of the yellow 6-methyl-2-pyrazinol (XII). Recrystallization from anhyd. ethyl acetate furnished 4.4 g. of the yellow platelets, m.p. 240°.

Anal. Calcd. for $C_5H_6N_2O$: N, 25.44. Found: N, 25.80.

Preparation of azo coupled compounds of 6-methyl-2-pyrazinol (XIII). *A. Disodio salt of 6-methyl-5-azobenzenesulfonate-2-pyrazinolate* (XIIIA). Two ml. of 6*N* sodium hydroxide solution were added to a suspension of 1.8 g. (0.01*M*) of sulfanilic acid in 15 ml. of water. Solution was obtained on warming. Then 0.7 g. of sodium nitrite was added and the solution cooled to room temperature. Then this solution was poured into a mixture of 1.3 ml. of concentrated sulfuric acid, 26 g. of ice, and 20 ml. of water, and allowed to stand for 30 min. After which, a solution of 1.6 g. (0.01*M*) of 6-methyl-2-pyrazinol (XII) in 20 ml. of water and 10 drops of 20% sodium hydroxide was added to the diazotized sulfanilic acid. The reaction mixture was stirred for 5 min., after which 10% sodium hydroxide was added to make *p*H 6. After an orange precipitate had formed, 30 ml. of saturated sodium chloride solution was added and the mixture cooled for 10 min. Filtration produced 2.1 g. of orange yellow solid. The solid was recrystallized from 125 ml. of distilled water at 95°, to give 2 g. of bright yellow solid. Aqueous solutions are colored red in acid and orange red in alkaline solution. The solid did not melt up to 300°.

Anal. Calcd. for $C_{11}H_8O_4N_5SNa_2$: N, 16.38. Found: N, 15.01, 15.31.

B. Sodio salt of 6-methyl-5-p-nitrobenzeneazo-2-pyrazinol (XIIIB). A suspension of 1.4 g. of *p*-nitroaniline in 5 ml. of concentrated hydrochloric acid was prepared. Solution was obtained by heating to 80°. On cooling to room temperature, 10 g. of ice and a solution of 0.8 g. of sodium nitrite were added. To the diazotized *p*-nitroaniline, a solution of 1.3 g. of 6-methyl-2-pyrazinol (XII) in 20 ml. of water and 10 drops of 20% sodium hydroxide was added with stirring. The reaction mixture stood for 10 min. and then a solution of 0.6 g. of anhydrous sodium acetate in 2 ml. of water was added. After 15 min., the solid was filtered, washed with ice water, and dried. The dried solid was digested with a small amount of benzene to remove unchanged *p*-nitroaniline. For analysis, a sample was recrystallized from 95% ethanol; no m.p. up to 300°.

Anal. Calcd. for $C_{11}H_8O_3N_5Na$: N, 24.90. Found: N, 24.73.

Preparation of 5-amino-6-methyl-2-pyrazinol (XIV). To a solution of the disodio salt of 5-azobenzenesulfonate 6-methyl-2-pyrazinolate (XIIIA) in 60 ml. of water at 85°, there was added a solution of 8 g. stannous chloride in 20 ml. of concentrated hydrochloric acid. The mixture was warmed until the dye color was lost. Then the mixture was cooled in an ice salt bath until there was no further precipitation of sulfanilic acid. After filtration of the sulfanilic acid, sodium hydroxide solution (20%) was added to precipitate stannic oxide. The filtrate was evaporated to dryness on the steam bath and then extracted with absolute methanol, 300 ml. in 3 portions. The alcoholic extracts were combined and reduced in volume to 25 ml. Cooling to 0°, produced a light tan solid. The solid was recrystallized from absolute methanol to yield 0.5 g. of pale yellow solid (62%), which did not melt up to 300°.

Anal. Calcd. for $C_5H_6ON_3Na$: C, 40.81; H, 4.11. Found: C, 41.11; H, 4.22.

Preparation of 5-amino-6-methyl-2-(2,4-dinitrophenylhydrazone) pyrazinone (XV). A saturated solution of 2,4-dinitrophenylhydrazine in 2*M* hydrochloric acid–methanol was added dropwise to a solution of 1.5 g. of 5-amino-6-methyl-2-pyrazinol (XIV) until precipitation was complete. The yellow orange micro crystals were recrystallized from hot methanol-water to yield 2 g. of product. The hydrazone gave a dark red color on addition of 2*M* alcoholic potassium hydroxide solution indicating the aromatic nature of the pyrazine ring. The hydrazone was dried, m.p. 125°.

Anal. Calcd. for $C_{11}H_{11}O_4N_7$: C, 45.32; H, 3,63. Found: C, 45.56; H, 3.44.

ULTRAVIOLET ABSORPTION MAXIMA AND MINIMA

	Max., Mμ	Min., Mμ
7-Methyllumazine (I) acid solution	325	270
7-Methyllumazine (I) sodio salt	275, 342	255, 292
2-Acetamido-5-methylpyrazine (V)	300	260, 400
6-Methyl-2-pyrazinol (XII)	250	324, 410
2-Amino-3-bromo 6-pyrazinoic acid (XI)	243, 340	285, 400
5-Amino-6-methyl 2-pyrazinol (XIV)	253	236, 360
5-Benezenesulfonate-6-methyl-2-pyrazinolate disodio salt (XIIA)	362	260
5-Benzenesulfonate-6-methyl-2-pyrazinolate disodio salt (XIIIA) at *p*H 11	410	700

BROOKLYN 10, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

Chromatographic Separation of Nitration Products of Ester-Blocked 2-Hydroxybiphenyl[1]

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Nitration of the benzenesulfonate of *o*-hydroxybiphenyl yields 2′- and 4′-mononitro derivatives. Hydrolysis of these esters and nitration of the resulting mononitrohydroxybiphenyls lead to mononitro and dinitro substitution in the phenolic ring. A satisfactory separation of the nitrohydroxybiphenyls has been accomplished by chromatographic methods.

The direction of entering nitro groups to positions in the nonphenolic ring of the hydroxybiphenyls by the "ester block" method has been reported by Bell and Kenyon,[2] Hazlet *et al.*[3,4] and others. In addition to the 4′-mononitro derivative,

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[1] Abstracted from a thesis submitted by D. Paul Denny to the faculty of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1957.

[2] F. Bell and J. Kenyon, *J. Chem. Soc.*, 129, 3044 (1926).

[3] S. E. Hazlet, G. Alliger, and R. Tiede, *J. Am. Chem. Soc.*, 61, 1447 (1939).

[4] S. E. Hazlet, L. C. Hensley, and H. Hass, *J. Am. Chem. Soc.*, **64**, 2449 (1942).

Campbell and Morrill,[5] working with 4-biphenylyl benzoate, reported the 2′-derivative.

This directional effect has been explained on the basis of steric hindrance. While there is some agreement that the extent of this type of substitution increases with increase in size of the blocking group, Campbell and Morrill's[5] experiments indicate that the steric factor may be of only moderate influence. Evidence for a change in the directional influence of the phenolic hydroxy group comes from work with ester-blocked 3- and 4-hydroxybiphenyl.[3,6] In 3-hydroxybiphenyl, a blocking group might affect both ortho positions and substitution at the para position might be hindered by the phenyl group. In 4-hydroxybiphenyl, substitution at the ortho positions might be hindered by a blocking group and since the para position is substituted by the phenyl group no test of spatial crowding *vs.* electronic effects beyond the ortho position can be obtained. In 2-hydroxybiphenyl the para position is unhindered by spatial crowding. Nitration of the benzenesulfonate of 2-hydroxybiphenyl should provide useful information since dominant entry of the nitro group into the unsubstituted ring rather than the position para to the phenolic hydroxyl group would indicate the significance of electronic rather than steric effects.

In the present research nitration occurred almost exclusively in the non-phenolic ring of ester-blocked 2-hydroxybiphenyl. The compounds obtained were the benzene sulfonates of 4′-nitro-2-hydroxybiphenyl and to a lesser extent 2′-nitro-2-hydroxybiphenyl. When the reaction mixture of these esters was hydrolyzed and placed on the chromatographic column 4′-nitro-2-hydroxybiphenyl was accompanied by trace amounts of a second phenol whose melting point was the same as that of 5-nitro-2-hydroxybiphenyl. The blocking group causes deactivation of all positions on the phenolic ring even though one of these positions is far removed from the blocked phenolic group.

Failure to isolate a phenolic ring mononitration product in significant amounts and production of the 4′ and 2′-mononitro derivatives lends strength to the assumption that electronic effects are of major significance in the reaction. While steric hindrance may be of importance to ortho positions the degree of activation or deactivation of each ring by its substituents determines nitration products of 2-hydroxybiphenyl. Since only the 2′- and 4′-mononitro derivatives were found, it is apparent that the ester-blocked phenolic ring is ortho, para directing.

The use of chromatographic techniques provided the tool for the separation of the nitrohydroxybiphenyls. Differences in solubilities and acidities cause the nitro derivatives of the hydroxybiphenyls to be spaced on an adsorbent column as colored bands. This technique was not used by early workers in the field.

General nitration procedure involved dropwise addition of fuming nitric acid to the ester contained in an equal volume of reaction solvent. The reaction was allowed to proceed during a period of heating and finally stopped with ice water. The benzene sulfonate of 4′-nitro-2 hydroxybiphenyl was crystallized from an ethanol solution of the gummy nitration products. After removal of the ethanol, the residue was a light-yellow, oily sirup. Hydrolysis of the 4′-mononitro ester derivative with alcoholic KOH produced 4′-nitro-2-hydroxybiphenyl in 57 to 81% yields. This was the only nitro derivative isolated directly from the crude nitrated ester products. In later runs the entire crude product was hydrolyzed and the hydrolyzate chromatographed. Since 2′-nitro-2-hydroxybiphenyl was recovered from the column it was evident that the ester of 2′-nitro-2-hydroxybiphenyl was contained in the residual oil mentioned above.

Satisfactory nitration of the ester when nitromethane was used as solvent was governed by the amount of nitric acid used. Below an acid-ester mole ratio of 3:1, only unchanged starting materials were recovered. A ratio of 6:1 caused oxidation of the ring system and reduced yields. Best results were obtained using a 4:1 ratio.

When glacial acetic acid was used as the solvent, there was little oxidation even with an acid-ester mole ratio of 12:1. Although there was little nitration with a 6:1 acid-ester ratio, satisfactory yields were obtained with higher ratios. Glacial acetic acid was the solvent of choice.

TABLE I

RESULTS OF NITRATION OF ESTER-BLOCKED *o*-HYDROXYBIPHENYL UNDER VARYING CONDITIONS OF ACID STRENGTH, SOLVENT AND REACTION TEMPERATURES[a]

Acid-Ester Mole Ratio	Solvent	Total Solvent, ml.	Reaction Temp.	Percentage Yield of Mononitro Ester
3:1	Nm[b]	4	Room	14.41
4:1				41.92
6:1				28.21
6:1	G.a.a.			26.02
8:1				35.89
8:1			Reflux	Oxidation
8:1		6	Room	11.40
9:1		4	90°[c]	53.10
9:1			80°[c]	26.20
9:1		3	Room	47.58
10:1		4		52.05
10:1		3		49.22
10:1		2		33.24
12:1		4		49.04

[a] All reaction mixtures refluxed on water bath for 1.5 hr. after addition of nitrating mixture unless otherwise indicated. [b] Abbreviations: Nm—Nitromethane; G.a.a.—Glacial acetic acid. Total solvent indicates ml. per g. of ester. [c] Nitrated at temperature shown and held at this temperature for 1.25 hr. without any reflux period.

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(5) I. G. M. Campbell and D. J. Morrill, *Chem. and Ind.* (*London*), 1229 (1953).

(6) J. C. Colbert and C. F. Robinson, to be reported.

Reactions carried out at either room temperature or at temperature ranges between 80° and 90° gave about the same results. The temperature at which the nitrating agent is added does not appear to be a factor as long as a period of heating on the water bath follows the addition.

The volume of the solvent plays a role. Higher yields resulted when the total acetic acid was 3–4 ml. per gram of ester.

Since nitration of the hydroxybiphenyls has been shown to produce a variety of mono-, di-, and trinitro derivatives,[7] a column adsorbent was required which would permit separation of the principal products. An adsorbent of strong retaining power was necessary to slow the speed of mononitration products (low acidity and high solubility) down the column to the point where retention was of sufficient duration for bands to be separated. On the other hand the adsorbent had to be of sufficiently low retaining power so that the di- and trinitro derivatives (low solubility and high acidity) would move far enough down the column for individual bands to form and thus facilitate separation by extrusion. Magnesol[8] was found to hold highly soluble–low acidity type nitrophenols firmly enough to slow down the speed of elution and at the same time permit band formation from low solubility–high acidity type nitrophenols. Benzene solutions of the hydrolyzed, nitrated products from one-gram samples of the sulfonate ester were placed on the column and eluted with benzene under a working pressure of five pounds gage. Both the 4′- and 2′-nitro derivatives were recovered from the column by elution. Typical yields of the 4′-nitro and 2′-nitro derivatives were 30% and 20%, respectively.

The two principal products were separable in one run using a Magnesol column 4.5 cm. × 50 cm. when less than 2.5-gram samples of the sulfonate ester of 2-hydroxybiphenyl were nitrated and the column was packed with a benzene slurry under 10 pounds pressure followed by elution with benzene under five pounds pressure.

4′-Mononitro and 2′-mononitro-2-hydroxybiphenyl were further nitrated under milder reaction conditions[7] since the phenolic ring was now unencumbered with a blocking group. The 3,5,4′-trinitro derivative[9] was easily prepared and isolated. With a 4:1 mole ratio, fuming or concentrated nitric acid, to 4′-mononitro-2-hydroxybiphenyl using glacial acetic acid as the solvent, the trinitro derivative dropped out at room temperature. When 4-nitro-2-hydroxybiphenyl was further nitrated in glacial acetic acid with fuming nitric acid, (1:1 mole ratio, acid to sample), the reaction proceeded smoothly at room temperature. Reaction products formed two principal and two insignificant bands on the column. The two principal bands were more highly colored (orange to red) than those developed from the initial ester nitration. Nitrogen analysis of these two bands indicated dinitro compounds. The material from each band was further nitrated to the same 3,5,4′-trinitro derivative. It was assumed that one of these two products was the 3,4′- and the other the 5,4′-dinitro derivative. Since 3-nitro-2-hydroxybiphenyl melts at 63–64° and 5-nitro-2-hydroxybiphenyl at 124–126°, it is probable that further work will show that of the two dinitro phenols obtained by further nitration of 4′nitro-2-hydroxybiphenyl, the higher melting (226–228°) is 5,4′-dinitro-2-hydroxybiphenyl and the lower melting (194–195°) is 3,4′-dinitro-2-hydroxybiphenyl.

Samples of the 2′- derivative were nitrated using a 4:1 mole ratio, acid to sample, in glacial acetic acid, and a 1:1 mole ratio in nitromethane. Evidently the 2′- derivative is more difficult to nitrate than the 4′-nitro derivative since a light orange, fast-moving principal band associated with the 1:1 mole ratio in nitromethane yielded starting material. Only one product was isolated from the column other than this starting material. Considering the low acid-sample mole ratio and results obtained with the 4′-derivative, this product was assumed to be either the 3,2′-dinitro or the 5,2′-dinitro-2-hydroxybiphenyl.

In the reaction employing a 4:1 mole ratio, acid to sample, and glacial acetic acid as the solvent, only one principal band was observed. Since analysis indicated three nitro groups, the material may have been 3,5,2′-trinitro-2-hydroxybiphenyl.

Separation of the nitro derivatives of the hydroxybiphenyls by chromatographic methods proved satisfactory. Not only was the technique effective for fast-moving mononitro products but was applicable to the dinitro derivatives by extrusion and extraction methods. Proofs of structure for the three dinitrophenols obtained will be offered when further work has been carried out.

EXPERIMENTAL

The benzenesulfonate of 2-hydroxybiphenyl. Twenty-five grams (0.147 mole) of 2-hydroxybiphenyl was dissolved in 75 ml. of pyridine and 20 ml. of benzenesulfonyl chloride (6.6% excess) was added to the pyridine solution with the temperature held below 10°. After standing for 1 hr., the reaction mixture was heated on the water bath for an additional hour. Overnight, long needle crystals of the benzenesulfonate separated and were collected on the filter. The mother liquor was poured over 200 g. of crushed ice and a further yield of the ester removed by filtration. Recrystallization from 95% ethanol gave 40.5 g., 88.9% m.p. 66–67°.

Nitration of the benzenesulfonate of 2-hydroxybiphenyl. One gram, (0.003 mole) of the ester was dissolved in 2 ml. of warm glacial acetic acid. A nitration mixture made up of 1.25 ml. of fuming nitric acid (0.029 mole) and an equal volume of

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(7) J. C. Colbert, D. W. Fox, and C. Matuszak, *J. Am. Chem. Soc.*, **77**, 2447 (1955).

(8) Magnesol, a synthetic magnesium silicate, was obtained from Westvaco Chlor-Alkali Division of the Food Machinery and Chemical Corporation.

(9) H. B. Hill and W. J. Hale, *Am. Chem. J.*, **33**, 1–21 (1905).

glacial acetic acid was added dropwise with shaking to the solution at room temperature. The reaction mixture was heated on the water bath for 1.5 hr. during which the color became a reddish brown. The mixture was poured into 50 ml. of ice water after standing for 20 hr. There was an immediate precipitation of a gummy, white, mass which took on a pinkish cast upon standing. This crude product was washed free of acid on the filter with distilled water and dissolved in 15 ml. of hot 95% ethanol. Within 1 to 2 hr., following addition of water, whitish yellow crystals were precipitated. These crystals were washed with cold dilute ethanol and dried in the desiccator. The yield was 0.544 g., 47.6% on a mononitro basis, m.p. 136–137°.

Two samples of the sulfonate ester (1 g. each) were dissolved in separate 3-ml. portions of glacial acetic acid and each sample nitrated with 1.25 ml. (0.029 mole) of fuming nitric acid mixed with 1 ml. of glacial acetic acid. One sample was heated at 90° during the period of dropwise nitration and held at this temperature for 75 min. The second sample was similarly treated at 80°. Employing the general procedure outlined above, the first sample produced 0.608 g., 53.7% of the nitrated ester m.p. 136–137°. The yield from the second sample was 0.30 g. (26.2%).

Hydrolysis of the nitrated ester of m.p. 136–137°. One gram of the nitrated ester was dissolved in 15 ml. of 95% ethanol and 1.0 g. of KOH in 3 ml. of distilled water was added to the alcoholic solution. There was immediate reaction and appearance of a dark red color characteristic of alkali salts of nitrated phenols. The hydrolysis mixture was refluxed for 3 hr. and was then poured into 50 ml. of distilled water. The wine red solution was acidified with hydrochloric acid and extracted with 15-ml. portions of chloroform until only a faint yellow color was shown by a chloroform portion. The chloroform solution was extracted with 15-ml. portions of 5% KOH solution until no further color was shown by the alkali extract. The alkali solution was acidified with hydrochloric acid and the slightly acidic solution exhaustively extracted with 15-ml. portions of benzene. The benzene extract was reduced in volume to 25 ml. and washed twice with 5-ml. portions of cold water to which 2 drops of dilute hydrochloric acid had been added. Two washings with cold water followed. The benzene solution was dried over anhydrous sodium sulfate, 10 ml. of *n*-heptane were added after which the solution was evaporated to dryness on the hot plate. The weight of nitrated phenols was 0.494 g., 81.6% yield on a mononitro basis.

Hydrolysis of the nitrated ester and recovery on the column. The crude, gummy nitration products (4.772 g.) from two 5-g. samples of the sulfonate ester were dissolved in 75 ml. of 95% ethanol and hydrolyzed, using the procedure described earlier. The final benzene extract was dried over anhydrous sodium sulfate, made up to 50 ml., the solution divided, and the 2 equal portions placed on like columns of Magnesol. The chromatograph was then developed with benzene. The materials from bands 3 and 4 (the only significant bands) were crystallized from their concentrated benzene solutions with *n*-heptane. Total yield from the 4.772 g. of nitrated sulfonate esters was 1.8516 g. of nitrated phenols. This is a 64.07% yield on a mononitro basis.

4'-Nitro-2-hydroxybiphenyl. Two and one half grams (0.008 mole) of the sulfonate ester dissolved in 7.5 ml. of glacial acetic acid was nitrated at room temperature with a nitrating mixture composed of 3.4 ml. of fuming nitric acid (sp. gr. 1.49–1.5) (0.078 mole) and an equal volume of glacial acetic acid. The gummy nitration products were hydrolyzed and, following the usual procedure, the nitrohydroxybiphenyls were dissolved in 25 ml. of benzene and placed on a Magnesol column. Yields of the first and second colored bands, which moved rapidly down the column, were insignificant. The third and fourth colored bands contained the principal products—the 4'- and 2'-mononitro derivatives.

The material from band number three, which was of a pronounced yellow color, was crystallized from benzene-*n*-heptane as a mixture of yellow prisms and pale, yellow needle clusters. The 0.52 g. obtained represented a 30% yield on a mononitro basis. Both crystal forms melted at 122–123°. A mixed melting point of the 2 forms showed no depression. When both crystal forms were heated to 115° a slight amount of material sublimed to form long, pointed needles melting at 125–126°. This is the melting point of 2-hydroxy-5-nitrobiphenyl.

Anal. Calcd. for $C_{12}H_9O_3N$: N, 6.51. Found: N, 6.36.

Oxidation of 4'-nitro-2-hydroxybiphenyl. A solution of chromic acid (2.1 g., 0.02 mole) in 10 ml. of 65% acetic acid was added dropwise with stirring to 0.27 g. of the yellow prisms (described in the preceding section) dissolved in 4 ml. of glacial acetic acid. When addition was completed, the mixture was heated at a gentle reflux for 90 min. and a 40% formaldehyde solution added dropwise to the reaction mixture until reaction ceased. A further 0.5 ml. of formaldehyde was added to ensure reduction of the excess chromic acid. The mixture was cooled to room temperature and an equal volume of concentrated hydrochloric acid added. The mixture was extracted with four 10-ml. portions of ether and the ether extract washed twice with 10 ml. of ice water. Evaporation of the ether gave 0.11 g. of a product which melted at 236°. This melting point is 4 degrees lower than that recorded for *p*-nitrobenzoic acid.

2'-Nitro-2-hydroxybiphenyl. The material in the fourth band, which followed the third colored band just described, required roughly twice the volume of eluent used for the third band. Recrystallization from benzene-*n*-heptane as well as from chloroform-*n*-heptane, gave moderately large, dark yellow prisms m.p. 139–141°. Recrystallization from boiling water, in which solubility was slight, gave crystals lighter in color, m.p. 142–144°. The dark yellow crystals sublimed at 120° to small, well formed, light yellow prisms. The 0.36 g. recovered represents a 20.9% yield based on *o*-hydroxybiphenyl. Chromic acid oxidation produced *o*-nitrobenzoic acid, m.p. 147–148°.

Anal. Calcd. for $C_{12}H_9O_3N$: N, 6.51. Found: N, 6.68.

3,5,4'-Trinitro-2-hydroxybiphenyl. One and eight tenths ml. (0.042 mole) of fuming nitric acid in 2 ml. of glacial acetic acid were added to a sample of 4'-nitro-2-hydroxybiphenyl (2.15 g., 0.01 mole) dissolved in 15 ml. of glacial acetic acid. Precipitation was observed during addition of the nitrating mixture. The temperature was held at 25° by cooling with tap water. The reaction mixture stood for 2 hr. after addition of the nitrating agent. The precipitate was washed with a 5% solution of sodium bicarbonate followed by water. The crystal mass was dissolved in a mixture composed of 15 ml. of benzene and 10 ml. of *n*-heptane. The solvent was evaporated to a volume of 3 ml. on the hot plate. This treatment was repeated and the crystal mass dissolved in 15 ml. of benzene followed by drying over anhydrous sodium sulfate. Crystallization was obtained by addition of 10 ml. of *n*-heptane. The crystals were thin, brownish yellow needles, yield 2.285 g., 71.9%, m.p. 162–163°. Crystals were also obtained from hot, dilute alcohol. Chromic acid oxidation produced *p*-nitrobenzoic acid.

Anal. Calcd. for $C_{12}H_7O_7N_3$: N, 13.76. Found: N, 13.76.

Nitration of 4'-nitro-2-hydroxybiphenyl to 3,4'- and 5,4'-dinitro-2-hydroxybiphenyl. A (0.5 g., 0.0023 mole) sample of 4'-nitro-2-hydroxybiphenyl was dissolved in 7 ml. of glacial acetic acid and nitrated at room temperature using 1 ml. of a nitration mixture composed of 1 ml. of fuming nitric acid (0.023 mole) and 9 ml. of glacial acetic acid. The dark-colored reaction mixture was set aside for 2 hr. and poured into 50 ml. of ice water. The yellow precipitate was washed on the filter with cold dilute acetic acid and with water. The precipitate was dissolved in 15 ml. of *n*-heptane and the solution evaporated to near-dryness on the hot plate. The precipitate was again dissolved in benzene and the treatment with *n*-heptane repeated. The crystals were dissolved in 25 ml. of benzene, the solution was dried over anhydrous sodium sulfate and placed on the column. Four bands appeared, however, material was recovered from only the first two. The first band was treated by elution and the second by extrusion and extraction with ethanol. The material from the first band crystallized readily from benzene, *n*-heptane as yellow needles with a slight greenish cast, m.p. 194–195°. The yield was 0.19 g., 31.59% on a dinitro basis.

Anal. Calcd. for $C_{12}H_8O_5N_2$: N, 10.77. Found: N, 10.73.

After extrusion and extraction with 95% ethanol, the material from the second band was crystallized from chloroform–*n*-heptane as shiny plates of pale yellow color, m.p. 226–228°. The yield was 0.073 g., 12% on a dinitro basis. When the compounds from the first and second bands were oxidized using chromic acid, and the products separately mixed with *p*-nitrobenzoic acid and heated, no lowering of the m.p. was observed. This shows that the second nitro group enters the phenolic ring.

Anal. Calcd. for $C_{12}H_8O_5N_2$: N, 10.77. Found: N, 10.56.

Further nitration of 3,4′- and 5,4′-dinitro-2-hydroxybiphenyl to 3,5,4′-tri-nitro-2-hydroxybiphenyl. A sample (0.208 g.) of the compound from the first band was dissolved in 10 ml. of glacial acetic acid and nitrated at room temperature with 1.0 ml. (0.0023 mole) nitric acid. A stock of this nitrating mixture was made up by mixing 1.3 ml. of fuming nitric acid and 8.7 ml. of glacial acetic acid. The mixture was set aside for 2 hr. and poured into 25 ml. of ice water. The yellow precipitate was collected on the filter, washed free of acid with water, and taken up in benzene. The benzene solution was twice taken to dryness with added *n*-heptane and the residue redissolved in 15 ml. of benzene. Addition of an equal volume of *n*-heptane caused a precipitate of brown-yellow needles m.p. 162–163° following recrystallization. A mixed melting point with 3,5,4′-trinitro-2-hydroxybiphenyl, previously prepared, showed no depression. A sample of the compound from the second band (0.186 g.) was dissolved in 10 ml. of glacial acetic acid and nitrated at room temperature with 1 ml. of the nitrating mixture previously described. The reaction mixture was refluxed on the water bath for 30 min. The product was worked up in the same manner as that described for the material from band 1. The purified product melted 161–163°. The melting point was not lowered by admixture with previously prepared 3,5,4′-trinitro-2-hydroxybiphenyl.

Further nitration of 2′-nitro-2-hydroxybiphenyl. A sample of 2′-nitro-2-hydroxybiphenyl (0.25 g., 0.0012 mole) was dissolved in 5 ml. of nitromethane and 1 ml. of nitration mixture (0.0012 mole nitric acid) added dropwise at room temperature. The nitrating mixture was made up with 0.5 ml. of fuming nitric acid and 9.5 ml. of nitromethane. There was immediate darkening of the reaction mixture and a moderate increase in temperature. The reaction mixture was set aside for 2 hr. and poured into 25 ml. of ice water. The precipitated material was prepared for the column in the usual manner. The first band, when eluted, gave 0.06 g. of starting material. The second band was extruded and extracted with 95% ethanol. Crystallization from hot benzene,*n*-heptane gave pale yellow fernlike leaflets which, when heated, showed a change of state above 200° forming rectangular plates, m.p. 228–229°, yield 0.09 g., 40.95%. This product was assumed to be either the 3,2′- or the 5,2′-dinitro derivative.

Further nitration of 2′-nitro-2-hydroxybiphenyl in glacial acetic acid. A sample of 2′-nitro-2-hydroxybiphenyl (0.25 g., 0.0012 mole) was dissolved in 5 ml. of glacial acetic acid and nitrated with 4 ml. of a nitrating mixture made up of 0.5 ml. fuming nitric acid dissolved in 9.5 ml. glacial acetic acid (0.0047 mole nitric acid). The reaction mixture darkened at once and a precipitate came down during the latter part of the addition period. The product was worked up as usual and placed on the column. Three bands developed of which the first was narrow, dim yellow in color and moved, under moderate elution with benzene, with sufficient speed to enable extrusion of a second band which was the principal one. This was the only band from which material could be isolated. The material from this band crystallized readily from benzene,*n*-heptane as yellow needles, m.p. 152–153°. The weight was 0.17 g., 48.02%. These yellow, needlelike crystals were assumed to be 3,5,2′-trinitro-2-hydroxybiphenyl. A sample of these crystals when oxidized with chromic acid formed a product whose m.p. of 146–147° approximated that of *o*-nitrobenzoic acid.

Anal. Calcd. for $C_{12}H_7O_7N_3$: N, 13.77. Found: N, 13.60.

NORMAN, OKLA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage Studies of Some Organogermanium Compounds

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n-Butyltriethylgermane, benzyltriethylgermane, and 2-biphenylyltriethylgermane were prepared and characterized. *n*-Octadecyldiphenyl-2-phenylethylgermane was prepared *via* two independent routes from diphenyl-2-phenylethylgermyllithium and *n*-octadecyl bromide or from *n*-octadecyldiphenylgermyllithium and 2-phenylethyl bromide.

The cleavage of tetraethylgermane was investigated under a variety of experimental conditions. When lithium wire or lithium dispersion was employed, there was little evidence of reaction; but when sodium-potassium alloy was used, it appeared that triethylgermylpotassium was formed but immediately reacted in some unknown manner with the solvent. Attempts were also made to cleave other R_4Ge and $R_3R'Ge$ compounds.

The only trialkylgermylmetallic compound which has been successfully synthesized and characterized is triethylgermylpotassium,[1] prepared from hexaethyldigermane and potassium in ethylamine.

Triphenylgermylmetallic reagents have been more completely investigated. Kraus and Foster[2] cleaved hexaphenyldigermane with sodium in ammonia, forming triphenylgermylsodium. Triphenylgermyllithium was prepared initially by the cleavage of triethylsilyltriphenylgermane in ethylamine.[3] The preparation of triphenylgermyl-

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[1] C. A. Kraus and E. A. Flood, *J. Am. Chem. Soc.*, **54**, 1635 (1932).

[2] C. A. Kraus and L. S. Foster, *J. Am. Chem. Soc.*, **49**, 457 (1927).

[3] C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).