TABLE II

DERIVATIVES OF 2-HYDROXY-2′-NITROBIPHENYL

Derivative, 2-(2-nitrophenyl)-phenyl-	Formula	Yield, %	M.p., °C.	Analytical data Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Benzoate	$C_{19}H_{13}O_4N$	50	116	71.5	71.3	4.1	3.9	4.4	4.4
4-Nitrobenzoate	$C_{19}H_{12}O_6N_2$	70	116	62.6	62.5	3.3	3.2	7.7	7.8
3,5-Dinitrobenzoate	$C_{19}H_{11}O_8N_3$	70	180					10.3	10.2
4-Nitrobenzene sulfonate	$C_{18}H_{12}O_7N_2S$	90	147					7.0	6.9
3-Nitrobenzene sulfonate	$C_{18}H_{12}O_7N_2S$	50	161	54.0	54.2	3.0	2.8	7.0	7.0
4-Methylbenzene sulfonate	$C_{19}H_{15}O_5NS$	40	100					3.8	3.7
2,4-Dinitrophenyl ether	$C_{18}H_{11}O_7N_3$	10	118					11.0	11.1

minated product. The crystals were filtered, dissolved in chloroform, the solution dried over sodium sulfate, concentrated and precipitated by addition of petroleum ether. The light yellow material melted at 149°. Since 2-hydroxybiphenyl readily yields 3,5-dibromo-2-hydroxybiphenyl[8] the present product is assumed to be 2-hydroxy-3,5-dibromo-2′-nitrobiphenyl. A yield of 1.2 g. (70%) was obtained.

Anal. Calcd. for $C_{12}H_7O_3Br_2N$: Br, 42.9. Found: Br, 42.7.

This procedure was repeated using 1 g. of 2-methoxy-2′-nitrobiphenyl. The dibrominated ether weighed 1.25 g. (70%) and melted at 108° following recrystallization from chloroform and petroleum ether.

Anal. Calcd. for $C_{13}H_9O_3Br_2N$: Br, 41.3. Found: Br, 41.0.

Hydrolysis of the dibrominated ether was accomplished by heating 0.2 g. of the ether for two days at 90° with 2 ml. each of acetic anhydride and hydrobromic acid. Fifteen milligrams of 2-hydroxy-3,5-dibromo-2′-nitrobiphenyl was isolated. This hydrolysis product melted at 149° when mixed with that obtained by bromination of 2-hydroxy-2′-nitrobiphenyl. The dibromoether is assumed to be 2-methoxy-3,5-dibromo-2′-nitrobiphenyl.

Derivatives of 2-Hydroxy-2′-nitrobiphenyl.—Seven derivatives involving the –OH group of 2-hydroxy-2′-nitrobiphenyl were prepared. All were prepared by well known methods. In general, the phenol was dissolved in pyridine and the acid chloride added in slight excess. Refluxing for 30 minutes was followed by pouring the reaction mixture over ice or into cold water. The precipitate was dissolved in a suitable solvent such as chloroform or alcohol and a crystalline product obtained. Table II supplies details.

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[8] Auwers and Wittig, *J. prakt. Chem.*, **108**, 99 (1924).

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Colored Complexes with Inorganic Salts Mounted on Silica Gel

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Jura, Grotz and Hildebrand[1] have reported that mesitylene reacts with the salts of 19 metals on a silica gel surface to form colored complexes, and attributed the color formation to a generalized acid–base interaction between mesitylene and the respective cations. Evidence is listed below, however, which shows that the colors reported by these investigators can be attributed to the presence of an as yet unidentified trace impurity in mesitylene. This evidence does not, of course, exclude the possibility of the existence of genuine mesitylene complexes that have characteristic absorption bands outside of the visible spectrum.

Sulfates of four of the 19 ions reported to give colored mesitylene complexes—Cu^{++}, Zn^{++}, Mg^{++} and Al^{+++}—were mounted on silica gel. When mesitylene from two different sources was added to these salts, two types of reactions were observed. Mesitylene from the first source, which we will denote mesitylene I, produced an intense red-purple color with each of the above four salts. A sample of mesitylene used by Jura, *et al.*,[2] gave a red-purple color that was not as intense as was the case for mesitylene I. However, mesitylene from the second source (denoted as mesitylene II) produced no color change of any kind with these same salts. A mixture of I and II gave the red-purple color reaction. These results were already strong evidence for the presence of a color-producing impurity in mesitylene I that was absent from mesitylene II.

The attempts to isolate and identify the color-producing impurity—henceforth denoted as X—in mesitylene I can be summarized as follows: (1) Simple distillation or chromatographic treatment with silica gel did not remove impurity X. (2) Ten equal fractions were obtained by distillation of mesitylene I through a 60-plate fractionating column at a reflux ratio of *ca.* 60:1. Since impurity X did not appear in the first nine fractions, but was found in the higher boiling residue (fraction 10), a tenfold concentration of impurity X was effected. (3) After learning that mesitylene I was probably synthesized from acetone, two of the possible higher boiling by-products of this synthesis—phorone and isophorone—were added to the mounted salts. No color reaction was observed. (4) Chromatographic treatment using copper sulfate mounted on silica gel as the adsorbent completely removed impurity X, as was evidenced by the appearance of an extremely intense red-purple zone localized at the top of the chromatographic column. Attempts to remove impurity X from the colored adsorbent by sublimation in high vacuum resulted in decomposition of the adsorbed material. In this respect, the adsorption seemed irreversible. (5) Ultraviolet analysis of mesitylene I revealed no absorption peaks other than those characteristic of mesitylene itself. (6) The above-mentioned mesitylene samples were analyzed mass-spectrometrically at each stage of purification and isolation. In making an intercomparison of the mass spectra of these samples, it was assumed (because of the results described in 2) that impurity X had a molecular weight higher than that of mesitylene. Although it was not possible to assign

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[1] G. Jura, L. Grotz and J. H. Hildebrand, American Chemical Society Meeting Abstracts, September, 1950, p. 56Q.

[2] The writer gratefully acknowledges the coöperation of Professor George Jura, who kindly supplied this sample of mesitylene.

a particular parent peak to impurity X, it was evident that any of the peaks that were likely possibilities arose from impurities that were present at concentrations lower than 0.01% in the original sample of mesitylene I.

Further attempts to identify impurity X were abandoned upon exhaustion of the supply of mesitylene I.

It is interesting to compare the color reactions of impurity X with metal salts to the work of Walling.[3] This investigator has shown that indicators exhibiting color changes at low *p*H's in aqueous solutions give their acid colors when adsorbed on surfaces of iron, magnesium, silver and copper salts, and on other acidic surfaces. Since indicators are a class of substances having huge extinction coefficients and since it is likely that impurity X falls into such a class, it seems reasonable to postulate that impurity X is an indicator that exhibits a red-purple color on highly acidic surfaces.

Experimental

Mounted Salts.—Ten ml. of 0.5 *M* solutions of each of the four salts was added to 10-g. portions of pure silica gel, stirred on a hot-plate until the product seemed dry, and dried overnight in a 200° drying oven. Copper sulfate mounted on silica gel was used to follow the course of impurity (X) during the purification steps.

Mesitylene.—Both mesitylene I and mesitylene II were Eastman Kodak White Label products. Through the kind coöperation of the Eastman Kodak Company, it was learned that mesitylene I, which was distributed before about 1950, was most likely synthesized from acetone. Mesitylene II, the current Eastman Kodak product, probably was made from a coal tar distillate.

Color Tests.—The intense red-purple color could be brought about by the addition of a few drops of mesitylene I to *ca.* 0.1 g. of mounted salt on a spot plate. The full intensity developed in 5–10 minutes at room temperature, but could be greatly accelerated by warming 1–2 minutes at *ca.* 100°.

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[3] C. Walling, THIS JOURNAL, **72**, 1164 (1950).

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Polar Effects in N-Bromosuccinimide Brominations

BY ELIAS J. COREY

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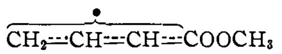
The reaction between N-bromosuccinimide and unsaturated compounds which results in the substitution of bromine for hydrogen is generally considered as involving free radical intermediates.[1] The allylic bromination of an olefin, for example, has been postulated to occur by dissociation of N-bromosuccinimide into bromine atoms and succinimide radicals, radical displacement on hydrogen by the succinimide radical to give a mesomeric radical and, finally, reaction of this radical with the reagent to give a succinimide radical and the allylic bromide.

According to this interpretation the reaction of N-bromosuccinimide with two isomeric substances which are converted by radical displacement on an allylic hydrogen to the same free radical should lead to the same product (or products).[2]

Methyl crotonate (I) and methyl vinylacetate (II) are such a pair of isomeric substances and their study seemed especially advantageous since only two allylic substitution products are possible and since, as Ziegler and co-workers have already reported, the reaction of methyl crotonate with N-bromosuccinimide produces methyl γ-bromocrotonate in good yield.[3] One might anticipate that methyl γ-bromocrotonate would also be formed from methyl vinylacetate.

$CH_3CH{=}CHCOOCH_3$ I $\qquad$ $CH_2{=}CHCH_2COOCH_3$ II



$$\overset{\bullet}{\overparen{CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} COOCH_3}}$$

III

We have found that under the same conditions which are favorable for the conversion of methyl crotonate to methyl γ-bromocrotonate, methyl vinylacetate reacts *more slowly* and yields chiefly methyl β,γ-dibromobutyrate (IV) along with an insignificant amount of monobrominated product. Some tarry material is also formed. The structure of IV was proved by debromination to methyl vinylacetate and by synthesis from methyl vinylacetate and bromine.

We and, very recently, others[4] have also observed that a similar situation exists with the corresponding nitriles, crotononitrile and vinylacetonitrile.

Regardless of what the mechanism of formation of dibromide is,[5] the relative inertness of the α-methylene group in methyl vinylacetate and vinylacetonitrile in succinimide radical displacements must still be explained. Since significant steric effects can hardly be operative in the case of vinylacetonitrile, it seems reasonable to suppose that the impediment to radical attack associated with the proximity of the cyano function (or in the case of II, the carbomethoxy group) is primarily electrical in nature.

Experimental

Reaction of Methyl Vinylacetate (II) with N-Bromosuccinimide.—Methyl vinylacetate, b.p. 107° (742 mm.), $n^{25}\text{D}$ 1.4060, was prepared by the action of diazomethane on pure vinylacetic acid,[6] b.p. 72.5–73.5° (14 mm.), $n^{25}\text{D}$ 1.4210. A mixture 10.0 g. (0.10 mole) of methyl vinylacetate, 17.8 g. (0.10 mole) of N-bromosuccinimide, 0.01 g. of benzoyl peroxide and 50 ml. of pure carbon tetrachloride was heated at reflux for 8 hours, after which time all of the N-bromosuccinimide had disappeared and a brown oil had settled out. The layers were separated by decantation and the oil extracted with two 10-ml. portions of carbon tetrachloride. The carbon tetrachloride solution (plus washings) was cooled to 0°, filtered to remove the precipitate of succinimide (7.2 g.) and concentrated. Distillation of the residual liquid through a semi-micro column yielded 6.14 g. (68.4% based on N-bromosuccinimide) of methyl β,γ-dibromobutyrate (IV), b.p. 70.5° (0.8 mm.), $n^{25}\text{D}$ 1.5114 and a small amount (0.48 g.) of a low-boiling fraction, b.p. 48–70°, which probably contained monobromide.

Anal. Calcd. for $C_5H_8O_2Br_2$: C, 23.10; H, 3.10; Br, 61.49. Found: C, 23.28; H, 3.28; Br, 61.78.

Debromination of IV.—A mixture of 3.30 g. of the dibromoester IV and 2 g. of zinc dust in 10 ml. of ether containing a few drops of methanol was heated to reflux for one hour. The resulting mixture was filtered and the filtrate

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[1] G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

[2] This point had apparently not been considered in connection with the reaction of N-bromosuccinimide with ketene dimer, A. T. Blomquist and F. H. Baldwin, THIS JOURNAL, **70**, 29 (1948).

[3] K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 118 (1942).

[4] P. Couvreur and A. Bruylants, *Bull. soc. chim. Belg.*, **61**, 253 (1952).

[5] See E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

[6] *Org. Syntheses*, **24**, 95 (1944).