the reaction at atmospheric pressure below the boiling point of liquid ammonia (−50°). These are illustrated by the following instances.

Dibenzylmalononitrile (Method A). To a mixture of 3.3 g. (0.05 mole) of malononitrile and 12.7 g. (0.1 mole) of benzyl chloride contained in a glass pressure vessel[4] was added 50 cc. of liquid ammonia. In a moment the exothermic reaction occurred,[5] and a great deal of crystalline solids began to separate. The reaction mixture was allowed to stand at room temperature for about 24 hr.; then the ammonia was evaporated. The remaining solids were washed with water and recrystallized from ethanol; yield, 9.1 g. (74%) of dibenzylmalononitrile, m.p. 127.5–129°. An additional recrystallization from ethanol raised the m.p. to 130–131°.

2-Allyl- and 2,2-diallylcyanoacetamide (Method B). Allyl bromide (36.3 g., 0.3 mole) was added dropwise to a stirred solution of 12.6 g. (0.15 mole) of cyanoacetamide in 150 cc. of liquid ammonia contained in a three necked flask equipped with a mechanical stirrer and a Dewar reflux condenser over a period of 1 hr. while maintaining the reaction temperature at −50°. After the addition was completed, the mixture was stirred for 3 hr., and then the ammonia was evaporated. The residue was washed with water. The remaining solids were dissolved in boiling water, and the solution was allowed to stand at room temperature. 2,2-Diallylcyanoacetamide was precipitated rapidly from the still warm solution; yield, 10.5 g. (43% based on cyanoacetamide) which melted at 128–129°. 2-Allylcyanoacetamide was isolated thereafter as a crystalline product from the filtrate by cooling with ice water; it melted at 101–104°, 4.0 g. (21% based on cyanoacetamide).

2-Acetamido-2-ethylcyanoacetamide (Method B). To a stirred solution of 7.1 g. (0.05 mole) of 2-acetamidocyanoacetamide and 150 cc. of liquid ammonia, 7.8 g. (0.05 mole) of ethyl iodide was added dropwise at −50°. Stirring was continued for 2 hr.; then the ammonia was evaporated. The resulting mixture was washed with water and recrystallized from water. The yield of 2-acetamido-2-ethylcyanoacetamide, m.p. 204–205° dec., was 6.0 g. (71%). Upon repeated recrystallization from water it melted at 205° dec.

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(4) K. Shimo and S. Wakamatsu, *J. Org. Chem.*, 24, 19 (1959).

(5) External cooling with cold water was desired until the reaction was completed (for about 0.5 hr.).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, NATIONAL RESEARCH CENTRE]

The Stobbe Condensation with *o*- and *p*-Chlorobenzaldehyde

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o- and *p*-Chlorobenzaldehyde condense with methyl succinate to give methyl hydrogen *cis*-γ-*o*-chlorophenyl-, and methyl hydrogen *cis*-γ-*p*-chlorophenylitaconate together with di-*o*-chlorobenzylidene-, and di-*p*-chlorobenzylidenesuccinic acid. The itaconates are cyclized by acetic anhydride and sodium acetate to methyl 4-acetoxy-8-, and -6-chloro-2-naphthoate which are converted into 5-, and 7-chloro-1-naphthol, respectively. The anhydride of the di-*o*-chlorobenzylidenesuccinic acid is cyclized by the action of heat to the corresponding 1-phenylnaphthalene derivative.

Continuation of the investigation of the Stobbe condensation on substituted aromatic aldehydes,[1] *cis*-β-half esters, methyl hydrogen *cis*-γ-*o*-(Ia;R_3 = CH_3) and *cis*-γ-*p*-chlorophenylitaconate (Ib; R_3 = CH_3) together with di-*o*-chlorobenzylidene- (VIa) and di-*p*-chlorobenzylidenesuccinic acid (VIb)[2] were obtained in about 52% and 14% yield respectively by Stobbe condensation of *o*- and *p*-chlorobenzaldehyde with dimethyl succinate and *t*-butyl alcohol potassium *t*-butoxide.[3] In the case of *p*-chlorobenzaldehyde, a small amount of *p*-chlorobenzoic acid was also isolated. Repeating the reaction under nitrogen atmosphere gave no such acid. The structure and the *cis* configuration of the half esters (Ia and b) were confirmed by their cyclization with fused sodium acetate in acetic anhydride[1,4] to methyl 4-acetoxy-8-(IIa;R_3 = CH_3, R_4 = Ac) and -6-chloro-2-naphthoate (IIb; R_3 = CH_3, R_4 = Ac) in a good yield. Alkaline hydrolysis of the acetoxy esters gave 8-, and 6-chloro-4-hydroxy-2-naphthoic acid (IIa and b; R_3 = R_4 = H), respectively.

These phenolic acids were converted by methyl sulfate and potassium carbonate in acetone into the corresponding methoxy esters (IIa and b; R_3 = R_4 = CH_3) which were hydrolyzed to the methoxy acids (IIa and b; R_3 = H, R_4 = CH_3) and then decarboxylated by quinoline and copper-bronze to give 5-, and 7-chloro-1-methoxynaphthalene, respectively.

The structure of these naphthol ethers was confirmed by their cleavage with hydriodic acid to the known 5-, and 7-chloro-1-naphthol.[5]

Hydrolysis of the *cis*-β-half esters (Ia and b; R_3 = CH_3) with boiling barium hydroxide solution gave the *cis*-itaconic acids (Ia and b; R_3 = H). These were converted into their *cis*-anhydrides (IVa and b), which on boiling with methanol gave the *cis*-α-half esters (Va and b) which were different from the *cis*-β-half esters (Ia and b; R_3 = CH_3) obtained by the Stobbe condensation.

The anhydride (VII) was cyclodehydrogenated

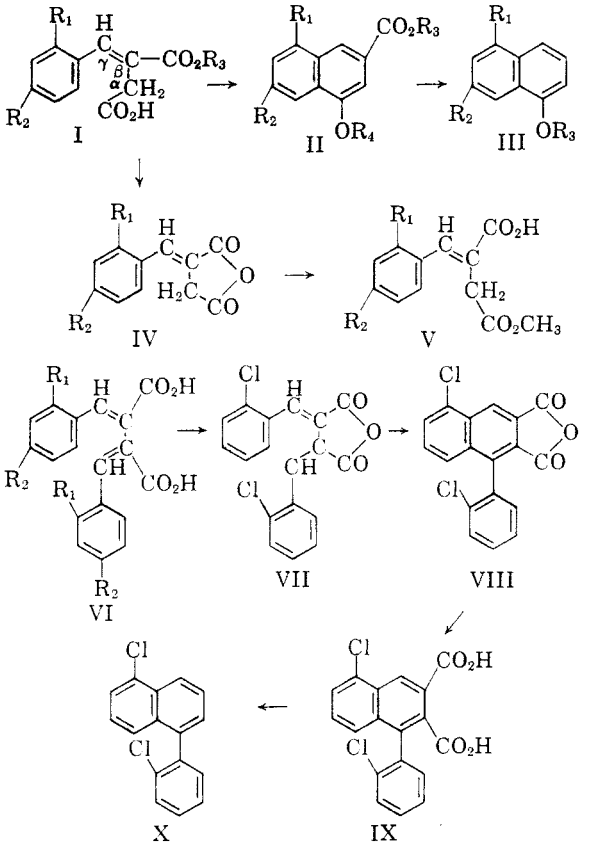
(1) A. M. El-Abbady and Lanson S. El-Assal, *J. Chem. Soc.*, 1024 (1959).

(2) F. G. Baddar, L. S. El-Assal, N. A. Doss, and A. H. Shehab, *J. Chem. Soc.*, 1016 (1959).

(3) *Cf.* W. S. Johnson and G. H. Daub, *Org. Reactions*, VI, 1 (1951).

(4) W. Borsche, S. Kettner, M. Gillies, H. Kuhn, and R. Manteuffel, *Ann.* **526**, 1 (1936).

(5) H. Erdmann and R. Kirchhoff, *Ann.* **247**, 366 (1888).



a. $R_1 = Cl$, $R_2 = H$
b. $R_1 = H$, $R_2 = Cl$

by heat[6] into 2′:5-dichloro-1-phenylnaphthalene-2:3-dicarboxylic anhydride (VIII), which on hydrolysis with dilute alkali gave the corresponding dibasic acid (IX). This on decarboxylation yielded 2′:5-dichloro-1-phenylnaphthalene (X).

EXPERIMENTAL

Stobbe condensation of o-chlorobenzaldehyde with methyl succinate. A solution of *o*-chlorobenzaldehyde (28 g., 1 mole) and methyl succinate (35 g., 1.2 moles) in *t*-butyl alcohol (30 ml.) was added to a boiling solution of potassium *t*-butoxide [from metallic potassium (11.5 g.) in *t*-butyl alcohol (170 ml.)] during 15 min., and the whole refluxed for a further 45 min. The cold mixture was acidified (litmus) with concentrated hydrochloric acid. Evaporation under reduced pressure left an orange brown viscous oil which was treated with ice-water and extracted with ether. The ethereal solution was washed with water and repeatedly extracted with cold sodium bicarbonate solution, then acidified. The oily product (31.4 g.) was digested with boiling benzene, and filtered. The solid insoluble part (ca. 5 g.) on crystallization from aqueous methanol gave di-*o*-chlorobenzylidenesuccinic acid (VIa), m.p. 240°.

Anal. Calcd. for $C_{18}H_{12}O_4Cl_2$: C, 59.5; H, 3.3; Cl, 19.5. Found: C, 59.6; H, 3.6; Cl, 19.1.

The benzene solution on evaporation afforded methyl hydrogen *cis*-γ-*o*-chlorophenylitaconate as viscous brown oil (*ca.* 20 g.) which on hydrolysis (4.5 g.) with concentrated barium hydroxide solution (3 hr., refluxing) gave a solid substance (4 g.). This on repeated crystallization from aqueous methanol yielded *cis*-γ-*o*-chlorophenylitaconic acid (Ia; R_3 = H), m.p. 194–195°.

Anal. Calcd. for $C_{11}H_9O_4Cl$: C, 54.9; H, 3.8; Cl, 14.8. Found: C, 55.5; H, 4.2; Cl, 14.9.

Methyl 4-acetoxy-8-chloro-2-naphthoate (IIa; $R_3 = CH_3$ $R_4 = Ac$). The above crude oily half ester (5.5 g.) and sodium acetate (2 g.) in acetic anhydride (25 ml.) were refluxed for 5 hr., then worked up by removing the acetic anhydride under reduced pressure, adding water, then extracting the precipitate with ether. The ethereal solution was washed with sodium bicarbonate solution, water, and dried. Evaporation left methyl 4-acetoxy-8-chloro-2-naphthoate (*ca.* 4.6 g.), m.p. 90–91° which after crystallization from aqueous acetone formed needles, m.p. 101°.

Anal. Calcd. for $C_{14}H_{11}O_4Cl$: C, 60.3; H, 4.0; Cl, 12.7. Found: C, 60.03; H, 4.21; Cl, 12.35.

This ester (2 g.) with 10% sodium hydroxide solution (40 ml.) (2 hr. refluxing) gave 8-chloro-4-hydroxy-2-naphthoic acid (IIa; $R_3 = R_4 = H$) in pale yellow plate (1.5 g.), m.p. 282–284° (from acetic acid).

Anal. Calcd. for $C_{11}H_7O_3Cl$: C, 59.3; H, 3.1; Cl, 15.95. Found: C, 58.85; H, 3.27; Cl, 15.39.

Methyl 8-chloro-4-methoxy-2-naphthoate (IIa; $R_3 = R_4 = CH_3$). The above phenolic acid (3 g.), dimethyl sulfate (9 g.), and anhydrous potassium carbonate (12 g.) in acetone (90 ml.) were refluxed for 12 hr., affording methyl 8-chloro-4-methoxy-2-naphthoate (3.1 g.) pale yellow needles (from aqueous ethanol), m.p. 93–94°.

Anal. Calcd. for $C_{13}H_{11}O_3Cl$: C, 62.27; H, 4.39. Found: C, 62.46; H, 4.65.

Hydrolysis of this (1 g.) with 10% sodium hydroxide solution (20 ml.) (2.5 hr. refluxing) as above gave the methoxy acid (IIa; R_3 = H, $R_4 = CH_3$), m.p. 279° (from ethanol).

Anal. Calcd. for $C_{12}H_9O_3Cl$: C, 60.88; H, 3.8; Cl. 15.01. Found: C, 60.69; H, 3.89; Cl, 14.28.

5-Chloro-1-methoxynaphthalene (IIIa; $R_3 = CH_3$). A solution of the preceding acid (0.5 g.) in 5 ml. of quinoline was treated with about 0.5 g. of copper-bronze and heated to reflux (sand-bath) for 1 hr. The quinoline solution was diluted with ether, filtered and extracted with dilute hydrochloric acid to remove the quinoline and with dilute alkali to remove any unchanged acid. After distillation of the ether; the residue (0.4 g.) was crystallized from methanol (charcoal) to give 1-chloro-5-methoxynaphthalene, m.p. 49°.

Anal. Calcd. for $C_{11}H_9OCl$: C, 68.57; H, 4.67; Cl, 18.44. Found: C, 68.48; H, 4.3; Cl, 19.06.

5-Chloro-1-naphthol (IIIa; $R_3 = H$). The above ether (0.2 g.) was boiled with hydriodic acid (5 ml.) for 1 hr. After cooling the precipitated naphthol (0.15 g.) was purified through its sodium salt then crystallized from water to give 5-chloro-1-naphthol in colorless needles, m.p. 130–131°[5].

Anal. Calcd. for $C_{10}H_7OCl$: C, 67.22; H, 3.92; Cl, 19.77. Found: C, 67.8; H, 4.15; Cl, 19.2.

cis-γ-o-Chlorophenylitaconic anhydride (IVa). *cis*-γ-*o*-Chlorophenylitaconic acid (Ia; R_3 = H) (3.2 g.) was boiled with a mixture of acetic anhydride (15 ml.) and acetyl chloride (30 ml.) for 2 hr. After evaporation, the residue crystallized from acetic acid, to give the anhydride (*ca.* 2 g.), m.p. 143–144°.

Anal. Calcd. for $C_{11}H_7O_3Cl$: C, 59.32; H, 3.14; Cl, 15.95. Found: C, 59.19; H, 3.25; Cl, 15.38.

α-Methyl β-hydrogen cis-γ-o-chlorophenylitaconate (Va). The anhydride (IVa) (0.5 g.) was refluxed in methanol (10 ml.) for 3 hr. Evaporation and crystallization of the residue (0.3 g.) from benzene-petroleum ether (b.p. 40–60°) gave α-methyl β-hydrogen *cis*-γ-*o*-chlorophenylitaconate, m.p. 112–114°.

Anal. Calcd. for $C_{12}H_{11}O_4Cl$: C, 56.6; H, 4.33; Cl, 13.94. Found: C, 56.76; H, 4.44; Cl, 13.01.

Di-o-chlorobenzylidenesuccinic anhydride (VII). The acid (VIa) (3 g.) was refluxed with a mixture of acetyl chloride (60 ml.) and acetic anhydride (30 ml.) for 2 hr. The solution was then concentrated to a small volume and left overnight.

(6) H. Stobbe, *Ber.*, **40**, 3372 (1907); F. G. Baddar, L. S. El-Assal, and M. Gindy, *J. Chem. Soc.*, 1270 (1948).

The precipitate was collected (2.7 g.) and crystallized from acetic acid, from which di-*o*-chlorobenzylidenesuccinic anhydride separated in yellow crystals, m.p. 176–177°.

Anal. Calcd. for $C_{18}H_{10}O_3Cl_2$: C, 62.6; H, 2.90; Cl, 20.6. Found: C, 62.6; H, 3.2; Cl, 20.7.

2′,5-Dichloro-1-phenylnaphthalene-2,3-dicarboxylic acid (IX). The anhydride (VII) (2.5 g.) was heated at 270° (ethyl cinnamate bath) until the evolution of hydrogen ceased. The yellow glassy product (VIII) was hydrolyzed with aqueous sodium hydroxide solution (10%) (1 hr.). The dibasic acid precipitated on acidification was treated with charcoal and crystallized from benzene–petroleum ether (b.p. 70–80°) from which 2′,5-dichloro-1-phenylnaphthalene-2,3-dicarboxylic acid separated in colorless crystals (1.4 g.), m.p. 213–214° (from benzene).

Anal. Calcd. for $C_{18}H_{10}O_4Cl_2$ C, 59.83; H, 2.74; Cl, 19.66. Found: C, 60.25; H, 3.06; Cl, 18.25.

2′,5-Dichloro-1-phenylnaphthalene (X). A solution of the above dibasic acid (IX) (0.3 g.) in 3 ml. of quinoline was treated with about 0.2 g. copper-bronze and heated to reflux for 0.5 hr. (sand bath). Further copper-benzene (0.2 g.) was added during a further 0.5 hr. with continuous heating. Then the whole was worked up as described before, affording 2′,5-dichloro-1-phenylnaphthalene as colorless crystals (0.2 g.), m.p. 172–173° (from methanol).

Anal. Calcd. for $C_{16}H_{10}Cl_2$: C, 70.32; H, 3.66. Found: C, 70.36; H, 4.21.

Stobbe condensation of p-chlorobenzaldehyde with methyl succinate. *p*-Chlorobenzaldehyde (28 g., 1 mole) and methyl succinate (35 g., 1.2 moles) in *t*-butyl alcohol (50 ml.) were added to a boiling solution of potassium *t*-butoxide [from metallic potassium (11.5 g.) and the alcohol (190 ml.)] during 20 min., and the whole was refluxed for a further 45 min., then worked up as described for the *ortho* isomer. The solid product (*ca.* 38 g.) was digested in boiling benzene and the solution was filtered while hot from the insoluble residue (*ca.* 5 g.). This insoluble part on crystallization from aqueous methanol gave di-*p*-chlorobenzylidenesuccinic acid (VIb), m.p. 240° (*cf.* reference 2, m.p. 225–226°).

Anal. Calcd. for $C_{18}H_{12}O_4Cl_2$: C, 59.5; H, 3.3; Cl, 19.5. Found C,59.6; H, 3.69; Cl, 19.14.

The hot benzene filtrate on cooling gave the known *p*-chlorobenzoic acid as needles (*ca.* 2 g.) m.p. 240–241° (from benzene).

Anal. Calcd. for $C_7H_5O_2Cl$: C, 53.67; H, 3.19; Cl, 22.68. Found: C, 53.68; H, 3.20; Cl, 22.59.

The benzene filtrate on concentration to a small volume afforded methyl hydrogen *cis-γ-p*-chlorophenylitaconate which on crystallization from benzene had m.p. 123–124° (*ca.* 13 g.).

Anal. Calcd. for $C_{12}H_{11}O_4Cl$: C, 56.6; H, 4.33; Cl, 13.94. Found: C, 57.07; H, 4.34; Cl, 13.65.

When the above experiment was repeated under nitrogen atmosphere, no *p*-chlorobenzoic acid was isolated.

Methyl 4-acetoxy-6-chloro-2-naphthoate (IIb; R_3 = CH_3, R_4 = *Ac*). The preceding half ester (5 g.) was cyclized with sodium acetate (2 g.) in boiling acetic anhydride (40 ml.) (5 hr.) in the usual manner. The naphthoate (*ca.* 4.4 g.) on crystallization from acetone, had m.p. 126°.

Anal. Calcd. for $C_{14}H_{11}O_4Cl$: C, 60.32; H, 4.0; Cl, 12.75. Found: C, 60.12; H, 3.99; Cl, 12.68.

Hydrolysis of this ester (2 g.) as for its isomer (3.5 hr. refluxing) gave 6-chloro-4-hydroxy-2-naphthoic acid (IIb; R_3 = R_4 = H) in colorless crystals (*ca.* 1.5 g.), m.p. 297° from acetic acid).

Anal. Calcd. for $C_{11}H_7O_3Cl$: C, 59.32; H, 3.14; Cl, 15.95 Found: C, 59.33; H, 3.43; Cl, 15.65.

Methyl 6-chloro-4-methoxy-2-naphthoate (IIb; R_3 + R_4 = CH_3). The above phenolic acid (2 g.), dimethyl sulfate (6 g.), and anhydrous potassium carbonate (8 g.) in acetone (60 ml.) were refluxed for 12 hr. affording methyl 6-chloro-4-methoxy-2-naphthoate (*ca.* 2 g.), m.p. 130–132° (from methanol).

Anal. Calcd. for $C_{13}H_{11}O_3Cl$: C, 62.27; H, 4.39; Cl, 14.17. Found: C, 62.59; H, 4.68; Cl, 13.35.

Hydrolysis of this (1.5 g.) with 10% sodium hydroxide solution (30 ml.) (2 hr. refluxing) gave the methoxy acid (IIb; R_3 = H, R_4 = CH_3) (1.4 g.), m.p. 304° (from ethanol).

Anal. Calcd. for $C_{12}H_9O_3Cl$: C, 60.88; H, 3.8; Cl, 15.01. Found: C, 60.71; H, 3.92; Cl, 14.39.

7-Chloro-1-naphthol (IIIb; R_3 = *H*). A solution of the above acid (0.4 g.) in 4 ml. of quinoline was treated with about 0.4 g. of copper-bronze and heated above 300° (sand bath) for 2 hr. The whole was worked up in the usual manner, affording 7-chloro-1-methoxynaphthalene (IIIb; R_3 = CH_3) as a pale brown oil. This ether (0.25 g.) on boiling with hydriodic acid (5 ml.) for 1 hr. gave after cooling a phenolic precipitate (0.15 g.). This was purified through its sodium salt then crystallized from water to give 7-chloro-1-naphthol in colorless needles, m.p. 121–122°.

Anal. Calcd. for $C_{10}H_7OCl$: C, 67.22; H, 3.92; Cl, 19.8. Found: C, 67.42; H, 4.23; Cl, 18.54.

cis-γ-p-Chlorophenylitaconic acid (Ib; R_3 = *H*). The *cis-β*-half ester (Ib: R_3 = CH_3) (2 g.) was hydrolyzed with a concentrated barium hydroxide solution (40 ml.) (3 hr. refluxing), and the precipitated barium salt was filtered off, washed with water and with alcohol and dried. Acidification with dilute hydrochloric acid liberated an acid which was filtered off, washed and dried (*ca.* 2 g.). Crystallization from aqueous methanol gave *cis-γ-p*-chlorophenylitaconic acid, m.p. 205°.

Anal. Calcd. for $C_{11}H_9O_4Cl$: C, 54.9; H, 3.8; Cl, 14.75. Found: C, 55.23; H, 3.94; Cl, 14.37.

Cis-γ-p-Chlorophenylitaconic anhydride (IVb). *cis-γ-p*-Chlorophenylitaconic acid (1.5 g.) was boiled with a mixture of acetic anhydride (10 ml.) and acetyl chloride (20 ml.) for 2 hr. After evaporation the residue crystallized from acetic acid, to give the itaconic anhydride (1.1 g.), m.p. 176°.

Anal. Calcd. for $C_{11}H_7O_3Cl$: C, 59.32; H, 3.14; Cl, 15.9. Found: C, 59.46; H, 3.38; Cl, 14.9.

α-Methyl β-hydrogen cis-γ-p-chlorophenylitaconate (Vb). The anhydride (IVb) (0.5 g.) in methanol (10 ml.) gave as in the preceding case, α-methyl β-hydrogen *cis-γ-p*-chlorophenylitaconate (0.5 g.), m.p. 141° (from aqueous methanol), depressed on admixture with the β-half ester.

Anal. Calcd. for $C_{12}H_{11}O_4Cl$: Cl, 13.95. Found: Cl, 13.58.

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