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.

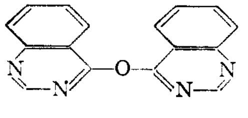
O-Ethers are very easily cleaved by acid in contrast to N-ethers which are stable.[3] The diquinazolyl ether prepared above reacted very readily with dilute hydrochloric acid to yield almost quantitatively a product ($C_{15}H_{13}N_3O$) which contained a quinazoline unit bound apparently to a degraded 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.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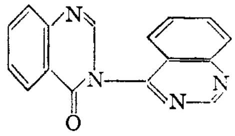
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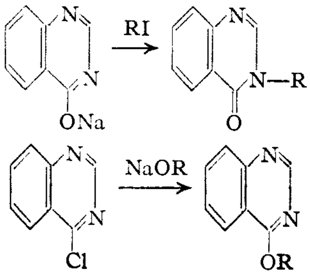

Fig. 1.

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.

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 14, 1947

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).

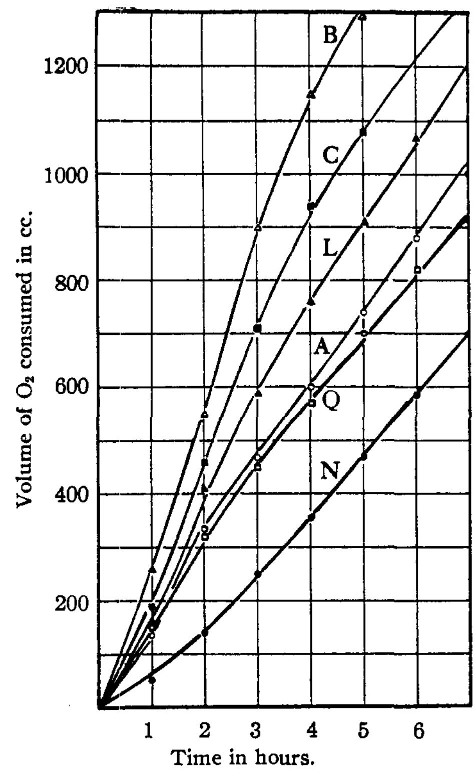

Fig. 1.—Effect of the addition of 0.001 *M* quantities of oxidation catalysts on the oxygen uptake in the oxidative condensation of 2-methoxy-4-nitrotoluene: ●, no catalyst, N; □, anthraquinone, Q; O, acetone, A; ▲, cyclohexanol, L; ■, cyclohexanone, C; △, benzoquinone, B.

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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SCHIEFFELIN & CO.
NEW YORK 3, N. Y.

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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. 11, 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.