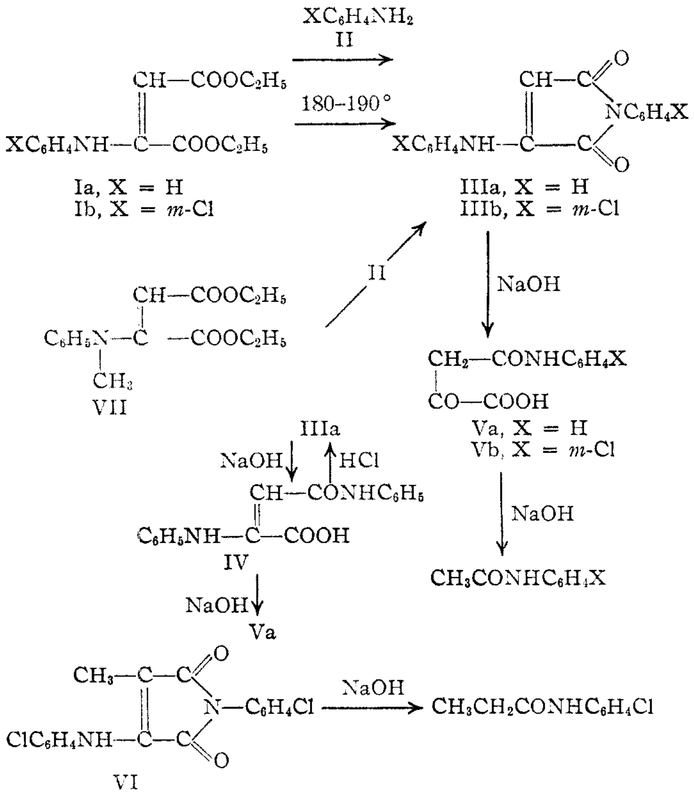
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL COMPANY, INC.]

The Preparation of N-Aryl-α-arylaminomaleimides

BY A. R. SURREY AND R. A. CUTLER

In the course of investigations on the preparation of substituted quinoline compounds by the method of Conrad and Limpach,[1] a study was undertaken to determine the optimum conditions for the ring closure of the ethyl α-arylaminomaleates (I), which have now for the first time been purified by distillation. As a result of this study, it seemed advisable to effect ring closure as rapidly as possible and in the absence of the aniline used in the preparation of I. In the presence of the aniline (II), N-aryl-α-arylaminomaleimides (III) are formed which are yellow crystalline solids not readily separated from the main product. In addition, it has now been found that in some instances it is possible to form the imide (III) by heating the pure I for several hours at 180–190°.

CHART I



When ethyl α-(m-chloroanilino)-maleate (Ib) is subjected to ring closure in mineral oil at 250° in the presence of some m-chloroaniline, a large amount of yellow material is produced. Attempts to separate the mixture of quinoline isomers from the yellow material resulted in the isolation of a yellow crystalline product (VIII), m. p. 228–229°, that proved to be a molecular compound. VIII could also be prepared by heating equimolecular quantities of ethyl 7-chloro-4-hydroxy-2-quinolinecarboxylate,[2] m. p. 250–251°, and ethyl α-(m-chloroanilino) - N - (m - chlorophenyl) - maleimide (IIIb), m. p. 221–222°, in pyridine.[3] The molecular compound was separated into its constituents with difficulty by prolonged heating with glacial acetic acid. Alkaline hydrolysis yielded the anticipated equivalent amount of 7-chloro-4-hydroxy-2-quinolinecarboxylic acid and m-chloroaniline and the analytical data conformed with this ratio. When heated alone at 180–190° for several hours, Ib yielded the same molecular compound (VIII) and, consequently, ring closure was accompanied with formation of IIIb.

It has been known for some time[4] that ethyl α-anilinomaleate reacts with aniline to yield α-anilino-N-phenylmaleimide (IIIa), the ease of formation of which has been shown in many reactions[5] wherein it appears mainly as a by-product. The formation of III by heating I alone, however, involves cleavage of aniline which then reacts with more I to yield III. Under the same conditions, ethyl α-(m-chloroanilino)-β-methylmaleate yields, instead of the maleimide, mainly the ring-closed product ethyl 5- and 7-chloro-4-hydroxy-3-methyl-2-quinolinecarboxylate, yet reacts with m-chloroaniline to yield α-(m-chloroanilino)-N-(m-chlorophenyl)-β-methylmaleimide (VI).

Attempts to prepare α-(m-chloroanilino)-N-phenylmaleimide by the action of aniline upon Ib resulted in a mixture from which IIIa was isolated. The formation of IIIa from Ib might proceed through addition of aniline upon Ib followed by cleavage of m-chloroaniline and reaction of the liberated ethyl α-anilinomaleate (Ia) with aniline to yield IIIa. This mechanism accounts for the formation of a mixture of products. The

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[1] Conrad and Limpach, *Ber.*, **20**, 944 (1887).

[2] Surrey and Hammer, THIS JOURNAL, **68**, 113 (1946).

[3] A mixture of the two pure constituents melted at 227–230°. This unusual phenomenon was not encountered with the other maleimides studied.

[4] Wislicenus and Spiro, *Ber.*, **22**, 3351 (1889).

[5] (a) Reissert and Tiemann, *ibid.*, **19**, 626 (1886); (b) Michael *ibid.*, **19**, 1377 (1886); (c) Wohl and Freund, *ibid.*, **40**, 2303 (1907); (d) Bischoff and Walden, *Ann.*, **279**, 139 (1894); (e) Le Sueur and Hass, *J. Chem. Soc.*, **97**, 179 (1910); (f) Chattaway and Parkes, *ibid.*, **123**, 663 (1923); **125**, 464 (1924); (g) Clarke and Bolton, THIS JOURNAL, **36**, 1906 (1914); (h) Zetzsche and Hubacher, *Helv. Chim. Acta*, **9**, 291 (1926).

reaction of Ia and *m*-chloroaniline gave a mixture from which IIIa was isolated. The latter was obtained from the above mixtures without serious difficulty since it appeared to be the most insoluble imide of those present.

In the reactions of ethyl α-N-methylanilinomaleate (VII) with aniline and *m*-chloroaniline, substantially pure products, IIIa and IIIb, respectively, separated from the reaction mixtures. The action of aniline upon ethyl α-(*m*-chloroanilino)-β-methylmaleate resulted in a mixture of products from which α-anilino-β-methyl-N-phenylmaleimide[6] was isolated and identified by direct comparison with the product obtained by condensation of ethyl oxalylpropionate with aniline.

The data in the literature on the hydrolysis of IIIa is confusing and the reactions have, therefore, been re-examined. Reissert's[7] initial product (m. p. 176°) melting as did that previously isolated by Michael[5b] and assigned structure IV, yielded, on further hydrolysis, a second acid the structure of which was designated at first, as β-anilinoacrylic acid. However, the work was subsequently[8] repudiated, because the properties of the esterified acid differed from those reported by von Pechmann[9] for the ester obtained by the action of aniline upon ethyl sodioformylacetate. Chattaway and Parkes[5f] also postulated a hydrolysis to β-anilinoacrylic acid, involving intermediatory formation of anilinomaleic acid.

Hydrolyses of IIIa, either by heating in a 5% sodium hydroxide solution or allowing to stand in 5% sodium hydroxide in 50% alcohol, gave a product (m. p. 150–151°) designated as α-anilinomaleanilic acid (IV), which on warming with dilute hydrochloric acid reformed IIIa. Treatment of IV with sodium hydroxide yielded aniline and another acid which analyzed for the monoanilide of oxalacetic acid (V). This appears to be the same compound prepared by Wohl and Lips[10] from the action of aniline upon the pyridine salt of hydroxymaleic anhydride which they designated as β-hydroxyfumaranilic acid. By analogy with ethyl ethoxalylacetate[11] and as was anticipated, alkaline hydrolysis of V gave aniline, acetanilide and oxalic acid. Hydrolysis of IIIb in the same manner omitting, however, isolation of the acid corresponding to IV, gave Vb,[12] which further hydrolyzed to *m*-chloroacetanilide. Hydrolysis of α-(*m*-chloroanilino)-N-(*m*-chlorophenyl)-β-methylmaleimide (VI) yielded the expected *m*-chloropropionanilide. Formation of these anilides confirms the structures assigned to IV and V.

Acknowledgment.—The authors wish to express their appreciation to Drs. C. M. Suter and J. S. Buck for their advice and interest in this work.

Experimental[13]

Ethyl α-*m*-Chloroanilinomaleate (Ib).—Ethyl sodioethoxalylacetate, 210 g. (1.0 mole), was added to a well-stirred solution of 204 g. (1.6 mole) of *m*-chloroaniline in 460 ml. of glacial acetic acid and stirring was continued for five hours. After standing for fifteen hours the reaction mixture was diluted with ice-water, neutralized with sodium hydroxide solution and the oil which separated was extracted with ether. The ether solution was washed three times with a total of 2 liters of 1 *N* hydrochloric acid and twice with a total of 1500 ml. of 1 *N* sodium hydroxide solution, dried over anhydrous sodium sulfate and distilled. The residue, 216 g. (72%), was distilled at 149–150° at 0.2 mm. (bath temp. 160°), $n^{27}\mathrm{D}$ 1.5671.

Anal. Calcd. for $C_{14}H_{16}NO_4Cl$: C, 56.50; H, 5.42; N, 4.71. Found: C, 56.76; H, 4.71; N, 4.94.

Ethyl α-Anilinomaleate (Ia).—Essentially the same method as described above was used in the preparation of Ia, yield, 70%. The product distilled at 124–125° at 0.15 mm., $n^{24}\mathrm{D}$ 1.5610.

Anal. Calcd. for $C_{14}H_{17}NO_4$: N, 5.32. Found: N, 5.31.

Ethyl α-(*m*-Chloroanilino)-β-methylmaleate.—A mixture of *m*-chloroaniline (3 moles) and ethyl ethoxalylpropionate (2 moles) was allowed to stand at room temperature for three days and then worked up as above; yield, 80%. The product distilled at 149–150° at 0.2 mm., $n^{25}\mathrm{D}$ 1.5570.

Anal. Calcd. for $C_{15}H_{18}NO_4Cl$: N, 4.49. Found: N, 4.46.

Ethyl α-N-Methylanilinomaleate (VII).—A mixture of 53 g. (0.5 mole) of N-methylaniline, 94 g. (0.5 mole) of ethyl ethoxylalylacetate and 500 ml. of benzene was refluxed on a steam-bath for sixteen hours using a water separator. The benzene solution was worked up as above. The oil, 68 g. (48%), was distilled: b. p., 148–150° at 0.2 mm., $n^{25}\mathrm{D}$ 1.5433. The product crystallized from Skellysolve A to yield a white solid, m. p., 43–44°.

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 64.54; H, 6.65; N, 4.69.

α-Anilino-N-phenylmaleimide (IIIa).—Essentially the same method as described by Wislicenus and Spiro[4] was used in the preparation of the N-aryl-α-arylaminomaleimides.

A mixture of 115 g. (0.44 mole) of ethyl α-anilinomaleate (Ia), 45 g. (0.48 mole) of aniline and 1 ml. of glacial acetic acid was heated for seven hours at 180–190°. Alcohol was added to the cooled mixture and the yellow crystalline solid which separated from the reaction mixture was filtered off; yield 44 g. (38%), and recrystallized from pyridine; m. p., 230–230.5°.

α-(*m*-Chloroanilino)-N-(*m*-chlorophenyl)-maleimide (IIIb).—This product was prepared from ethyl α-(*m*-chloroanilino)-maleate (Ib) and *m*-chloroaniline; yield 52%. A sample recrystallized from pyridine gave a light yellow-colored product which melted at 220–221°.

Anal. Calcd. for $C_{16}H_{10}N_2O_2Cl_2$: C, 57.68; H, 3.03; N, 8.41. Found: C, 57.73; H, 2.70; N, 8.50.

α-(*m*-Chloroanilino)-N-(*m*-chlorophenyl)-β-methylmaleimide (VI).—The compound was prepared from ethyl α-(*m*-chloroanilino)-β-methylmaleate and *m*-chloroaniline; yield 30%. A sample recrystallized from alcohol gave yellow leaflets which melted at 150–151°.

Anal. Calcd. for $C_{17}H_{12}N_2O_2Cl_2$: N, 8.07. Found: N, 7.88.

Reaction of Ia and *m*-Chloroaniline.—A mixture of 20 g. (0.076 mole) of ethyl α-anilinomaleate (Ia) and 10 g.

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(6) Ref. 4; the authors prepared this compound by the reaction of ethyl oxalylpropionate and aniline.

(7) (a) Reissert, *Ber.*, **19**, 1644 (1886); (b) **20**, 3105 (1887).

(8) Reissert, *ibid.*, **26**, 1759 (1893).

(9) v. Pechmann, *ibid.*, **25**, 1051 (1892).

(10) Wohl and Lips, *ibid.*, **40**, 2297 (1907).

(11) Wislicenus, *Ann.*, **246**, 326 (1888).

(12) On the basis of the work of Wohl and Lips (ref. 10) this would be *m*-chloro-β-hydroxyfumaranilic acid.

(13) All melting points are uncorrected; microanalyses by the Misses P. Curran and G. Barnett.

(0.079 mole) of *m*-chloroaniline was heated at 180–190° for five hours. On cooling, the crude product which separated was filtered off, dissolved in 50 ml. of hot pyridine and 100 ml. of methanol added to yield 2.7 g. of a yellow mixture, which melted at 190–204°. The mixture was dissolved in 250 ml. of alcohol, approximately one-half of the solvent was distilled, and the separated solid (m. p. 218–223°) filtered from the hot solution. Four recrystallizations from dioxane gave 0.05 g. of product melting at 228–230° which did not depress the melting point of a pure sample of IIIa.

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: N, 10.60. Found: N, 10.93.

Reaction of Ib and Aniline.—A mixture of 22 g. (0.074 mole) of ethyl α-(*m*-chloroanilino)-maleate (Ib) and 7.5 g. (0.08 mole) of aniline was heated at 180–190° for five hours. The crude product was dissolved in 30 ml. of hot pyridine and 100 ml. of methanol was added; yield 5.1 g., m. p. 182–200°. The isolation of IIIa from this mixture was carried out in the same manner as described above to give 0.08 g., m. p. 230–232°.

Reaction of Ethyl α-(*m*-Chloroanilino)-β-methylmaleate and Aniline.—A mixture of 10 g. (0.032 mole) of ethyl α-(*m*-chloroanilino)-β-methylmaleate and 3 g. (0.032 mole) of aniline was heated for eight hours at 185–200°. After standing at room temperature for a week, the solid which slowly crystallized from the reaction mixture was removed by filtration; yield 1 g., m. p. 133–145°. After six crystallizations from a mixture of benzene and Skellysolve C, a yellow crystalline solid (0.02 g.) was obtained melting at 153.5–155°. A mixed melting point determination with a sample of α-anilino-β-methyl-N-phenylmaleimide, prepared from ethyl ethoxalylpropionate and aniline,[4] m. p., 155–156°, showed no depression.

Reaction of VII and Aniline.—A mixture of 12 g. (0.043 mole) of ethyl α-N-methylanilinomaleate (VII) and 4 g. (0.043 mole) of aniline was heated for four and one-half hours at 180–190°. The solid which separated from the reaction mixture was filtered off and washed with ether; yield, 3 g., m. p. 229–231°. This was identified as IIIa.

Reaction of VII and *m*-Chloroaniline.—A mixture of 10 g. (0.036 mole) of ethyl α-N-methylanilinomaleate (VII) and 4.6 g. (0.036 mole) of *m*-chloroaniline was heated eight hours at 160°; yield 1.3 g., m. p. 213–217°. One recrystallization from a mixture of dioxane and alcohol raised the melting point to 220–221°. A mixed melting point determination with a pure sample of IIIb showed no depression.

Preparation of Molecular Compound VIII.—A mixture of 30 g. (0.1 mole) of ethyl α-(*m*-chloroanilino)-maleate (Ib) and 12.8 g. (0.1 mole) of *m*-chloroaniline was added with stirring to 200 ml. of mineral oil at 245°. The temperature was held at 240–245° for ten minutes after which the reaction mixture was allowed to cool to room temperature. The product was filtered off and washed with Skellysolve B; yield 21.4 g., m. p., 202–216°. After recrystallization from pyridine a yellow product (11 g.) was obtained melting at 226–230°. A sample was recrystallized several times from glacial acetic acid for analysis, m. p. 227–228°.

Anal. Calcd. for $C_{28}H_{20}N_3O_5Cl_3$: C, 57.50; H, 3.45; N, 7.19; Cl, 18.19. Found: C, 57.14, 57.32; H, 3.28, 3.58; N, 7.48, 7.53; Cl, 18.31, 18.50.

A mixture of 1.26 g. ethyl 7-chloro-4-hydroxy-2-quinoline carboxylate and 1.67 g. of IIIb was heated to solution in 15 ml. of pyridine. The solid which separated on cooling (m. p. 228–230°) was recrystallized from pyridine, m. p. 228–229°. A mixed melting point determination with a sample of VIII prepared above showed no depression.

Anal. Found: N, 7.17.

Separation of VIII into its Constituents.—Twenty grams of VIII was refluxed for two and one-half hours with 500 ml. of glacial acetic acid. The orange-yellow solution was allowed to cool slowly to 60° and the solid which gradually separated was filtered off; yield 4 g., m. p., 216–218°. One recrystallization from glacial acetic acid gave small yellow needles, m. p. 220–221°. A mixed melting point determination with a pure sample of IIIb showed no depression. When the filtrate had cooled to 40° it was filtered again to give 6.6 g. of the molecular compound VIII, m. p. 227–229°. At room temperature a third fraction was obtained from the acetic acid solution; yield, 2.5 g., m. p. 223–227°. Dilution of the filtrate with an equal volume of water gave 4.2 g. of product melting at 220–230°. Trituration of the latter or recrystallization with hot ethyl acetate gave a white solid, m. p., 248–249°, which was identified as ethyl 7-chloro-4-hydroxy-2-quinolinecarboxylate.

Hydrolysis of VIII.—Fifteen grams (0.026 mole) of VIII was refluxed for two hours with 140 ml. of 1.5 *N* sodium hydroxide (0.21 mole). The solution was diluted with water, extracted with ether and the latter washed with dilute hydrochloric acid, and distilled to give 1.3 g. of *m*-chloroacetanilide. The acid washings yielded 4.3 g. of *m*-chloroaniline. The residual alkaline solution was filtered hot with charcoal, acidified with dilute hydrochloric acid, and the solid which separated from the hot solution was filtered off and washed with water; yield 5.9 g. (0.025 mole) of 7-chloro-4-hydroxy-2-quinolinecarboxylic acid, m. p. 277–278°.[2]

Action of Heat on Ia.—Ten grams of freshly distilled ethyl α-anilinomaleate (Ia) was heated for six hours at 180–185° to yield 1 g. of a yellow-orange solid. One recrystallization from a large volume of alcohol gave a product melting at 230–231° which was identified as IIIa.

Action of Heat on Ib.—Ten grams of freshly distilled ethyl α-(*m*-chloroanilino)-maleate was heated for seven hours at 180–190°; yield, 0.95 g. of yellow crystalline solid melting at 228–230°, which was identified as the molecular compound VIII.

Action of Heat on Ethyl α-(*m*-chloroanilino)-β-methylmaleate.—Ten grams of ethyl α-(*m*-chloroanilino)-β-methylmaleate was heated at 170–185° for eight hours; yield, 0.7 g. of a white solid melting at 181–185°. This appeared to be a mixture of ethyl 5- and 7-chloro-3-methyl-4-hydroxy-2-quinolinecarboxylates. No yellow product was isolated.

Action of Heat on VII.—Ten grams of ethyl α-N-methylanilinomaleate (VII) heated for eight hours at 160° darkened somewhat but was otherwise unchanged as evidenced by the constancy of the refractive index.

Preparation of α-Anilinomaleanilic Acid (IV).—Ten grams (0.038 mole) of α-anilino-N-phenylmaleimide (IIIa) was added with stirring to 45 ml. of a solution of 5% sodium hydroxide in 50% alcohol. After standing at room temperature for forty hours, the clear yellow solution was cooled in an ice-bath and acidified with glacial acetic acid; yield 5 g. (48%) of a yellow powder melting at 148–150°. Recrystallization from ethyl acetate gave yellow needles, m. p., 150–151°.

Anal. Calcd. $C_{16}H_{14}N_2O_3$: N, 9.93. Found: N, 9.80.

IV was also obtained by boiling 10 g. of IIIa in a 5% aqueous solution of sodium hydroxide for about one minute. The clear solution was cooled rapidly in an ice-bath and worked up as above; yield 2.4 g.

A sample of IV was warmed with 6 *N* hydrochloric acid on a steam-bath for about one minute. A yellow solid separated (m. p. 220–228°) which after one recrystallization from pyridine gave pure IIIa, m. p. 230–231°.

Preparation of β-Hydroxyfumaranilic Acid (Va).—One and one-half grams (0.0053 mole) of IV was refluxed for twenty-five minutes with 30 ml. of 0.35 *N* sodium hydroxide (0.0106 mole). The aniline which separated was removed from the cold solution by ether extraction, the alkaline solution was filtered with charcoal and the ice-cooled filtrate acidified with 1 ml. of concentrated hydrochloric acid. The solid which separated (0.7 g. (70%), m. p., 131–135°) was triturated with hot benzene to give a white solid which melted at 142–143°. An aqueous solution gave a deep red color with ferric chloride solution.

Anal. Calcd. for $C_{10}H_9NO_4$: N, 6.76. Found: N, 6.98.

Va was also prepared directly from 10 g. of IIIa in 45 ml. of 0.18 *N* sodium hydroxide (0.08 mole) by refluxing for one hour and working up as above; yield, 5.3 g. (67%).

Alkaline Hydrolysis of Va.—A solution of 2.07 g. (0.01 mole) of Va in 15 ml. of 0.2 *N* sodium hydroxide (0.03 mole) was refluxed for ninety minutes. After cooling, the solution was extracted with ether, the latter washed with dilute hydrochloric acid; 0.1 g. of acetanilide (m. p., 113–114°) and 0.3 g. of aniline were isolated from the final ether and acid solutions, respectively. The residual alkaline solution, after extraction with ether, was filtered with charcoal, cooled and acidified with concentrated hydrochloric acid to give 0.1 g. of unchanged acid. The filtrate was made alkaline and treated with calcium hydroxide solution, to yield 0.95 g. of a white solid identified as 60% calcium oxalate and 40% calcium carbonate.

Preparation of *m*-Chloro-β-hydroxyfumaranilic Acid (Vb).—Five grams (0.015 mole) of IIIb was refluxed for thirty minutes in 25 ml. of 0.12 *N* sodium hydroxide (0.03 mole) to yield 1.8 g. of *m*-chloroaniline, and 3.5 g. (96%) of a yellowish-white acid, m. p., 118–119°. Recrystallization from a mixture of ether and Skellysolve A gave a white powder, m. p., 122–123°. An aqueous solution gave a deep red color with ferric chloride solution.

Anal. Calcd. for $C_{10}H_8NO_4Cl$: N, 5.80. Found: N, 5.65.

Alkaline Hydrolysis of Vb.—A solution of 3.7 g. (0.015 mole) of Vb in 25 ml. of 0.16 *N* sodium hydroxide was refluxed for two hours. The following products were isolated according to the procedure for the hydrolysis of Va: *m*-chloroaniline (0.34 g.); *m*-chloroacetanilide (0.75 g.), identified by a mixed melting point determination with an authentic sample; 0.46 g. of unchanged acid; 0.74 g. of calcium oxalate, and 0.49 g. of calcium carbonate.

Hydrolysis of VI.—Ten and one-half grams (0.03 mole) of VI was refluxed with 45 ml. of 0.19 *N* sodium hydroxide (0.086 mole) for one and one-half hours. The products isolated were *m*-chloroaniline (4.23 g.) and *m*-chloropropionanilide (3.48 g.).

Summary

Four pure ethyl α-arylaminomaleates have been prepared.

The formation of α-anilino-N-phenylmaleimide by heating ethyl α-anilinomaleate alone or in the presence of aniline is described. When ethyl α-(*m*-chloroanilino)-maleate is heated alone or in the presence of some *m*-chloroaniline, a molecular compound of α-(*m*-chloroanilino)-N-(*m*-chlorophenylmaleimide and ethyl 7-chloro-4-hydroxy-2-quinolinecarboxylate is formed. The stepwise alkaline hydrolysis of α-anilino-N-phenylmaleimide and α-(*m*-chloroanilino)-N-(*m*-chlorophenyl)-maleimide is reported. Alkaline hydrolysis of α-(*m*-chloroanilino)-N-(*m*-chlorophenyl)-β-methylmaleimide gives *m*-chloropropionanilide as one of the products.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Trimethylthallium[1]

BY HENRY GILMAN AND R. G. JONES

Triethylthallium,[2,3] triphenylthallium[4,5] and tri-*i*-butylthallium[4] are the only R_3Tl compounds hitherto described, and each of these has been prepared by the reaction of a diorganothallium halide with an organolithium compound.

$$R_2TlX + RLi \longrightarrow R_3Tl + LiX \qquad [I]$$

Rochow and Dennis[3] were unable to obtain trimethylthallium by reactions between thallium and dimethylmercury, thallium and methyl iodide, or a sodium–thallium alloy and methyl iodide.

Incidental to studies on the reactions of finely divided metals, we have found that trimethylthallium is produced in almost quantitative yields from a thallous halide, methyllithium and methyl iodide. The following sequence of reactions is the best present description of the process.

$$3CH_3Li + 2TlX \longrightarrow (CH_3)_3Tl + 2Tl + 3LiX \qquad [II]$$

$$2CH_3I + 2Tl \longrightarrow (CH_3)_2TlI + TlI \qquad [III]$$

$$CH_3Li + (CH_3)_2TlI \longrightarrow (CH_3)_3Tl + LiI \qquad [IV]$$

Addition of II, III and IV gives the following reaction V.

$$2CH_3Li + CH_3I + TlX \longrightarrow (CH_3)_3Tl + LiX + LiI \qquad [V]$$

We have shown that reaction II takes place quantitatively.[6] When an excess of methyllithium in ether solution was allowed to react with thallous iodide, two-thirds of the thallium was reduced to the metal and one-third appeared as trimethylthallium. Methylthallium is probably formed first, but then undergoes immediate disproportionation.

$$3CH_3Li + 3TlX \longrightarrow 3LiX + [3CH_3Tl] \longrightarrow (CH_3)_3Tl + 2Tl$$

Although methyl iodide does not react with ordinary forms of metallic thallium,[3] the very finely divided metal, produced according to reaction II, reacts readily with methyl iodide in ether solution at room temperature or even at 0°. Reaction III might have been written as

$$3CH_3I + 2Tl \longrightarrow (CH_3)_2TlI + CH_3TlI_2$$

However, the existence of methylthallium diiodide seems doubtful. Aromatic $RTlI_2$ compounds decompose immediately to give RI + TlI.[7] The scope and limitations of the reactions of thallous halides with reactive RM compounds

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[1] Paper LI in the series: "Relative Reactivities of Organometallic Compounds." The preceding article is: *J. Org. Chem.*, **8**, 224 (1943).

[2] Groll, THIS JOURNAL, **52**, 2998 (1930).

[3] Rochow and Dennis, *ibid.*, **57**, 486 (1935).

[4] Birch, *J. Chem. Soc.*, 1132 (1934).

[5] Gilman and Jones, THIS JOURNAL, **61**, 1513 (1939).

[6] Similar reactions of thallous halides with other RLi and RMgX compounds have been reported: see Menzies and Cope, *J. Chem. Soc.*, 2862 (1932); Gilman and Jones, THIS JOURNAL, **62**, 2357 (1940); also ref. 4.

[7] Challenger and Parker, *J. Chem. Soc.*, 1462 (1931).