinazolyl)-4-quinazolone. The product recrystallized from alcohol as thin, wool-like fibers, m. p. 232.5°, was insoluble in water, soluble in both dioxane and hot benzene. It was stable to long boiling in water.

Anal. Calcd. for $C_{16}H_{10}N_4O$: C, 70.06; H, 3.68; N, 20.43: Found, C, 70.02; H, 3.85; N, 20.43.

Acid Hydrolysis Product of 3-(4'-Quinazolyl)-4-quinazolone.—The 3-(4'-quinazolone)-4-quinazolone (10.6 g.) was dissolved in hot dilute hydrochloric acid. In a few seconds the hydrochloride of the cleavage product precipitated. The mixture was cooled and filtered. The solid material and liquors were separately treated with excess sodium bicarbonate. The free base was then filtered, washed with water and dried. Combined fractions amounted to 9.3 g. (96%) of the crude product. After recrystallization from pyridine–water, fine, white, needle-like crystals melting at 244–225° were obtained.

Anal. Calcd. for $C_{15}H_{13}N_3O$; C, 71.69; H, 5.21; N, 16.72; mol. wt., 251. Found: C, 71.69; H, 5.23; N, 16.87; mol. wt.,[7] 255, 232, 257.

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[3] Bogert and May, This Journal, **31**, 507 (1909).

[4] For other examples of this terminology, see ref. 3, p. 508.

[5] Bogert and Seil, This Journal, **29**, 526 (1907).

[6] All melting points are corrected. All N-analyses are by the Dumas method.

[7] Niederl and Niederl, "Micromethods of Quantitative Organic Analysis," 2d ed., John Wiley & Sons, New York, N. Y., 1942, p. 217.

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Investigation of the Oxidative Condensation of 2-Methoxy-4-nitrotoluene. The Use of Oxidative Catalysts

By Gino R. Treves

The oxidation of various substituted 4-nitrotoluenes to stilbenes was described by Green and Baddiley.[1] They also prepared 2,2'-dimethoxy-4,4'-dinitrostilbene by a two stage air oxidation of 2-methoxy-4-nitrotoluene. Recently Ashley and Harris[2] repeated the work of Green and Baddiley but were unable to obtain the stilbene. They report that the reaction ceased at the bibenzyl stage. When we carried out the reaction only minute quantities of condensation products were obtained. It was then decided to run the reaction with oxygen instead of air under more carefully controlled conditions.

The reaction mixture was shaken in the Adams shaker and the rate of oxygen consumption observed. The contact was continued for twenty-two hours and the product consisted of a mixture of the bibenzyl and the stilbene in 30% yield.

Compounds of high oxidation potential were tried in the hope that they would catalyze the reaction by functioning as hydrogen carriers. Results are shown in Fig. 1. Of special interest was the fact that cyclohexanol was almost as effective as cyclohexanone. This indicates that cyclo-

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[1] Green and Baddiley, *J. Chem. Soc.*, **93**, 1721 (1908).

[2] Ashley and Harris, *ibid.*, 567 (1946).

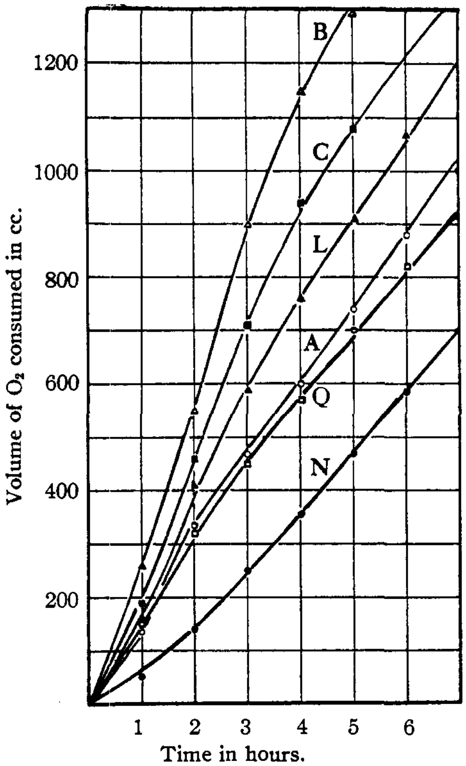

Fig. 1.—Effect of the addition of 0.001 M quantities of oxidation catalysts on the oxygen uptake in the oxidative condensation of 2-methoxy-4-nitrotoluene: ●, no catalyst, N; □, anthraquinone, Q; ○, acetone, A; ▲, cyclohexanol, L; ■, cyclohexanone, C; △, benzoquinone, B.

hexanol may be oxidized first to cyclohexanone which then acts as a catalyst. The total oxygen consumption was well above the expected theoretical amount. Therefore, oxygen was also used up in some side reaction.

Atmospheric oxygen as in the original method[1] was then tried in the presence of a catalyst and it proved to be effective. When benzoquinone was used and air bubbled through the reaction mixture for seven hours a 55% yield of the bibenzyl was obtained. When acetone was used and air bubbled through for twenty-two hours, 60% yield of a mixture of two parts of the bibenzyl and one part of the stilbene was obtained.

Experimental

Preparation of 2,2'-Dimethoxy-4,4'-dinitrobibenzyl.—Air is bubbled through a suspension of 10 g. of pure 2-methoxy-4-nitrotoluene in 200 ml. of 33% solution of methanolic potassium hydroxide containing one gram of benzoquinone for seven hours. The product is filtered, washed with dilute hydrochloric acid then with hot methanol and recrystallized from ethyl acetate, m. p. 179°; yield 5.5 g. On bromination it gives α,α'-dibromo-2,2'-dimethoxy-4,4'-dinitrobibenzyl, m. p. 247–249°.

Preparation of 2,2'-Dimethoxy-4,4'-dinitrobibenzyl and 2,2'-Dimethoxy-4,4'-dinitrostilbene.—Forty grams of 2-methoxy-4-nitrotoluene is placed in 800 ml. of 33% methanolic potassium hydroxide and 20 ml. of acetone. The mixture is well stirred and air is bubbled through at room temperature. After twenty-two hours the precipitate is filtered off. The mixture is then taken up in boiling ethyl acetate which dissolves the bibenzyl. The stilbene is filtered off and weighs 7.5 g. On cooling 16 g. of bibenzyl is collected from the ethyl acetate. The stilbene on bromination gives the same α,α'-dibromo-2,2'-dimethoxy-4,4'-dinitrobibenzyl as was obtained by brominating the bibenzyl.

Procedure Followed to Determine the Rate of Oxygen Consumption (see Fig. 1).—Ten grams of 2-methoxy-4-nitrotoluene and 0.001 M quantities of the different oxidation catalysts were placed in 200 ml. of 33% methanolic potassium hydroxide and shaken for twenty-two hours in the Adams shaker in the presence of oxygen at atmospheric pressure. The yield of mixture of the bibenzyl and the stilbene for all the catalysts tried varied between 30% and 38%. The mixture contained about equal quantities of the two substances.

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COMMUNICATIONS TO THE EDITOR

STUDIES ON THE MECHANISM OF THE DEAMINATION OF DIAZONIUM SALTS WITH HYPOPHOSPHOROUS ACID

Sir:

In an attempt to introduce a deuterium atom into the *meta* position of nitrobenzene, a deamination reaction with hypophosphorous acid[1] was carried out. Thus, to a solution of diazotized *m*-nitroaniline containing 30% deuterium oxide was added a solution of hypophosphorous acid in water which contained 50% of deuterium oxide. Before use the hypophosphorous acid solution was allowed to stand at room temperature for twenty-four hours. Much to our surprise *the nitrobenzene which was obtained was found to contain no deuterium.* This was determined for us by Mrs. James L. Johnson and Dr. Foil A. Miller with an infrared spectrometer.[2] Similarly, aniline hydrochloride prepared from this sample of nitrobenzene was found to show no absorption in the region of the C–D stretching frequencies (2270 cm.$^{-1}$).

We are not yet in a position to comment on the mechanism of the reaction, but this result is par-

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[1] See Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 277.

(2) The lower limit of the sensitivity of this method for the detection of deuterium in an aromatic ring has not yet been completely determined. From dilution experiments conducted with deuterobenzene in benzene, however, it appears that if 1–2% of the nitrobenzene molecules contained deuterium, it could be detected.