

retitrated as before. This process was repeated three more times; 200 mg. of crystals was obtained. They were dissolved in alcohol and reprecipitated with distilled water, m. p. 175°.

Anal. Calcd. for $C_{20}H_{18}O_7$: C, 64.83; H, 4.9. Found: C, 64.93; H, 5.08.

Dibenzylideneglucose from 4,6-Benzylideneglucose.—4,6-Benzylideneglucose (2.1 g.) previously dried over phosphorus pentoxide was mixed with phosphorus pentoxide (2 g.) in a dry Erlenmeyer flask. All precautions were taken to avoid moisture. To this mixture was added freshly distilled benzaldehyde (7 cc.), previously cooled to 0°. The reaction flask was stoppered quickly and shaken in an ice-water-bath for ten minutes. Then it was taken out of the ice-bath and shaken twenty minutes at room temperature. Dry ether was added to extract the substance and the ether solution was washed with saturated sodium chloride solution made alkaline with a little ammonium hydroxide. The ether layer was separated and, after partially evaporating the ether, petroleum ether was added. The crystals formed were separated, boiled with water, filtered off from the hot water and then recrystallized from ether and finally from methanol, m. p. 163°. It does not reduce Fehling's solution. Mixed melting points of this substance were tried (a) with dibenzylideneglucose from the mercaptoglucose method before the oxidation to dibenzylideneglucuronic acid, m. p. 143–148°, and (b) with the residue which had not oxidized, m. p. 142–148°; mixed melting points of dibenzylideneglucose from (a) with residue from (b), m. p. 163°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 67.39; H, 5.92.

The author wishes to express his appreciation to Dr. L. Zervas for the interest which he has shown in this work, and to Mr. D. Rigakos of the Rockefeller Institute for Medical Research for the microanalyses for carbon and hydrogen.

Summary

1. 6-Monobenzoyldibenzylideneglucose was prepared by treating 6-monobenzoyldiethylmercaptoglucose with benzaldehyde and anhydrous zinc chloride. It does not reduce Fehling's solution.
2. Dibenzylideneglucose was prepared from 6-monobenzoyldibenzylideneglucose. The compound does not reduce Fehling's solution.
3. Dibenzylidene glucose was oxidized to dibenzylideneglucuronic acid.
4. Dibenzylideneglucose was prepared from 4,6-benzylideneglucose. It does not reduce Fehling's solution. It was found to differ from the dibenzylideneglucose prepared from 6-benzoyldiethylmercaptoglucose.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

On 1,2- and 1,4-Addition.¹ II. Nitrogen Tetroxide and Trimethylethylene

BY ARTHUR MICHAEL AND G. H. CARLSON

Probably no other reagents act so diversely upon ethylenic hydrocarbons as the higher oxides of nitrogen and the reactions, although repeatedly investigated, are still understood very incompletely. The relative negativity of the possible addenda components, formed by intramolecular fission of nitrogen tetroxide, should decrease in the order. $ONO_2 > ONO > NO_2 > NO$ and, correspondingly, the polarity differences between the paired addendum groups of the following combinations should decrease as follows: $ONO_2 + NO > ONO + NO_2$. Alkenes in which the polarities of the Δ -carbons differ considerably should, therefore, add the tetroxide to form the nitroso-nitrate and less of the nitro-nitrite. This relationship has not been realized experimentally with alkylenes owing, largely, to the protean chemical character of the addendum. It may

(1) For a previous paper in this series see, THIS JOURNAL, 59, 744 (1937).

function not only as the balanced system $2NO \rightleftharpoons O_2N-O-NO$, but as a powerful oxidant upon the alkene; further, as a polymerizing reagent upon alkenes easily susceptible to that process and the polymers may be reacted upon by the tetroxide.

Schmidt² passed the gas formed by heating lead nitrate into a cooled, ether solution of trimethylethylene until "saturated" and obtained mainly a greenish-blue oil with a varying yield (maximum 25%) of crystalline trimethylethylene nitrosate.³ This compound was shown

(2) Schmidt, *Ber.*, 35, 2336 (1902). Guthrie [*J. Chem. Soc.*, 13, 35, 129 (1861)] by the action of nitric acid, or of nitrogen tetroxide, upon trimethylethylene obtained, besides unidentified oily products, a colorless crystalline compound $C_6H_{10}N_2O_4$. This substance was prepared by Wallach [*Ann.*, 262, 324 (1891)] by the action of nitric acid upon a solution of the alkene and isoamyl nitrite in acetic acid. From its chemical behavior, Wallach concluded the product is $C_6H_{10}(NO)(ONO_2)$ or $C_6H_9(=NOH)(ONO_2)$.

(3) The strongly oxidative, undried gas was used in a large excess and the solution stood at room temperature for a long time. Besides oxygen, nitrous and nitric acids were introduced into the reaction

TABLE I

| Expt. no. | I | II | III | IV | V | VI | VII | VIII | |
|------------------------|--------|-------|------|------|------|----------|----------|-----------|-----|
| Tetroxide, g. | 18.8 | 19.4 | 22.2 | 19.8 | 11.0 | 21.0 | 8.0 | 2.4 | |
| Amylene { g. | 20.0 | 25.0 | 25.0 | 20.0 | 12.0 | 22.0 | 20.0 | 8.0 | |
| Excess { % | 40.0 | 69.0 | 48.0 | 32.0 | 43.0 | 37.5 | 230 | 340 | |
| Solvent, cc. { Ether | 150 | 75 | 100 | | | No solv. | No solv. | Gas phase | |
| Solvent, cc. { Petrol | | | | 150 | 100 | | | | |
| Temp., °C. | -15 | -15 | -2 | -15 | 0 | -7 | -80 | 30 | |
| Time of addition, min. | 60 | 60 | 180 | 60 | 330 | 90 | 120 | 120 | |
| Product, g. { | Solid | 0.05 | 2.1 | 3.2 | 12.3 | 7.6 | 18.1 | 6.1 | 2.0 |
| | Liquid | 36.3 | 35.0 | 39.0 | 21.0 | 12.0 | 18.7 | 8.0 | 1.2 |
| | Total | 36.35 | 37.1 | 42.2 | 33.3 | 19.6 | 36.8 | 14.1 | 3.2 |
| | Calcd. | 33.2 | 34.2 | 39.2 | 34.9 | 19.4 | 37.0 | 14.1 | 4.2 |
| Nitrosate, % | 0.15 | 6.2 | 8.2 | 35.2 | 39.2 | 49.0 | 43.2 | 47.6 | |

by Schmidt to be dimeric in a cold, colorless solution, but to dissociate appreciably, at 30°, into the blue, monomeric form. When fused, the bis-nitrosate, in contrast to the bis-nitrosite,⁴ could not be depolymerized, but completely decomposed; accordingly, only in a dilute solution is there any indication of the existence of the monomeric form. Yet, Schmidt concluded that the main reaction product, the greenish-blue oil, principally because of its color and because a small amount of the bis-nitrosate gradually separated from the oil, consisted, mainly, of the monomeric trimethylethylene nitrosate, notwithstanding that the oil could not be purified, did not analyse correctly, became discolored and decomposed on standing.

Schmidt believed that the polymerization of the mono- to the bis-nitrosate was a slow process, but Klingstedt⁵ noticed that the separation of the bis-nitrosate was complete after two to four hours and concluded that the blue oil is not the monomeric nitrosate. In support of this view, he showed that the bis-nitrosate with aniline gave trimethylethylene nitrolamine, whereas the blue oil gave undefined products.

Previous work^{2,6} has shown that reduction with metals, in acidic, basic or neutral media, is generally not a satisfactory method for establishing the structure of the nitrogen tetroxide addition products. Catalytic reduction, too, under varied conditions, gave us indefinite results; ammonia was formed invariably and amines were isolated in yields too low to permit of identification. Since potassium thio-

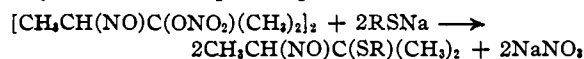
mixture. Wieland [*Ber.*, **54**, 1782 (1921)] stated that nitrogen tetroxide acts upon ether with formation of nitrous and nitric ethyl esters; accordingly, at least six reactants were present in Schmidt's experiments, which cannot be considered, therefore, as representing the addition of nitrogen tetroxide to trimethylethylene.

(4) Schmidt, *ibid.*, **35**, 2323 (1902).

(5) Klingstedt, *ibid.*, **58**, 2363 (1925).

(6) Demjanov, *Ann., Inst. Agronomique Mos.*, **4**, 155 (1899).

phenylate reacts with benzyl nitrate and yields potassium nitrate and benzyl phenyl sulfide quantitatively,⁷ it seemed probable that the mercaptide might be used to characterize ester groups formed in the addition of nitrogen tetroxide to alkenes. Sodium thiophenylate and the ethyl mercaptide replace, quantitatively, the nitric ester radical in bis-trimethylethylene nitrosate to yield the corresponding thio ethers



The thio ethers gave colorless solutions in hot benzene, but were partially associated in the freezing solvent, in this respect behaving like β -triazole- β -methylbutan- γ -oxime.⁸ The thio ethers unite rapidly with phenyl isocyanate to form the corresponding urethan derivatives, but this reaction does not prove the presence of an isonitroso group in the original thio ether, for the isocyanate cannot differentiate with certainty between nitroso and isonitroso groups in compounds easily capable of tautomerization. A summary of the experimental details of this work is given in Table III. The mercaptide reaction, however, is not of general applicability; with some of the liquid, nitrogen tetroxide addition products, oxidative reactions occurred, resulting in formation of disulfides, as the main and sometimes the only product of reaction which could be identified.

Anhydrous, pure nitrogen tetroxide, distilled into cold ether solutions of trimethylethylene, in excess of equimolecular proportion, formed blue solutions from which bis-trimethylethylene nitrosate separated in varying yields. Typical results are given in Table I.

The maximum yield of bis-nitrosate (8.2%) appeared in experiment III, but under equally

(7) T. Carlson, *Ber.*, **40**, 4191 (1907).

(8) Forster and Gelderen, *J. Chem. Soc.*, **99**, 239 (1911).

favorable conditions (II) the yield was 2% lower and only a negligible amount was formed in experiment I. No general relation can be discerned between the yield of bis-nitrosate and the experimental conditions. The yield of bis-nitrosate was invariably higher (35.2–39.2%) when petrol was used as diluent (experiments IV and V). Since the bis-nitrosate is difficultly soluble in petrol and only slightly more so in ether, the large variation between yields of bis-nitrosate formed in the two solvents cannot depend solely upon the slight difference between the solubility in the respective solvents. Without solvent, the amount of bis-nitrosate formed at -80° (experiment VII) was 5.8% lower than that produced at -7° (experiment VI) and 4.4% less than that formed slightly above room temperature in a gas phase reaction (experiment VIII). In these experiments, again, no direct relation appears between the yield of bis-nitrosate and the experimental conditions. Since in the absence of a diluent a variation of temperature of about 100° alters the yield of solid product by only 4.4%, the actual yield fluctuating between 43.2–47.6%, whereas the maximum yield produced in ether solution was only 8.2%, evidently, the effect of solvent upon the course of addition of nitrogen tetroxide to alkenes is far greater than that of the reaction temperature.

A comparison of the results obtained in petrol solution with those obtained without solvent, or in the gas phase, shows unmistakably that the degree of dissociation of the addendum has no material influence upon the extent of the bis-nitrosate formation. At -7° , without solvent, conditions under which the addendum consisted almost entirely of O_2N-ONO , 49% of the bis-nitrosate appeared, while in the gas phase, where the tetroxide was considerably more dissociated, almost the same percentage of the bis-nitrosate was formed; even at -80° , the proportion of bis-nitrosate differed but slightly. From these, and results with other ethylenic hydrocarbons, it is evident that the course of the addition depends only slightly upon the relative proportions in which the components of the addendum appear in the equilibrium, $2NO_2 \rightleftharpoons O_2N-ONO$; apparently, the dominant chemical factor is the relative polarity of the Δ -carbons of the alkene. In no experiment with trimethylethylene did we succeed in isolating a dinitro addition product, nor a corresponding dinitrite.

The green oils formed in petrol solution decomposed so easily that purification by fractionation was impossible, nor could the oily products obtained from the crude oils by benzylation, or treatment with acetic anhydride and sulfuric acid, be identified. According to Schaarschmidt and Hofmeier,⁹ the action of nitrogen tetroxide upon alkenes is more complex and the products less stable, the lower the reaction temperature. However, on adding the tetroxide to reaction mixtures cooled only to 0° , the yield of bis-nitrosate (39.2%) obtained approximated that found (35.2%) at -15° : the liquid products slowly decomposed, even at 0° , liberating a colorless gas and depositing a small amount of ammonium nitrate. Although decomposing slowly, the liquid product in one experiment was subjected to distillation at the pressure of a mercury pump and the volatile as well as the non-volatile oil treated with sodium thiophenylate in alcoholic solution, but organic sulfur derivatives suggestive of the constitution of the original, green addition product could not be isolated. Likewise, in the absence of diluent, other than excess trimethylethylene, green, unstable oils were formed which could not be identified: the oils deposited ammonium nitrate, at 0° , and decomposed with evolution of nitrous fumes when subjected to steam distillation. The green liquid distilled at the pressure of the mercury pump and at 30° to give a blue distillate and a non-volatile, yellow oil, neither of which could be identified directly, nor through the reaction products formed with sodium thiophenylate. We were, therefore, unable to determine whether these oils contained the blue product and the nitro-nitrite formed in the presence of ether.

The blue oil, formed by interaction of nitrogen tetroxide and trimethylethylene in ether solution, is a mixture and may be separated by distillation into an easily volatile, blue and a less volatile, greenish oil. A summary of a typical fractionation is given in Table II. Although the refractive index of the blue oil, purified by repeated fractionation, indicated that the material was nearly pure after one fractionation, yet the empirical constitution (approximate formula, $C_6H_8NO_2$) could not be established from the values obtained on analysis. Molecular weight determinations in freezing benzene gave the values 120 and 112, which indicate that the blue oil is monomeric

(9) Schaarschmidt and Hofmeier, *Ber.*, **66**, 1047 (1925).

and of lower molecular weight than monomeric trimethylethylene nitrosate. The deep blue coloration is characteristic of monomeric nitroso derivatives, but, whereas the latter generally polymerize to crystalline solids, the purified, blue oils did not solidify at -80° . The catalyst and the experimental conditions were varied, but catalytic hydrogenation invariably stopped when relatively a small amount of hydrogen was absorbed and ammonia was the only reaction product identified; reduction with metals gave no better results. The blue oil is inert toward hot formic acid and 40% hydrobromic acid, did not react with phenyl isocyanate, nor with dimethylaniline. With phenylhydrazine and semicarbazide, oxidation occurred and the products could not be identified. Samples of blue oil separated from the reaction mixture by steam distillation had properties and gave results on analysis which compare favorably with those of preparations purified by low pressure distillation (Table II). In contrast, bis-trimethylethylene nitrosate is completely decomposed by steam distillation and under no conditions could it be depolymerized to a stable, blue oil. Attempts to convert the blue oil to a more stable product, by treatment with ozone, gave mixtures which could be separated only incompletely and could not be identified. Reduction of the blue oil with aqueous potassium hydrosulfide gave a complex mixture of products which could not be separated, nor could the nature of the main reaction product be established. The blue oil, isolated by methods which permit of semi-quantitative separation, constituted about 20-25% of the total reaction product.

By cooling the greenish-yellow oil, remaining as a residue after the liquid reaction product had been steam distilled, a crystalline, waxy solid (A), m. p. 60° , was obtained in low yield. The same material was subsequently isolated, in better yields, by cooling the greenish-yellow oil which was volatile with steam, or by diluting the original, liquid, reaction product with ether and cooling to -80° . The composition, $C_8H_{10}N_2O_4$, and the values (157 and 168) obtained in molecular weight determinations, together with the products, sodium nitrite and 3-nitro-2-methylbutanthiol-2-phenyl ether, quantitatively formed in the reaction with sodium thiophenylate, establish the structure of the waxy product as the nitrous ester of 3-nitro-2-methylbutanol-2. The quantitative details of

the reactions which confirm the structure of the nitrous ester are given in Table III. Semi-quantitative isolation of the nitrous ester was not realized, but, based on the best separations, although steam distillation was employed entailing loss of about 15% of material, the minimum quantity produced in ether solution may be estimated as approximating 35% of the total reaction product.

The influence of a solvent upon the course of addition of hydrogen bromide to certain alkenes has long been known,¹⁰ but in the above reaction the solvent exerts a decisive influence upon the chemical manner in which a reagent functions as an addendum. In petrol, or without solvent, the tetroxide functions with the component parts $—ONO_2 + NO$, yielding considerable amounts of the polymerized nitrosate; the oily by-products decomposed so easily that no pure compound could be isolated. On the other hand, the amount of bis-nitrosate formed in ether was relatively small, but the distillable oil contained up to 35% of the nitro-nitrite, formed by addition of the addendum components $—ONO + NO_2$ to the Δ -carbons.

Besides the blue oil and the nitrous ester, non-volatile, liquid products are formed constituting approximately 10% of the total reaction product. With sodium thiophenylate, no sulfur derivative indicative of the structure of the complex oil could be obtained. The molecular weight (208 and 307) of the non-volatile oil suggested that, in the presence of nitrogen tetroxide, trimethylethylene may have been polymerized to di- and triisoamylenes and these acted upon by the tetroxide. Greenish-yellow oils were produced by the action of nitrogen tetroxide upon di- and triisoamylenes, but, since no blue oils were formed, the products were not investigated. It is evident from the above results that the blue-green oil, formed by interaction of nitrogen tetroxide and trimethylethylene in ether, which Schmidt² believed to be the slightly impure monomeric nitrosate, is a complex product, from which as

(10) The reversal of the mode of addition, observed in certain solvents [Ipatiev, *Jahresber.*, 738 (1903); 832 (1904); Michael and Zeidler, *Ann.*, **385**, 245 (1911); Sherrill, *This Journal*, **56**, 926, 1645 (1934)], may be the effect of the solvent, or of peroxide influences [Kharasch, *ibid.*, **57**, 2463 (1935); **58**, 57 (1936); *J. Org. Chem.*, **1**, 393 (1936)], which may function by retarding the formation of the polymolecule normally leading to the maximal degradation of energy on decomposition, or, by accelerating the formation of the type of polymolecule leading to production of the isomeric derivative, normally always formed in subordinate quantity [Michael, *Ber.*, **39**, 2138-2163 (1906)].

TABLE II

| Fractions | (A) 33 g. blue oil separated by low pressure distillation gave | | | | | |
|-------------|--|--------|--------------------|-----------------------------|--------|------------------|
| | (1) | (2) | (3) | Refractionation of (2) gave | | |
| G. | 2.4 | 13.4 | 13.2 green residue | (4) | (5) | (6) |
| B. p., °C. | >40 | 40-49 | | 2.8 | 4.6 | 4.9 blue residue |
| Press., mm. | 3 | 3 | | 34-36 | 36-38 | |
| n_D^{25} | | 1.4480 | | | | |
| n_D^{20} | | 1.4425 | | 1.4410 | 1.4440 | 1.4450 |
| d_{20} | | | | | 1.0365 | |

Analysis of fraction (5): C, 49.01; H, 6.68; N, 14.63; mol. wt., 112.

yet only the isomeric, monomeric nitro-nitrite has been isolated in a perfectly pure condition.

Experimental

Nitrogen tetroxide was prepared by heating anhydrous lead nitrate, the evolved gas passed through a tube of phosphoric anhydride and condensed in a weighed ampoule.

Trimethylethylene was prepared by heating tertiary amyl alcohol with 10% hydrochloric acid, fractionating the distillate, removing the last traces of alcohol and water with sodium and refractionating.

Ether was dried with phosphoric anhydride and distilled. Petroleum ether (b. p. 20-40°) was washed, successively, with concentrated sulfuric and nitric acids, water, dried with phosphoric anhydride and distilled.

The reaction vessel, in all experiments excepting VII and VIII, consisted of a three-necked flask, provided with a stirrer, a calcium chloride tube and a tube suitably arranged so that connection could be made rapidly with the nitrogen tetroxide ampoule which, just previously, had been cooled to -30° and unsealed.

An all-glass arrangement of vertical, concentric tubes, shaped as nozzles,¹¹ was used in experiment VIII. The reaction chamber was 3 cm. long and 12 mm. in diameter and was sealed to 20 cm. of 10-mm. tubing, terminating in a 50-cc. bulb which, cooled to -30°, served as a condenser. By means of concentric nozzles suitably arranged, nitrogen tetroxide was diluted with dry nitrogen and entered the reaction chamber into which was simultaneously admitted a stream of nitrogen, previously passed through trimethylethylene contained in a Leyden flask cooled to 0°. Bis-trimethylethylene nitrosate collected in the vertical tube immediately below the reaction chamber and the green, oily product drained into the bulb condenser.

In experiment VII, nitrogen tetroxide was diluted with dry nitrogen, using the mixing apparatus described above, and then passed through an 8-mm. tube into the side neck of a two-necked flask, equipped with a stirrer and a calcium chloride tube.

With ether as solvent, the solid reaction product was filtered off, solvent removed at reduced pressure from the filtrate and the residual, blue oil steam-distilled, or distilled at the pressure of a mercury pump. With petroleum ether, the liquids were decanted from the bis-nitrosate, the solid triturated with ether, filtered off and the residual oil, recovered from the filtrate, combined with that decanted with the petrol solution. When no solvent was used the oily product was decanted, the solid washed with ether

and the residual oil obtained from the filtrate combined with the decanted oil.

Separation of Liquid Products.—The liquids from two similar experiments were combined and the products separated by methods of which three typical examples are described. The low-pressure distillations were made in an all-glass apparatus, which was attached by a heavy rubber connector to a McLeod gage and a mercury vapor pump: distillation pressures were not recorded. A, B and C designate, respectively, the following compounds: the nitrous ester of 3-nitro-2-methylbutanol-2, 3-nitro-2-methylbutanthiol-2-phenyl ether and 3-nitro-2-methyl-2-phenylsulfone-butane.

Steam distillation of 55.6 g. of blue liquid gave (1) 25.8 g. of easily volatile, deep blue oil; (2) 13.9 g. of less volatile, greenish oil; and (3) 3.4 g. of residual oil. Distillate (1) was fractionated and gave 16.0 g. of deep blue distillate, b. p. 46-70° at 3 mm., leaving 6.8 g. of green, residual oil which, at -25°, deposited 1.5 g. of (A), m. p. 60°. *Anal.* Calcd. for $C_8H_{10}N_2O_4$: C, 37.05; H, 6.16; N, 17.3. Found: C, 37.23; H, 5.9; N, 16.6. The greenish oil (2) solidified at -25°, but only 3.2 g. of (A) could be isolated by filtration; the filtrate, diluted with ether and cooled to -80°, deposited 8 g. of crude (A), which was recrystallized from ether at -80° and gave 6 g. of pure product: mol. wt. calcd., 162. Found, in freezing benzene, (1) 157; (2) 168.

Low pressure distillation of 77 g. of blue oil yielded only 3.2 g. of blue distillate during three hours. The operation was discontinued, the residual, blue-green oil diluted with ether and cooled to -80° deposited 13.8 g. of (A). The oil (49.7 g.) from the filtrate was steam distilled and the oily distillate, cooled to -80°, gave 3 g. of (A). In another low pressure distillation, 71 g. of blue oil gave 24.0 g. of deep blue distillate, leaving 39.5 g. of greenish oily residue from which, after two recrystallizations at -80°, 6.7 g. of pure (A) was isolated. Three grams of (A) was added to a solution prepared from 0.8 g. of sodium, 20 cc. of methyl alcohol and 5 g. of thiophenol: the organic product (3.9 g.), insoluble in 10% alkali, distilled to give 3.2 g. of (B), b. p. 135° at 2 mm., which was treated with 3 g. of chromic anhydride in 10 cc. of glacial acetic acid and gave 3.1 g. of (C).

When steam distilled, the residual green oil (32.8 g.), from which the nitrous ester had been separated at -80°, gave (a) 20.8 g. of blue-green distillate and (b) 4.2 g. of viscous, yellow, residual oil. The blue-green oil (a) was fractionated: (1a) 3.3 g., of blue oil, b. p. 55-72° at 2 mm.; (2a) 16.2 g., nearly colorless oil, b. p. 80-100° (mostly at 87-100°) at 2 mm. Three grams of fraction (2a), treated with sodium thiophenylate as described above, gave, as the organic product, 3.7 g. of oil from which 3.5 g. of (B),

(11) Horn, Polanyi and Style, *Trans. Faraday Soc.*, **30**, 190 (1934).

TABLE III

| Expt. | Sub- stance | G. | Reagent | G. | Solvent | Temp. | Time | Products | Yield | | Properties, m. p., °C. |
|-------|----------------|----|-----------------------------------|-----|----------------------------------|-------|---------|--------------------------|--------------|------------|---------------------------|
| | | | | | | | | | Calcd. | Found | |
| I | (F) | 3 | C ₆ H ₅ SNa | 2.4 | CH ₃ OH | B. p. | 10 min. | NaNO ₃ (D) | 1.58 3.8 | 1.5 3.3 | 90 |
| II | (F) | 2 | C ₆ H ₅ SNa | 1.6 | CH ₃ OH | R. T. | 8 days | NaNO ₃ (D) | 1.05 2.6 | 0.7 2.3 | |
| III | (F) | 2 | C ₂ H ₅ SN | 1.1 | C ₂ H ₅ OH | B. p. | 10 min. | NaNO ₃ (E) | 1.05 1.99 | 1.0 2.0 | 60 |
| IV | (F) | 2 | C ₂ H ₅ SNa | 1.1 | C ₂ H ₅ OH | R. T. | 20 days | NaNO ₃ (E) | 1.05 1.99 | 1.0 1.5 | 59-60 |
| V | (A) | 2 | C ₆ H ₅ SNa | 1.6 | CH ₃ OH | B. p. | 15 min. | NaNO ₂ (B) | 0.85 2.78 | 0.8 3.0 | |
| VI | (A) | 2 | C ₆ H ₅ SNa | 1.6 | CH ₃ OH | R. T. | 6 days | NaNO ₂ (B) | 0.85 2.78 | 0.8 2.7 | |

NOTES ON TABLE III

D and E represent the phenyl and ethyl ethers, respectively, of 3-nitroso-2-methylbutanthiol-2; for reasons stated above, these compounds may have the isonitroso structure. F designates bis-trimethylethylene nitrosate, A, B and C the same compounds as before.

I. A suspension of (F) was heated with alcoholic sodium thiophenylate, most of the solvent removed and sodium nitrate filtered off. An ether solution of the filtrate was washed with water, dried and the solvent removed. The residual thio ether (D) melted at 90°. *Anal.* Calcd. for C₁₁H₁₅NOS: C, 63.16; H, 7.18; N, 6.7; S, 15.3; mol. wt. 209. Found: C, 63.25; H, 7.5; N, 7.15; S, (1) 15.9; (2) 15.4; mol. wt. (in freezing benzene), (1) 273, (2) 308. In ether solution, 1 g. of (D) and 0.6 g. of (D) (1 g.) and 0.6 g. of phenyl isocyanate gave 1.6 g. of addition compound, m. p. 113-114°. *Anal.* Calcd. for C₁₈H₂₀N₂O₂S: C, 65.85; H, 6.1; N, 8.54. Found: C, 65.87; H, 5.87; N, 9.1.

II. Products treated as above. *Anal.* Calcd. for NaNO₃: Na, 27.05. Found: Na, 26.9.

III. A suspension of (F) in a solution prepared from 0.3 g. of sodium, 25 cc. of alcohol and 0.8 g. of ethylmercaptan was heated, solvent distilled and sodium nitrate collected. *Anal.* Calcd. for NaNO₃: Na, 27.05. Found: Na, 27.3. The filtrate, in ether solution, was washed with water, dried and the solvent removed. The thio ether (E) was purified by sublimation at reduced pressure. *Anal.* Calcd. for C₇H₁₅NOS: S, 19.9; mol. wt., 161. Found: S, 20.3; mol. wt. (in freezing benzene), 231. In ether solution, 0.5 g. of (E) and 0.4 g. of phenyl isocyanate gave 0.8 g. of addition compound, m. p. 122°. *Anal.* Calcd. for C₁₄H₂₀N₂O₂S: N, 10.1; S, 11.43. Found: N, 10.12; S, 11.49.

IV. Bis-trimethylethylene nitrosate was suspended in a solution prepared from 0.3 g. of sodium, 25 cc. of alcohol and 1 g. of ethyl mercaptan. *Anal.* Calcd. for NaNO₂: Na, 27.05. Found: Na (1) 27.90; (2) 27.95. Solvent was removed from the filtrate, the residue, in ether solution, washed with water, dried and the solvent removed. The residual product (E) solidified completely.

V. A methyl alcohol solution of (A) and sodium thiophenylate was heated on the water-bath, most of the alcohol distilled and the sodium nitrite filtered off. *Anal.* Calcd. for NaNO₂: Na, 33.35. Found: Na, 33.23. Solvent was removed from the filtrate and the residual thio ether (B) distilled at 1 mm. with the bath temperature at 170°.

VI. Sodium nitrite (0.5 g.) was filtered off: the alcoholic filtrate, after concentration, yielded 0.3 g. of sodium nitrite. Both portions were analyzed. *Anal.* Calcd. for NaNO₂: Na, 33.35. Found: Na (1) 33.3; (2) 33.25. The liquid thio ether (B), treated with 2.7 g. of 30% hydrogen peroxide in acetic acid, was recovered unchanged; oxidized with 2.7 g. of chromic anhydride in 10 cc. of hot acetic acid, gave the sulfone (C) (2.3 g.), m. p. 102-103°. *Anal.* Calcd. for C₁₁H₁₅NO₄S: C, 51.4; H, 5.84. Found: C, 51.25; H, 5.84.

b. p. 132° at 2 mm., was obtained, oxidation of (B) with chromic anhydride, after two treatments, yielding 1.9 g. of (C).

The oil, non-volatile with steam, gave the value 307 in a molecular weight determination in freezing benzene. Incomplete separation may account for the lower value (208), found for the residual oil remaining after the liquid product had been distilled at low pressure.

The easily volatile, deep blue oil, isolated by steam or low pressure distillation, was fractionally distilled, using a jacketed column of beads. A typical fractionation is given in Table II.

(B) Properties of Blue Oil Separated by Steam Distillation.—B. p. 43-47° at 2 mm.; *n*_D²⁰ 1.4512; *d*₂₀ 1.044; mol. wt., 120. Analysis of three preparations gave the average results: C, 48.72; H, 7.25; N (one determination), 12.58.

Table III is a summary of the data obtained in the study of the action of sodium mercaptides upon bis-trimethylethylene nitrosate and the nitrous ester of 3-nitro-2-methylbutanol-2.

Summary

1. The action of nitrogen tetroxide upon trimethylethylene has been re-investigated. The course of the reaction varies slightly with the temperature but greatly with the solvent. In ether, comparatively little bis-trimethylethylene nitrosate is formed; the yield of the latter varied from 28-39% in petrol and without solvent from 42-49%, although the temperature varied from -80 to 30°. Since the proportion of NO₂ to O₂NONO in the system 2NO₂ ⇌ O₂NONO increased considerably, the course of formation of bis-nitrosate is relatively independent of the degree of dissociation of the addendum.

2. The liquid reaction product formed in petrol solution, or without solvent, is unstable and decomposed on vacuum distillation. The chemical nature of the oil could not be established.

3. The blue-green liquid formed in ether solution, contrary to the conclusion of Schmidt, is

not, or to any appreciable extent, the monomeric trimethylethylene nitrosate. The blue coloration is caused by a distillable, blue liquid, constituting only 20–25% of the total reaction product, which could not be polymerized, nor solidified at -80° . Oxidation as well as addition apparently enters into its formation. The re-

mainder of the liquid reaction product is composed of the nitrous ester of 3-nitro-2-methylbutanol-2, constituting at least 35% of the total reaction product, and high boiling, complex oils, representing 10% of the total product, which could not be characterized.

CAMBRIDGE, MASS.

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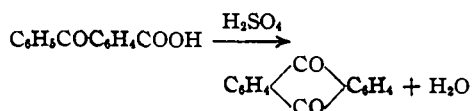
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Kinetic Study of the Sulfuric Acid Condensation of *o*-Benzoylbenzoic Acid¹

BY CHARLES W. DEANE

Both for considerations of kinetic theory and for its practical interest as the principal step in the industrial synthesis of the dye intermediate, anthraquinone, an extension of the velocity measurements on the decomposition of *o*-benzoylbenzoic acid, particularly in fuming sulfuric acid concentrations, appears especially valuable.

The major historical points appeared in an earlier report² on this reaction



Since 1929 Wiig,³ also Hammett and his co-workers,^{4,5} have used the data upon *o*-benzoylbenzoic acid in dealing, respectively, with Taylor's theory of negative catalysis and with correlations of the kinetics to the acidity function, H_0 .

With reference to Fig. 1, a graphical analysis using the data of Gleason and Dougherty shows that rather than as reported to the contrary,² *o*-benzoylbenzoic acid is not exceptional, but is like oxalic acid in having the velocity constant k , as a logarithmic or exponential function of the water present. The extra dotted line shows the result of using Gleason and Dougherty's kinetic value obtained at a decomposition of but 4% which resulted from employing an inflexible four-hour period to measure the reaction rate.

(1) The summary of a thesis presented to the Graduate School of The University of Rochester in partial fulfillment of the requirements for the degree of Master of Science.

(2) Gleason and Dougherty, *THIS JOURNAL*, **51**, 310 (1929).

(3) Wiig, *ibid.*, **52**, 4742 (1930).

(4) Hammett, *Chem. Rev.*, **16**, 67 (1935).

(5) Hammett and Deyrup, *THIS JOURNAL*, **54**, 2721 (1932).

The main objectives in the present work have been to extend the data by certain basic improvements in the general method of Gleason

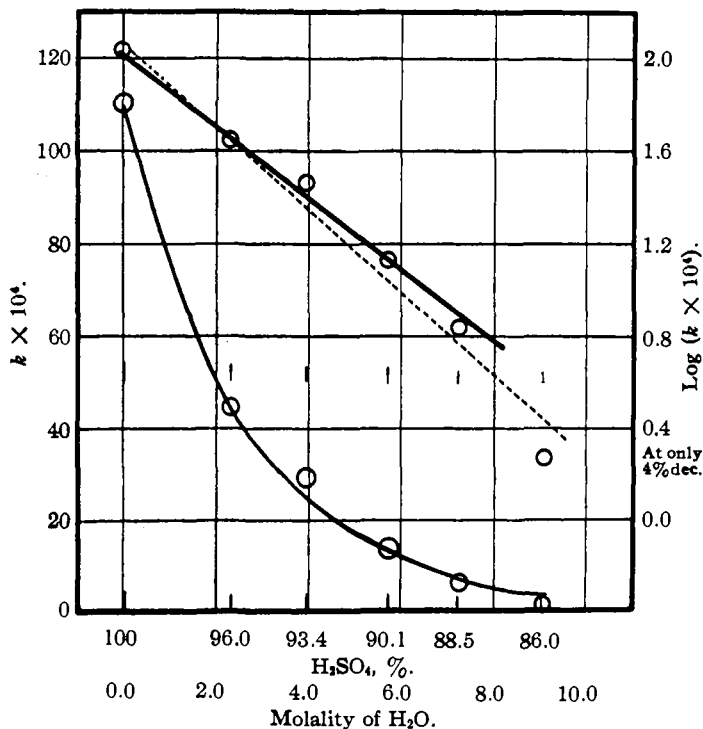


Fig. 1.—The velocity constant k for the condensation of *o*-benzoylbenzoic acid by sulfuric acid at 75° . Analysis of data obtained by Gleason and Dougherty.²

and Dougherty,² and to obtain precise results at the far higher reaction speeds due to fuming sulfuric acid. This extension of data was undertaken to check general theoretical predictions of the kinetic effects³ in the unexplored regions of fuming sulfuric acid.

Among the exceptional features and advantages afforded by this reaction for kinetic studies