Anal. Calcd. for $C_{14}H_{14}N_4O_6$: C, 48.00; H, 4.00. Found: C, 47.81; H, 4.00.

Oxidation of 3-Methyl-4-ethylpyridine.—3-Methyl-4-ethylpyridine (15 g.) in water (100 ml.) was treated at 60° with a 5% potassium permanganate solution until the pink color was permanent. The solution was cooled and filtered from the manganese dioxide. The filter cake was washed twice with 100-ml. portions of water and the washings combined with the original filtrate. Acidification of the filtrate to *p*H 6–6.5 followed by the addition of 40 ml. of 5% copper sulfate solution precipitated the cinchomeronic acid as the copper salt. The free acid was obtained by decomposing the copper salt with hydrogen sulfide and evaporating the solution. Recrystallization from ethanol gave crystals melting at 262–264° which did not lower the melting point of a sample prepared from isoquinoline.[18]

4-(β-Hydroxyethyl)-piperidine.—4-(β-Hydroxyethyl)-pyridine (100 g.) was reduced in 1-butanol (900 ml.) with sodium (150 g.) in a similar manner to that used for 4-ethylpyridine. The reduction mixture was diluted with 400 ml. of water and the sodium hydroxide layer discarded. The alcohol–amine layer was acidified with 6 *N* hydrochloric acid and the 1-butanol removed by steam distillation. The residue was made strongly alkaline with 20% sodium hydroxide solution and extracted with ether using a continuous extractor. The yield of product was 60 g.; b.p. 140–145° (16 mm.). This product did not cyclize to quinuclidine when treated with anhydrous hydrogen bromide and thionyl bromide or with aqueous hydrobromic acid (sp. gr. 1.42).

The above product (30 g.) upon catalytic reduction in glacial acetic acid gave a solution which was made strongly alkaline with 20% sodium hydroxide. Extraction with ether using a continuous extractor gave 26 g. of 4-(β-hydroxyethyl)-piperidine; b.p. 131–136° (16–18 mm.).

Refluxing this amine with hydrobromic acid (sp. gr. 1.42) for two hours followed by treatment with alkali gave quinuclidine melting at 155–156°.

Sodium 4-Ethylpyridine-3-sulfonate.—This salt was prepared from 4-ethylpyridine (90 g.) following the directions[7] used for sodium 4-methylpyridine-3-sulfonate. The yield of sodium salt varied from 50–90 g. The salt was not purified further but used as such in the next reaction.

3-Cyano-4-ethylpyridine.—This compound was prepared in a manner similar to that used for 4-methylnicotinonitrile.[7] Yields based on 40 g. of sodium-4-ethylpyridine-3-sulfonate were 2.4–3.2 g.; b.p. 72–74° (2 mm.).

Anal. Calcd. for $C_8H_8N_2$: C, 72.65; H, 6.06. Found: C, 72.48; H, 6.19.

Hydrolysis of 3-cyano-4-ethylpyridine (4 g.) in 75% sulfuric acid gave 3.2 g. of 4-ethylnicotinic acid; m.p. 137–138°. Gabriel and Colman[19] report a melting point of 135.5–136°.

This acid was also obtained by treating sodium 4-ethylpyridine-3-sulfonate (21 g.) with sodium formate (34 g.) according to the directions used for aromatic acids.[8] The yield of product was 1.4 g.; m.p. 133–135°. No lowering in melting point was observed when the two different preparations were mixed.

(18) L. Ternajgo, *Monatsh.*, **21**, 446 (1900).

(19) S. Gabriel and J. Colman, *Ber.*, **35**, 1358 (1902).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactivity of the Heterocyclic Nuclear Halogen in the Friedel–Crafts Reaction: The Preparation of Some Dihydroxyphenylquinoline and -benzothiazole Derivatives

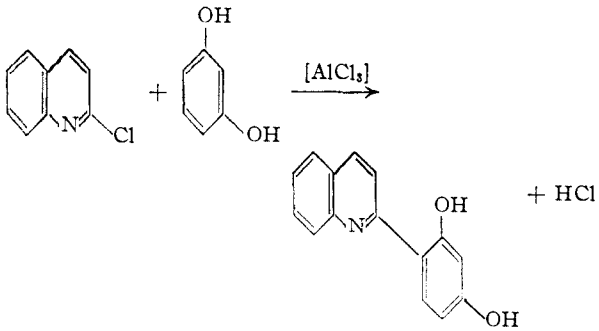
BY GABRIELLO ILLUMINATI AND HENRY GILMAN

RECEIVED NOVEMBER 3, 1951

The active nuclear halogens in 2-chloroquinoline, 4,7-dichloroquinoline and 2-chlorobenzothiazole undergo Friedel-Crafts reactions with resorcinol and 4-chlororesorcinol to give dihydroxyphenyl- or chlorodihydroxyphenylquinoline and benzothiazole derivatives. The products obtained are colored. A suitable solvent for these reactions is dry quinoline. Such a medium, in many respects similar to nitrobenzene, was profitably used in reactions which either had been unsuccessful or had resulted in somewhat lower yields when carried out in nitrobenzene. The molecular compounds of 4-chlororesorcinol with 2-chloroquinoline and 4,7-dichloroquinoline are also described.

Friedel–Crafts reactions involving the use of chloroquinoline and chlorobenzothiazole derivatives as the organic halogen components do not appear in the literature. More generally, Friedel–Crafts reactions involving nuclear halogen have been observed only in a few cases.[1] Since the chlorine atom attached to the positions 2 and 4 of quinoline and to the position 2 of benzothiazole shows high reactivity in many instances such as its ready displacement by sodium alkoxides, a condensation of 2-chloroquinoline and the other similarly reactive heterocyclic compounds with some aromatic nuclei in the presence of aluminum chloride seemed to be likely to occur.

The present investigation deals with the condensation of 2-chloroquinoline, 4,7-dichloroquinoline and 2-chlorobenzothiazole with resorcinol or 4-chlororesorcinol. The typical reaction takes place according to the equation



Evidence that the product was a dihydroxyphenyl- or chlorodihydroxyphenylquinoline or -benzothiazole derivative, and not the monohydroxyphenoxy- or chloromonohydroxyphenoxy- isomer, was obtained in the case of 2-(2,4-dihydroxyphenyl)-quinoline (1) by infrared absorption measurements, (2) by unsuccessful attempts at ether-cleavage, and (3) analyses for active hydrogen.

The reactivity of 4-chlororesorcinol is appreciably lower than that of resorcinol, the yields of the prod-

(1) See, for example, A. W. Weston and C. M. Suter, THIS JOURNAL, **61**, 2556 (1939); F. D. Chattaway, *J. Chem. Soc.*, **63**, 1185 (1893); E. Clar, *Ber.*, **65**, 846 (1932); E. B. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2631 (1923).

ucts obtained from the former being not higher than 12%.

All the reactions have been carried out at high temperature, namely, between 100–180°, over a period of 5 to 10 hours. Such somewhat forced conditions probably indicate the occurrence of some inhibitive factors depending on the markedly basic properties of the nitrogen atom in the heterocyclic component. In fact, resorcinol is known to possess a fairly high reactivity in Friedel–Crafts reactions conducted under milder conditions with benzyl or *p*-chlorobenzyl chloride.[2]

It may be of some interest in this connection to recall the known tendency of quinoline or benzothiazole derivatives to form salts with phenols. In the course of other studies in this Laboratory we happened to isolate and purify the salts formed with 4-chlororesorcinol. Such compounds are obtained in crystalline form and can be kept at room temperature without any apparent decomposition. Their melting points are generally higher than those of the corresponding basic components. The analytical data show that the phenol is combined with the basic component in a molar ratio 1:1.

Naturally, anhydrous aluminum chloride competes with the dihydroxybenzene derivatives in the formation of salts with the heterocyclic component. The occurrence of a complex between aluminum chloride and 8-hydroxyquinoline in the course of Friedel–Crafts reactions with acyl chlorides has been claimed by Rosenmund and co-workers[3] as an obstacle to the progress of the reaction itself. Rosenmund used a large excess of catalyst, namely, three moles of aluminum chloride per mole of 8-hydroxyquinoline.

In our case, however, an inhibitive action of the tertiary nitrogen is doubtful not only because in all the reactions the employed molar ratio of the catalyst to the chlorine compound was not higher than 1:1, but also because of the promising results obtained by running some of the experiments either in an excess of the chloro compound without any solvent or in dry quinoline as a solvent. Quinoline, like nitrobenzene, appeared to be an inert substance with regard to Friedel–Crafts reactions, since Borsche and Groth[4] proved its failure to undergo condensations with acyl chlorides. It forms exothermically a complex with anhydrous aluminum chloride, which it takes into solution somewhat in the cold and completely when hot. Attempts to condense the heterocyclic chloro compounds with 4-chlororesorcinol in nitrobenzene or in carbon disulfide have been unsuccessful, whereas the use of a moderate volume of quinoline or of just an excess of the chloro compound have led to the expected products even though in mediocre yields. Also, the corresponding reactions with resorcinol resulted in improved yields when quinoline was used instead of nitrobenzene. A similar reaction using phenol as the proton donor did not take place when 2-chloroquinoline, phenol and aluminum chloride were mixed in a ratio 1:1:1 or 1:2:1, dry quinoline acting as a medium.

(2) E. Klarman and J. Von Wowern, THIS JOURNAL, **51**, 605 (1929); E. Klarman, *ibid.*, **48**, 791, 2358 (1926).

(3) K. W. Rosenmund and G. Karst, *Arch. Pharm.*, **279**, 154 (1941).

(4) W. Borsche and H. Groth, *Ann.*, **549**, 238 (1941).

After the reactions carried out in quinoline or in an excess of the chloro compound were over, thick and glassy mixtures were obtained upon cooling. The decomposition of such mixtures by the usual way of adding a cold dilute hydrochloric acid solution could not be performed. We have used aqueous ethanol in various concentrations instead of water. The details are recorded in the experimental part.

All the products obtained are easily soluble in cold dilute sodium hydroxide solutions. Their hydrochlorides are insoluble in cold 10% hydrochloric acid, some being soluble in this solvent when hot. The alkaline solutions are dark brown, whereas the acid solutions or the hydrochlorides are pale yellow or green. The free compounds are high melting solids, insoluble in water, diethyl ether and petroleum ether, and soluble in ethanol and other polar organic solvents. Their color is tan or yellow-orange.

Because of their solubility properties, purification appeared to be very difficult and in some cases required the use of counter-current distribution methods[5] which were successfully applied. Precipitation of the dihydroxyphenyl compounds from their alkaline solutions by dropwise addition of dilute acetic acid begins at a *p*H within the range 10.2–10.5. The Craig procedure was carried out by choosing butanol and an aqueous solution having a *p*H adjusted between 10.7 and 11.0 as the system of immiscible liquids. Products satisfactorily pure for analytical purposes were obtained upon extension of the procedure over a series of 25 to 30 transfers. The purification was followed by taking melting points of the samples isolated by acidification of the alkaline aqueous solutions.

Experimental

As to the structure of the dihydroxyphenylquinoline and -benzothiazole derivatives reported below, we have assumed that resorcinol and 4-chlororesorcinol react at the carbon atom in the position 6 by analogy with similar reactions involving dihydroxybenzene derivatives.[6] From the experimental work which follows, evidence has been presented to indicate that the product from the reaction of resorcinol with 2-chloroquinoline is, in reality, 2-(2,4-dihydroxyphenyl)-quinoline. In the following description of the preparation of the compounds obtained we have surveyed the different procedures employed in the course of the present investigation.

2-(2,4-Dihydroxyphenyl)-quinoline.[7]—To a solution of 6.55 g. (0.05 mole) of anhydrous aluminum chloride and 11.0 g. (0.10 mole) of resorcinol in 50 ml. of nitrobenzene, 8.2 g. (0.05 mole) of 2-chloroquinoline in 15 ml. of nitrobenzene was slowly added at 5–10° with stirring. After the addition was completed, the mixture was slowly warmed up to 100° with the aid of a heating mantle and maintained under these conditions for 6 hours. Decomposition was effected by pouring the chilled reaction mixture into cracked ice and dilute hydrochloric acid. After the liquid was transferred into a separatory funnel, the nitrobenzene layer was diluted with diethyl ether and extracted repeatedly with a sodium hydroxide solution. If the concentration of the alkaline solution is 10% or higher, the product may precipitate out of the combined extracts in the form of its sodium salt as orange needles. Therefore, either the crys-

(5) See, for example, L. C. Craig, *Anal. Chem.*, **21**, 85 (1949).

(6) L. Gattermann, *Ann.*, **357**, 313 (1907); H. Gilman and J. B. Dickey, *Rec. trav. chim.*, **52**, 389 (1933).

(7) This compound had first been prepared by Sadao Kitaura, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **20**, 967 (1941) [*C. A.*, **43**, 8386f (1949)], by a different procedure. The melting point reported by this author is 197–198°, in good agreement with ours (197.7–199.2°).

tals are taken up in hot 5% hydrochloric acid or the alkaline extract is neutralized by adding acetic acid. From the hot hydrochloric acid solution pale yellow needles of the hydrochloride of the product are obtained on cooling. This property made possible the purification of the free compound; the purification was effected by dissolving the hydrochloride, twice recrystallized, in dilute sodium hydroxide solution and by neutralizing the solution so obtained with 50% aqueous acetic acid. The yield was 2.8 g. (25%) of tiny golden-yellow and silky crystals melting at 197.7–199.2°.

Anal. Calcd. for $C_{15}H_{11}O_2N$: N, 5.66. Found: N, 5.75.

Proof of Structure of 2-(2,4-Dihydroxyphenyl)-quinoline.—1. **Attempted Cleavage with HI.** (Studies by Dr. J. Lewis Towle).—The compound was refluxed for 24 hours in a mixture of hydriodic acid (d. 1.5) and glacial acetic acid. An equal volume of water was added and the solution was neutralized with ammonium hydroxide. Orange crystals were filtered off, washed with water and dried. The product melted at 198–199° and a mixture with the starting material (m.p. 198–199°) melted at 198–199°. When mixed with 2-hydroxyquinoline (m.p. 199–200°) a melting point of 160–164° was observed. From this evidence it was concluded that no ether linkage was present.

In a parallel experiment, 2-phenoxyquinoline was treated in the same manner. 2-Hydroxyquinoline was isolated and identified by a mixed melting point determination. A strong odor of phenol also was detected. 2-Phenoxyquinoline has been cleaved with concentrated hydrochloric acid[8] to 2-hydroxyquinoline and phenol.

2. **Analysis for Active Hydrogen** (Studies by Mr. Donald L. Esmay).—Due to the solubility properties of the compound, Zerewitinoff analyses for active hydrogen[9] were carried out with difficulty. The most reliable results were obtained from one run in which anisole was used as the solvent and from two runs in which hot dioxane was used. The samples weighed 25–30 mg. The values obtained were 1.73, 1.68 and 1.67 active hydrogens, respectively. These results indicate the presence of two hydroxyl groups.

3. **Infrared Absorption Measurements.** (Studies by Dr. Velmer A. Fassel and Mr. Marvin Margoshes).—Infrared absorption measurements indicated the presence of a 1,2,4-trisubstituted benzene ring and the absence of an aromatic ether linkage.

4-(2,4-Dihydroxyphenyl)-7-chloroquinoline.—A solution of 7.2 g. (0.055 mole) of aluminum chloride in 30 ml. of nitrobenzene was added to a chilled solution of 11.0 g. (0.10 mole) of resorcinol in 25 ml. of nitrobenzene, and to the mixture so formed 10.0 g. (0.05 mole) of 4,7-dichloroquinoline in 25 ml. of nitrobenzene was added at −10° with stirring. The resulting dark brown mixture was warmed up to 120° over a period of an hour and kept in such condition for 6 hours.

Decomposition was effected by adding water to the stirred reaction mixture chilled at 5°. The resulting mixture was then diluted with 50 ml. of diethyl ether and shaken until the solid material which appeared during the decomposition was completely dissolved. After removal of the aqueous layer, the nitrobenzene layer was diluted with a large volume of diethyl ether and allowed to stand. The solid which separated (from the ether–nitrobenzene solution) was removed by filtration, vigorously shaken with a mixture of ether and a dilute aqueous ammonia solution and subsequently taken up in 10% sodium hydroxide. The dark brown alkaline solution so obtained was filtered and acidified while hot by slowly adding 20% aqueous acetic acid. A tan product separated melting at 248–253°. The yield was 3.7 g. (26%). A further purification for analytical purposes was carried out by using the procedure followed for the preceding compound. The pure compound is a light tan powder melting at 254–256°.

Anal. Calcd. for $C_{15}H_{10}O_2NCl$: N, 4.96; Cl, 12.61. Found: N, 4.84; Cl, 12.50.

2-(2,4-Dihydroxyphenyl)-benzothiazole.—To a well-stirred solution of 6.6 g. (0.06 mole) of resorcinol and 10.17 g. (0.06 mole) of 2-chlorobenzothiazole in 10 ml. of quinoline kept at 15° with the aid of a chilled water-bath, 8.8 g. (0.066 mole) of powdered anhydrous aluminum chloride was gradually added over 15 minutes. After the addition was completed the inside temperature was raised to 150° within half an hour and maintained at this level for 10 hours. At the end of this period the color of the liquid was red-brown.

Decomposition was effected by adding 150 ml. of 50% aqueous ethanol containing hydrochloric acid in 3% concentration and by stirring the mixture for an hour at 50°. In this manner only part of the material went into solution. The clear supernatant solution was slowly poured into a large volume of water with occasional stirring, while the oily residue was first taken up in ethanol and then added to the aqueous liquid. A rusty precipitate appeared and the resulting suspension was heated to boiling to facilitate a thorough coagulation. After filtration the solid was taken up in 8% sodium hydroxide solution, the resulting solution was filtered through a sintered glass funnel and finally treated with glacial acetic acid. The acid was added dropwise until a persistent acidity was attained. During the acidification the flask containing the hot suspension occasionally was stoppered and vigorously shaken. At the end of the operation the suspension was boiled for a few minutes and filtered. At this stage the product melted at 190–194°. A further purification was carried out by the counter-current distribution method (see General part). The pure compound is a tan powder melting at 194–195°. In two runs carried out under the same conditions the yields were 43 and 59%, respectively.

Anal. Calcd. for $C_{13}H_9O_2NS$: S, 13.19. Found: S, 13.10.

2-(5-Chloro-2,4-dihydroxyphenyl)-quinoline.—To a solution of 7.2 g. (0.05 mole) of 4-chlororesorcinol in 16.4 g. (0.10 mole) of 2-chloroquinoline, 10 g. (0.075 mole) of aluminum chloride was gradually added at 90°. The temperature of the mixture rose to 180° and was maintained at this level for two hours with the aid of a heating mantle. At the end of this period a slight suction was applied for another half-hour while the temperature was allowed to drop to 150°. On cooling, the reaction mixture turned to a hard solid mass. Decomposition was effected by adding 50 ml. of 80% ethanol into which some hydrogen chloride had been passed, and by refluxing the liquid for a few hours with stirring. The solution thus formed was allowed to stand overnight at 0°. A precipitate separated which was removed from the mother liquor by filtration and yielded 4 g. of crude material. The solid was extracted several times with refluxing dilute sulfuric acid solution by using 150 ml. of solvent each time. From the combined extracts the sulfate of the expected product (m.p. 250–255°) settled on cooling. Such a salt was then suspended in 200 ml. of hot water, was treated with a few drops of ammonia and was shaken vigorously several times. The free compound so obtained was filtered, dried at 100° for an hour, finely powdered and finally submitted to the same treatment with hot water and ammonia. The final yield was 1.6 g. (12%) of a yellow-orange powder melting at 213.5–214.5°.

Anal. Calcd. for $C_{15}H_{10}O_2NCl$: Cl, 12.61. Found: Cl, 12.95.

2-(5-Chloro-2,4-dihydroxyphenyl)-benzothiazole.—This compound was prepared according to the essential directions described for 2-(2,4-dihydroxyphenyl)-benzothiazole. Starting from 8.7 g. (0.06 mole) of 4-chlororesorcinol, 10.17 g. (0.06 mole) of 2-chlorobenzothiazole and 8.8 g. (0.066 mole) of aluminum chloride in 15 ml. of quinoline as a medium, the yield was 2.1 g. (12.5%) of a tan product melting at 244–247°.

Anal. Calcd. for $C_{13}H_8O_2NClS$: S, 11.52; Cl, 12.77. Found: S, 11.28; Cl, 12.45.

Complex of 4-Chlororesorcinol with 4,7-Dichloroquinoline.—This compound was obtained in 60% yield by dissolving equimolecular amounts of the two components in a common solvent, such as ethanol or diethyl ether, and by stirring the solution for two hours at room temperature. The residue obtained after removal of the solvent was recrystallized from a large volume of petroleum ether (b.p. 85–105°). The pure product melted at 131–132°.

Anal. Calcd. for $C_{15}H_{10}O_2NCl_3$ ($C_9H_5Cl_2N \cdot C_6H_5ClO_2$): Cl, 31.1. Found: Cl, 30.4.

Complex of 4-Chlororesorcinol with 2-Chloroquinoline.—This compound was obtained in the same manner as the preceding complex. The nearly pure crystals melted at 83–86°.

(8) A. E. Chichibabin and N. P. Jeletzky, *Ber.*, **57**, 1158 (1924).

(9) S. Siggia, "Quantitative Organic Analysis Via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 41.

Anal. Calcd. for $C_{15}H_{11}O_2NCl_2$ ($C_9H_6ClN \cdot C_6H_5ClO_2$): Cl, 22.88. Found: Cl, 22.78.

Both salts decompose when treated with a hot mixture of petroleum ether and water, the 4-chlororesorcinol going into solution in the water layer and the freed basic component in the organic layer.

Acknowledgment.—The authors are grateful to Drs. J. Lewis Towle and Velmer A. Fassel, and to Messrs. Marvin Margoshes, Robert K. Ingham and Donald L. Esmay for assistance.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE FACULTY OF SCIENCES, AND OF THE INSTITUTE "ALONSO BARBA," HIGHER COUNCIL FOR SCIENTIFIC RESEARCH, UNIVERSITY OF BARCELONA (SPAIN)]

The *cis*- and *trans*-2-Hydroxycyclopentanecarboxylic Acids[1]

BY JOSÉ PASCUAL AND JOSÉ CASTELLS[2]

RECEIVED OCTOBER 17, 1951

The 2-hydroxycyclopentanecarboxylic acids, reported previously as liquids, have been isolated in solid form. Derivatives have been prepared. A study of some of their physical constants led to the assignment of *cis*-configuration to the acid melting at 52–53.4° (cor.), and of *trans* to the acid melting at 68.3–69.0° (cor.).

By reduction of 2-ketocyclopentanecarboxylic acid ethyl ester followed by hydrolysis, a liquid mixture containing the *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acids is obtained.[3a,b,c,4] Boeseken, *et al.*,[3b] separated this mixture into two liquid components. One of them formed an isopropylidene derivative and enhanced the electrolytic conductivity of boric acid solutions, and, therefore, was considered to be the *cis*-acid. The other substance was impure *trans*-acid.

We have carried out the reduction of ethyl 2-ketocyclopentanecarboxylate with sodium amalgam, according to Dieckmann,[3a] and also by hydrogenation with the aid of platinum oxide. Both methods gave a mixture of esters of the same physical properties, and of the same chemical composition.

We tried the direct separation of the *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acids from the crude mixture by means of solid derivatives, like the acetates, the phenacyl and *p*-nitrobenzyl esters, and the benzylthiouronium salts, but we did not obtain satisfactory results.

However, from the mixture of ethyl esters prepared by hydrogenation we succeeded in separating the pairs of isomerides, a and b, reported in Table I. The 3,5-dinitrobenzoates were especially important, for by stepwise hydrolysis the pure isomeric 2-hydroxycyclopentanecarboxylic ethyl esters and acids were prepared, the latter in solid form. Thus we were able to prepare other pure derivatives which are listed as α- and β-isomerides in Table I.

TABLE I

MELTING POINTS (CORRECTED) OF DERIVATIVES

Name	α-Isomer (*cis*)	β-Isomer (*trans*)	a[a]	b
Hydroxy acid	52–3.4°	68.3–9°	.....	.....
Ethyl ester	B.p. 54–56.5 (0.1–0.2 mm.)	id. 57.5–60 (id.)	.....	.....
3,5-Dinitrobenzoate of ethyl ester	116–116.8	76.2–77.1	116.0–116.8	76.2–77.1°
Anilide	163.8–164.3	149–150.3	163.8–164.3	131.1–131.7
p-Toluidide	181.8–182.2	150–151.2	181.8–182.2	136–140
Hydrazide	155.8–156.5	135.3–137.2	153–154[b]	124–125[b]
Phenylurethan of ethyl ester	88.9–90.2	[c]	88.6–90	.....

[a] a is the main derivative separated from the reaction mixture. [b] We report here the melting points of the hydrazides prepared by Mousseron and Jacquier.[4] [c] The attempted preparation of this derivative gave a liquid substance which we did not study further.

Comparison of the values for the α- and β-derivatives with those listed for the a- and b-compounds shows that the substances in the b-group are not pure in spite of their apparently sharp melting points. In the preparation of the 3,5-dinitrobenzoyl derivatives we also obtained a product melting at about 70°, but it could be resolved by several recrystallizations into the pure components. In this connection we should like to point out that the low-melting hydrazide reported by Mousseron and Jacquier[4] melted about ten degrees below our β-hydrazide.[5]

Of the two methods employed, catalytic reduction gave by far the better yield, and thus we feel that the more reliable configurational inference can be drawn from the yields obtained in that way, *i.e.*,

(1) This paper includes part of the experimental work presented by J. Castells in partial fulfillment of the requirements for his Doctor's degree, and it was presented at the XIIth International Congress of Pure and Applied Chemistry. A preliminary note has been published in *Anales fís. y quím.*, **46**, 403 (1950).

(2) Research Fellow of the "Patronato Juan de la Cierva de Investigación Técnica," 1948–1950.

(3) (a) W. Dieckmann, *Ann.*, **317**, 64 (1901); (b) J. Boeseken, G. Sloff and J. M. Hoeffelman, H. E. Hirsch, *Rec. trav. chim.*, **52**, 881 (1933); (c) H. Stenz, Fr. Fichter and H. Arni, *Helv. Chim. Acta*, **19**, 392 (1936).

(4) M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, 238 (1950).

(5) Another recent example of confusing mixtures of isomers melting like pure compounds is given by N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, 1379 (1950).