lonic esters in basic media which may be of value with acid-sensitive intermediates.[4]

Experimental

Diethyl Isopropylacetamidomalonate.—This compound was prepared in 17% yield[5] by the usual alkylation procedure[2]; m.p. 74.5° from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{21}NO_5$: N, 5.40. Found: N, 5.42.

Diethyl Thenylacetamidomalonate.—This compound has been reported by Dittmer, Herz and Chambers.[6] It was prepared independently in these laboratories.

Anal. Calcd. for $C_{14}H_{19}NO_5S$: S, 10.23. Found: S, 10.25.

Hydrolysis with aqueous sodium hydroxide and acidification with hydrochloric acid gave a 79% yield of the acetamidomalonic acid, m.p. 143.5–145° dec. The crude reaction product was analyzed after drying.

Anal. Calcd. for $C_{10}H_{11}NO_5S$: S, 12.46; neut. equiv., 257. Found: S, 12.48; neut. equiv., 253.

Hydrolysis of the malonic acid with dilute (1:10) hydrochloric acid gave a 60% yield of β-2-thienylalanine, m.p. 265.6–266.9° cor. (lit.,[6] m.p. 273°).

Anal. Calcd. for $C_7H_9NO_2S$: N, 8.18; S, 18.73. Found: N, 8.15; S, 18.88.

General Procedure for Hydrolysis.—The alkylacetamidomalonic esters were refluxed overnight (about sixteen hours) with an equal weight of sodium carbonate dissolved in ten volumes of water. The alkylacetamidocyanoacetic esters were refluxed until evolution of ammonia had practically ceased (usually about sixty hours). The solution was then cooled and acidified to congo paper with hydrochloric acid. The acetyl-DL-amino acid was collected by filtration and recrystallized from water or aqueous alcohol. The lower molecular weight compounds had a tendency to form supersaturated solutions and it was found advisable to obtain seeds from a small portion of the solution before acidifying all of the reaction product. The relatively low yield (52%) for acetyl-DL-norleucine was due to partial hydrolysis to the amino acid in the acidic solution before crystallization could be induced.

***n*-Butyl 2-Acetamido-4-pentenoate.**—Allylacetamidomalonate[2] (15.5 g.) was refluxed with sodium carbonate solution and acidified with hydrochloric acid according to the above procedure. The resulting solution was extracted several times with butanol, dried with sodium sulfate, filtered and distilled to give 9.0 g. of butyl ester; b.p. 118° at 1.1 mm. (70% over-all yield).

Anal. Calcd. for $C_{11}H_{19}NO_3$: C, 60.61; H, 8.98; N, 6.58. Found: C, 60,76; H, 9.20; N, 6.53.

***n*-Propylacetamidomalonic Acid.**—In preparing a sample of N-acetyl-DL-norvaline for mixed m.p., the procedure of Snyder, Shekleton and Lewis[7] was followed, except that the acidified solution was cooled and filtered to give the malonic acid, m.p. 125–126° (dec.).

Anal. Calcd. for $C_8H_{13}NO_5$: neut. equiv., 102. Found: neut. equiv., 106.

Starting material RR'C(NHAc)COOEt R	R″	M. p. of acetyl-DL-amino acid, °C.	Yield, %	N Anal., % Calcd.	Obsd.
Isopropyl	COOEt	146[a]	72		
2-Methyl allyl[2]	COOEt	160	67	8.18	8.03[b]
n-Amyl[2]	COOEt	106	77	7.48	7.21
Benzyl[c]	COOEt	152[a]	75		
2-Thenyl[6]	COOEt	121	80	6.57	6.45[d]
n-Propyl[2]	CN	114[a]	69		
n-Butyl[2]	CN	104[e]	52		
n-Octyl[2]	CN	105	72	6.08	5.80
3-Indolemethyl[3]	CN	200[a]	81		

[a] Identity confirmed by mixed m.p. [b] *Anal.* Calcd. for $C_8H_{13}NO_3$: C, 56.12; H, 7.65. Found: C, 56.29; H, 7.48. [c] Albertson and Archer, THIS JOURNAL, 67, 308 (1945). [d] *Anal.* Calcd. for $C_9H_{11}NO_3S$: neut. equiv., 213. Found: neut. equiv., 212. [e] Identity confirmed by m.p. and analogy.

STERLING–WINTHROP RESEARCH INSTITUTE
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Unsymmetrical Azo Compounds from Diazotized Amines

BY EDWARD R. ATKINSON, DONALD N. REYNOLDS AND DONALD M. MURPHY

The reduction of a mixture of diazotized anthranilic acid and diazotized 3,5-dichloro-2-aminobenzoic acid by cupro-ammonia ion produces the unsymmetrical biaryl 4,6-dichlorodiphenic acid along with the expected symmetrical biaryls.[1]

We have now examined the reduction of a mixture of diazotized anthranilic acid and diazotized aniline and find that in addition to the expected symmetrical products, diphenic acid and azobenzene, the only unsymmetrical product is an azo compound, azobenzene-2-carboxylic acid. It is apparent that the tendency to form an azo compound, which diazotized aniline exhibits, predominates over the tendency to form a biaryl shown by diazotized anthranilic acid. As in the earlier work the reaction is of no great interest as a synthetic method but again demonstrates that whatever the intermediates may be, they possess the ability of reacting with one another.

Experimental Part

Solutions of diazotized aniline and diazotized anthranilic acid were prepared, mixed and reduced by the general procedure previously described[1]; identical results were obtained from mixtures reduced immediately after preparation or after standing at 0° overnight.

Azobenzene was filtered from the ammoniacal reaction mixture and purified by steam distillation. The procedure used for the separation of the acidic products, diphenic acid and azobenzene-2-carboxylic acid, depended on their relative quantities. In cases where the quantity of diphenic acid was not too great, the ammoniacal reaction mixture was slowly acidified at 90° with hydrochloric acid. The azo acid collected as an oil which was removed mechanically while the diphenic acid was obtained by further acidification and cooling overnight. This process took advantage of the tendency of diphenic acid to form supersaturated solutions in water. In other cases it was necessary to obtain a mixture of crude acidic products by acidification with excess acid, dissolve the crude in dilute bicarbonate solution at room temperature, filter free from entrained copper salts and then slowly acidify the bicarbonate solution.

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(4) Herz, Dittmer and Cristol, *J. Biol. Chem.*, **171**, 383 (1947), report that furfuryl acetamidomalonate could not be hydrolyzed to β-2-furylalanine because of the instability of the intermediates to acids. In this case, carbonate hydrolysis followed by caustic hydrolysis would probably give the amino acid.

(5) It will be noted that although acetamidomalonic ester gives low yields on alkylation with secondary halides, acetamidocyanoacetic ester gives just as good results with secondary as with primary halides; *cf.* ref. 3.

(6) Dittmer, Herz and Chambers, *J. Biol. Chem.*, **166**, 541 (1946).

(7) Snyder, Shekleton and Lewis, THIS JOURNAL, **67**, 311 (1945).

(1) Atkinson, Morgan, Warren and Manning, THIS JOURNAL, **67**, 1513 (1945).

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.

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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.*, **B6**, 242, 243, 259 (1930).