The azo acid obtained by either method above was reprecipitated from dilute bicarbonate solution before weighing. It melted over 10° ranges above 75°; further purification gave material whose melting point, neutralization equivalent and behavior on sublimation were identical with those described previously.[2] The diphenic acid obtained melted above 210°. Previous experience has shown that this material is at least 90% pure. Typical results are recorded in Table I.

TABLE I

Run	Moles, R_1/R_2[a]	Azobenzene, %	Azobenzene-2-carboxylic acid, %	Diphenic acid, %
1	1/1	24	16	17
2	1/1	25	15	29
3	3/1	32	40	9
4	3/1	32	47	14
5	3/1	32	34	11
6	1/3	10	23	38
7	1/3	12	36	46
8	1/3	6	38	45

[a] R_1 = diazotized aniline, R_2 = diazotized anthranilic acid.

To demonstrate the absence of biphenyl-2-carboxylic acid in the products the acidic products from a typical run were dissolved in concentrated sulfuric acid and the solution heated to 140° for five minutes. Under these conditions any biphenyl-2-carboxylic acid present would be quantitatively converted to fluorenone. The solution was cooled, poured on ice, and the resulting precipitate examined. The non-acidic portion of the product consisted of ether-insoluble tars, from which no fluorenone was isolated; these tars were shown in a separate experiment to be derived from azobenzene-2-carboxylic acid. The acidic portion of the product consisted of fluorenone-4-carboxylic acid, derived from diphenic acid.

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(2) Paal and Krecke, *Ber.*, **24**, 3060 (1891).

DEPARTMENT OF CHEMISTRY
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An Improved Synthesis of 2,4-Diacetoxymercurianiline

BY THOMAS C. BRUICE

In the course of a study of aromatic mercury derivatives, it became desirable to prepare large quantities of 2,4-diacetoxymercurianiline. The synthesis of this compound has been previously reported by Vecchiotti in 24% yield.[1] On attempting to repeat this earlier work, the author was unable to obtain the dimercuri compound in yields above 16%. A careful study of the best conditions for obtaining the diacetoxymercurianiline showed that control of *p*H was a primary factor in permitting isolation of the product in high yield. In a series of runs, carried out in buffered solutions of varying *p*H, it was found that at *p*H 4.25 a maximum amount (93.5%) of diacetoxymercurianiline could be isolated; and that deviations of even one *p*H unit from this optimum condition resulted in very decided lowering of yields. The solution of the preparative problem in the case of aniline is considered important, since the same problem will no doubt be encountered in the mercuration of other aromatic amines with mercuric acetate.

Experimental

To 479 g. (7.99 moles) of glacial acetic acid, stirred at room temperature, there was added 251 g. (2.99 moles) of sodium bicarbonate. After the foaming had subsided, 3.2 liters of water was added in such a manner that foaming was kept to a minimum. The *p*H of the resulting solution was found to be 4.30. One mole (318.6 g.) of C. P. mercuric acetate was added, and the *p*H was then found to be 4.25. With constant stirring, there was then added one mole (93 g.) of aniline, and the mixture was set aside in the dark for forty-eight hours to permit complete precipitation of the product. If the *p*H of the solution was carefully adjusted, as above, it was found that washing the precipitate freely with several portions of hot water and then drying in a vaccum desiccator over sodium hydroxide led to 285.3 g. (93.5%) of an excellent product, which melted at 209°, with decomposition. The value recorded in the literature is 208°.[1] The product was converted to 2,4-dibromoacetanilide (m.p. 146°) to confirm its identity.

Anal.[2] Calcd. for $C_{10}H_{11}O_4NHg_2$: C, 19.68; H, 1.82; Hg, 65.73. Found: C, 19.85; H, 1.88; Hg, 65.54.

If the adjustment of *p*H in the above preparation was not carefully made, or if different proportions of reagents than those described above were used, it was found that the yields of 2,4-diacetoxymercurianiline were sharply cut. With mercurating solutions of *p*H above 4.25 the product was contaminated with considerable proportions of *p*-acetoxymercurianiline, which could be removed to some extent by extracting with chloroform. At *p*H values below 4.25, the yield of the desired product was lowered by formation of the soluble 2,4-diacetoxymercurianilinium acetate.

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(1) L. Vecchiotti, *Gazz. chim. ital.*, **44**, II, 34-38 (1914).

(2) Analysis by Dr. A. Elek of the Elek Micro-analytical Laboratory.

DEPARTMENT OF CHEMISTRY
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X-Ray Diffraction Studies of the System: Zn_2TiO_4–$NiTiO_3$

BY H. BIRNBAUM AND R. K. SCOTT

By thermal combination, zinc oxide and oxides of elements of the fourth group of the periodic system, such as titanium, silicon, tin or zirconium, will react to form colorless or weakly colored compounds. If oxides of strong coloring elements, such as vanadium, chromium, manganese, iron, cobalt, nickel or copper, are substituted for part of the zinc oxide in these compounds, colored pigments of excellent stability can be produced.[1] Depth of color, as well as the color itself, can be varied by changing the proportions of the constituents and, in addition, the shade of a pigment of a given composition will change with proceeding reaction.

Since the structures of the pure titanates, zinc orthotitanate and nickel titanate, including their cell dimensions, have been worked out by N. W. Taylor,[2] we selected compositions of zinc oxide, nickel oxide and titanium dioxide for an X-ray diffraction study. Taylor's statement that zinc

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(1) U. S. Patent 2,068,294 (1937).

(2) Taylor, *Z. physik. Chem.*, **96**, 242, 243, 259 (1930).

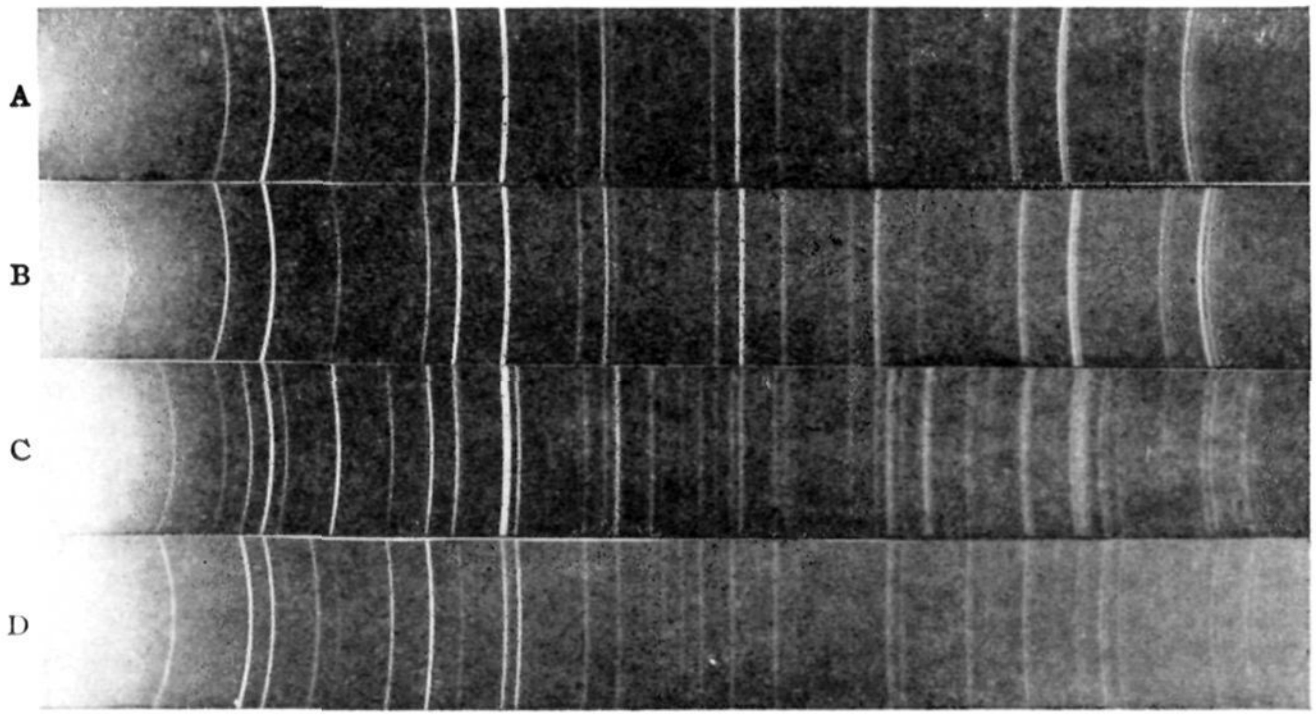

Fig. 1.—X-Ray diffraction patterns of (A) Zn_2TiO_4, (B) ZnO:NiO:TiO_2 = 1.1:0.9:1, (C) ZnO:NiO:TiO_2 = 0.3:1.7:1, (D) $NiTiO_3$. A pronounced change in the unit cell size is evident from (A) to (B) as solid solution occurs. The lack of such change from (D) to (C) is indicative of the inability of zinc to enter the $NiTiO_3$ lattice. The additional lines present in pattern C are those of nickel oxide.

and nickel form only one titanate by direct heating at temperatures up to 1200°, was substantiated by our own work. Furthermore, from our own X-ray data we concluded: (1) Zn_2TiO_4 forms more readily than $NiTiO_3$ under comparative conditions. (2) NiO readily substitutes for ZnO in Zn_2TiO_4 to the extent of approximately 45 mole per cent. as calculated by Vegard's law.[3] (3) ZnO will not enter the $NiTiO_3$ unit cell to any measurable extent. Attempts to obtain substitution of this type results in the formation of pure $NiTiO_3$ and the limit of substitution of NiO in Zn_2TiO_4. The fact that the "d" values of pattern C are slightly smaller than the corresponding "d" values of pattern B indicates that the actual limit of solid solution is slightly greater than the 45 mole per cent. NiO calculated on the basis of the contraction of the Zn_2TiO_4 unit cell. (4) $NiTiO_3$ is a yellow pigment of poor brilliance, and any green tinge in the absence of ZnO is due to unreacted NiO. (5) Zn_2TiO_4 is white. Substitution of zinc by nickel in the crystal lattice results in pure green pigments. The depth of shade depends solely on the extent of the substitution of NiO for ZnO. Nickel oxide present in excess of the limit of solid solution results in a gradual change of color to an olive green, due to the presence of $NiTiO_3$ and NiO.

Experimental

Since metal oxides do not react too rapidly in the dry state, it was considered advantageous to use the sulfates of the divalent metals. The reagents therefore used were: $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, TiO_2.

From these compounds compositions were prepared having the mole ratios: ZnO:NiO:TiO_2, 2.0:0.0:1 (zinc orthotitanate), Pattern A; 1.1:0.9:1 (substitutional solid solution), Pattern B; 0.3:1.7:1 (mixed titanates), Pattern C; 0.0:1.0:1 (nickel metatitanate), Pattern D; Those mixtures of the sulfates and TiO_2 were ground to a fine powder, digested twice with concentrated sulfuric acid, evaporated to dryness each time and heated to 1050° for extended periods. From time to time the reaction products were removed from the furnace for visual inspection and preparation of X-ray diffraction patterns. The heating was continued until the reaction was complete. However, in the case of mixtures where $NiTiO_3$ was one of the end products, the reaction temperature of 1200° was maintained until the uncombined NiO was reduced to an estimated 1%. Diffraction patterns were made by the Debye–Scherrer method, using a powder wedge in a cylindrical camera of 14.32 cm. diameter. A copper target tube was used with heavy filtration Kβ radiation.

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Structure Proof of 2,2-Bis-(4-fluorophenyl)-1,1-dichloroethane[1]

BY R. C. BLINN AND F. A. GUNTHER

Müller[2] reported the preparation of 2,2-bis-(4-fluorophenyl)-1,1-dichloroethane (I) by treating dichloroacetal with fluorobenzene in concentrated sulfuric acid. Bradlow and VanderWerf[3] subsequently reported that they had also prepared this compound by the catalytic hydrogenation of 2,2-bis-(4-fluorophenyl)-1,1-dichloroethylene (II). The compound prepared by

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[3] Vegard, *Z. Physik*, **5**, 16 (1921).

[1] Paper number 618 from University of California Citrus Experiment Station.

[2] Müller, *Helv. Chim. Acta*, **29**, 1560 (1946).

[3] Bradlow and VanderWerf, THIS JOURNAL, **69**, 662 (1947).