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REPLACEMENT OF NUCLEAR ALKOXYL GROUPS BY THE ACTION OF GRIGNARD REAGENTS

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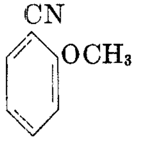
It was discovered by Richtzenhain and Nippus that replacement of the 2-alkoxyl group in 2,3-dialkoxybenzonitriles could be effected by the action of Grignard reagents (1, 2). Efforts to bring about a similar replacement in 2-methoxy-1-naphthonitrile were unsuccessful, however (3). Subsequently attention has been directed to certain methoxybenzonitriles closely similar to the 2,3-dimethoxy derivative employed by Richtzenhain. 2-Methoxy- (I), 2,6-dimethoxy- (II), and 2,5-dimethoxybenzonitrile (III) were found to undergo no replacement of methoxyl groups.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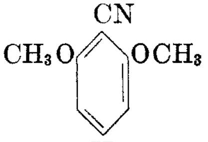
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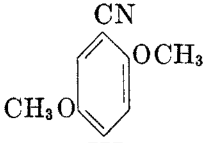
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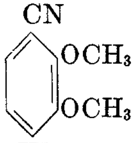
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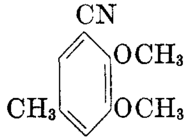
Under somewhat different conditions, Baker and Smith (4) obtained good yields of the expected dimethoxy ketones by the action of methyl and phenyl Grignard reagents on 2,3-dimethoxybenzonitrile (IV). It seemed possible, therefore, that our failure to effect replacement in similar compounds might have been due to a difference between our procedure and that of Richtzenhain. Accordingly, we attempted to repeat Richtzenhain's work with the ethyl and isopropyl Grignard reagents. Yields comparable with his were obtained only by decreasing the ratio of Grignard reagent to nitrile to 1.25:1. When isopropylmagnesium bromide was employed in this ratio, a yield of 83% of pure 2-isopropyl-3-methoxybenzonitrile was obtained. *t*-Butylmagnesium chloride, however, failed to effect replacement under these conditions. In fact, the only new examples of the replacement were realized with substituted 2,3-dimethoxybenzonitriles; namely, 2,3-dimethoxy-5-methylbenzonitrile (V) and a 2,3-dimethoxybromobenzonitrile (VI or VII).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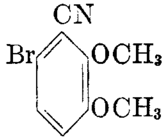
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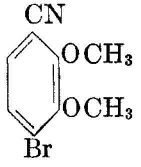
VII

The results of these experiments led to the conclusion that replacement of an alkoxyl group in the 2 position occurs only if the 3 position is occupied by a

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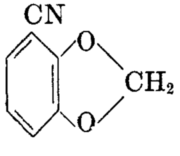
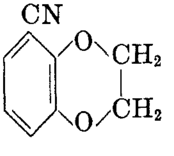
second alkoxyl group. Attempts to effect replacement with 2,3-methylenedioxy- (VIII) and 2,3-ethylenedioxy-benzonitriles (IX) gave only 1,2-addition products. A similar result was obtained with veratronitrile (X) and piperonylonitrile (XI) in which replacement of the group in the 4 position might have been expected.



VIII



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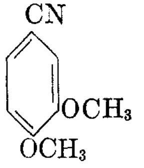
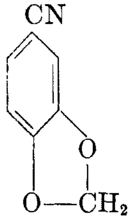
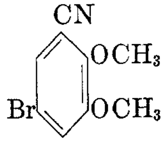


X



XI



XII

In all of the replacements so far mentioned the alkoxyl group involved is in a position *ortho* or *para* to a carbonyl or nitrile group and the reaction can, therefore, be represented as conjugate addition of the Grignard reagent followed by the loss of the elements of methanol. The conversion of 4,4′-dimethoxybiphenyl into a dimethoxy-*p*-terphenyl by the action of *p*-methoxyphenylmagnesium bromide by Price and Mueller (5) demonstrated, however, that a carbonyl or nitrile group is not necessary.

2,3-Dimethoxy-5-methylbenzonitrile (V), a new compound, was made from 2-methoxy-4-methylphenol. The phenol was converted by the Duff method, as modified by Liggett and Diehl (6), to 2-hydroxy-3-methoxy-5-methylbenzaldehyde, from which the nitrile was prepared by usual procedures.

The bromo compound (VI or VII) was formed by bromination of 2,3-dimethoxybenzonitrile (IV). In an attempt to identify the bromo compound, 2,3-dimethoxy-5-bromobenzonitrile (XII) was prepared; the two compounds proved to be unlike.

The ethylenedioxy compound (IX), also new, was synthesized from 2,3-dihydroxybenzoic acid by treatment with ethylene bromide followed by conversion of the ethylenedioxybenzoic acid to the nitrile.

EXPERIMENTAL[2]

Reaction of ethylmagnesium bromide with the benzonitriles. A. *2,6-Dimethoxybenzonitrile.* The nitrile (12 g.) suspended in a mixture of 50 ml. of ether and 50 ml. of benzene was added in four approximately equal portions at fifteen-minute intervals to a Grignard reagent prepared from 3.5 g. of magnesium, 16 g. of ethyl bromide, and 100 ml. of ether. After the addition was completed the mixture was stirred for four hours at room temperature and overnight under reflux. The products were isolated by usual procedures. A small amount (0.8 g.) of unchanged 2,6-dimethoxybenzonitrile was recovered along with 11 g. of the crude imine of 2,6-dimethoxypropiophenone (m.p. 68–72°). The imine was characterized by transformation into the hydrochloride. The salt was dissolved in chloroform and precipitated by the addition of ether; m.p. 168–170°.

Anal. Calc'd for $C_{11}H_{16}ClNO_2$: C, 57.51; H, 7.02.
Found: C, 57.07; H, 7.29.

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[2] Microanalyses were by Misses Theta Spoor and Betty Snyder.

B. *2-Methoxybenzonitrile.* 2-Methoxybenzonitrile was prepared by a method similar to that employed by Clark and Read (7) for the synthesis of *o*-tolunitrile. When 16.6 g. of this nitrile was treated with ethylmagnesium bromide by a procedure similar to that outlined for 2,6-dimethoxybenzonitrile, the only product which could be identified was a yellow oil (13 g.) that proved to be the corresponding imine. Its hydrochloride melted at 157–158°.

Anal. Calc'd for $C_{10}H_{14}ClNO$: C, 60.14; H, 7.07.
Found: C, 59.98; H, 7.05.

C. *2,5-Dimethoxybenzonitrile.* This nitrile, prepared by dehydration of the corresponding oxime, melted at 81–83° (8). When 10.5 g. of the nitrile was treated with ethylmagnesium bromide it yielded 9.5 g. of the imine of 2,5-dimethoxypropiophenone. The hydrochloride melted at 144–145°.

Anal. Calc'd for $C_{11}H_{16}ClNO_2$: C, 57.51; H, 7.02.
Found: C, 56.72; H, 7.25.

D. *2,3-Dimethoxybenzonitrile.* When this nitrile (12 g.) was treated with ethylmagnesium bromide according to the directions of Richtzenhain (1) 3.5 g. of 2-ethyl-3-methoxybenzonitrile was obtained. The product after recrystallization from low-boiling petroleum ether, melted at 35–36°. It became liquid when mixed with 2,3-dimethoxybenzonitrile at room temperature.

Anal. Calc'd for $C_{10}H_{11}NO$: C, 74.50; H, 6.88.
Found: C, 74.76; H, 7.07.

Reaction of 2,3-dimethoxybenzonitrile with Grignard reagents. A. *Ethylmagnesium bromide.* In view of the low yield obtained above, the ratio of Grignard reagent to nitrile was reduced. The following procedure was essentially that used in all subsequent reactions of nitriles with Grignard reagents, unless otherwise specified.

To a Grignard reagent prepared from 4.4 g. of magnesium turnings and 20 g. of ethyl bromide in 100 ml. of dry ether was added over a period of two hours a solution of 24 g. of the nitrile in 100 ml. of dry ether. After being stirred overnight at room temperature, the mixture was heated at reflux for four hours and cooled in an ice-bath; then it was poured into a mixture of ammonium chloride solution and ice. In the presence of ice, the ether layer was separated, washed with dilute sodium hydroxide solution, washed twice with saturated sodium chloride solution, and extracted repeatedly with dilute hydrochloric acid, the extracts being retained in an ice-bath for later neutralization and isolation of imines, if desired.

The ether layer was washed with ammonium chloride solution, and the nitriles isolated by usual procedures. Distillation of the crude product *in vacuo* at 92–95° (1 mm.) gave 14.4 g. (60% yield) of 2-ethyl-3-methoxybenzonitrile; m.p. 35–36°. A further decreased ratio was found to be unsatisfactory as was the use of a higher reflux temperature obtained by replacement of part of the ether by benzene.

B. *Isopropylmagnesium bromide.* When 12 g. of the nitrile was treated with this Grignard reagent according to the procedure described above, 10.5 g. (83% yield) of a colorless oil, b.p. 109–110° (1 mm.), $n^{20}{}_D$ 1.5240, was obtained. Richtzenhain and Nippus (2) reported the boiling point 91–93° (0.2 mm.) for 2-isopropyl-3-methoxybenzonitrile of 95% purity, which they obtained from the same reactants in 81% yield.

Anal. Calc'd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48.
Found: C, 75.64; H, 7.18.

C. *t-Butylmagnesium chloride.* Treatment of 12 g. of the nitrile with this Grignard reagent gave 7.4 g. of starting material and 4.3 g. of an oily yellow imine. The crude product melted at 34.5–35.5°. *t*-Butyl 2,3-dimethoxyphenyl ketimine hydrochloride, a white powder, melted at 205.5–206° with decomposition after purification by repeated precipitation from chloroform with ether.

Anal. Calc'd for $C_{13}H_{20}ClNO_2$: C, 60.57; H, 7.82.
Found: C, 60.71; H, 7.87.

2,3-Dimethoxybromobenzonitrile. To a refluxing solution of 12 g. of 2,3-dimethoxybenzonitrile in 20 ml. of carbon tetrachloride (to which had been added small amounts of iron powder and iodine) was added slowly a solution of 12.8 g. of bromine in 10 ml. of the solvent. When the evolution of hydrogen bromide appeared complete, conventional procedures for isolation gave 10.6 g. (59% yield) of white needles from methanol; m.p. 96–97°. A small amount was distilled *in vacuo*; b.p. 119–121° (1 mm.). Recrystallization from high-boiling petroleum ether gave white needles; m.p. 97.5–98.5°.

Anal. Calc'd for $C_9H_8BrNO_{21}$: C, 44.65; H, 3.33.
Found: C, 44.27; H, 3.40.

Reaction of 2,3-dimethoxybromobenzonitrile and ethylmagnesium bromide. A. When the above nitrile (15 g.) was treated with ethylmagnesium bromide according to the directions of Richtzenhain for 2,3-dimethoxybenzonitrile (1), the principal product was the imine portion, a dark viscous oil, weighing 10.9 g. Ethyl 2-ethyl-3-methoxybromophenyl ketimine hydrochloride was a light yellow powder sintering at 215° and melting at 226–228°, with decomposition.

Anal. Calc'd for $C_{12}H_{17}BrClNO$: C, 46.99; H, 5.59.
Found: C, 46.92; H, 5.50.

The nitrile fraction, a dark viscous oil, weighed 3 g. and deposited 0.39 g. of a solid which melted at 75–76° after recrystallization from low-boiling petroleum ether. It proved to be identical with the nitrile obtained in much better yield in the succeeding experiment.

B. Treatment of the nitrile (25 g.) with ethylmagnesium bromide in the reduced ratio described for 2,3-dimethoxybenzonitrile gave 7.7 g of imines and, after recrystallization from high-boiling petroleum ether, 9.0 g. (36% yield) of 2-ethyl-3-methoxybromobenzonitrile melting at 70–72°. Further purification involved excessive loss. A sample was distilled; b.p. 125–126° (1 mm.). After careful recrystallization from the same solvent, large colorless crystals were obtained; m.p. 75.5–76.5°.

Anal. Calc'd for $C_{10}H_{10}BrNO$: C, 50.02; H, 4.19.
Found: C, 49.92; H, 4.13.

2-Hydroxy-3-methoxy-5-bromobenzaldehyde. This compound was prepared by bromination of *o*-vanillin in carbon disulfide at room temperature for two days. A 51% yield of a product melting at 128–129° was obtained after recrystallization from high-boiling petroleum ether. The compound had been prepared previously by Rupp and Linck (9) by bromination in acetic acid, a procedure which could not be repeated satisfactorily. They reported the melting point 127°.

2,3-Dimethoxy-5-bromobenzaldehyde. Methylation with methyl sulfate according to the method of Davies (10) gave an almost quantitative yield of dimethoxy compound melting at 79–81° after recrystallization from aqueous ethanol; the reported melting point was 81°.

2,3-Dimethoxy-5-bromobenzaldoxime. The oxime separated from aqueous ethanol in white needles; m.p. 132.5–133.0°. The yield was practically quantitative. The compound sublimed *in vacuo* at 100°.

Anal. Calc'd for $C_9H_{10}BrNO_2$: C, 41.56; H, 3.88.
Found: C, 41.62; H, 3.86.

2,3-Dimethoxy-5-bromobenzonitrile. A mixture of 7 g. of the crude oxime, 7 g. of anhydrous sodium acetate, and 30 ml. of acetic anhydride was heated at reflux for 3 hours, cooled slightly, and poured into 150 ml. of cold water with stirring. When cooled, the nitrile solidified. Its solution in high-boiling petroleum ether, after decolorization with Darco, deposited 5 g. (72% yield) of white needles; m.p. 93–94°. The compound sublimed *in vacuo* at 56°.

Anal. Calc'd for $C_9H_8BrNO_2$: C, 44.65; H, 3.33.
Found: C, 44.92; H, 3.34.

That this compound was different from the bromination product of 2,3-dimethoxybenzonitrile was shown by a mixture melting point determination. A mixture of the two compounds melted at 72–74°.

2-Hydroxy-3-methoxy-5-methylbenzaldehyde. The Duff reaction as modified by Liggett and Diehl (6) was applied to creosol. A further modification, found advantageous in this reaction, consisted of grinding the creosol (50 g.) with an equal weight of hexamethylenetetramine until a thick paste was obtained. This material, when allowed to stand overnight in a thin layer, formed a dry solid. It was powdered and used in the modified procedure. The product of steam distillation of the reaction mixture was 24 g. (40% yield) of light yellow crystals; m.p. 75-77°. The melting point 77° has been reported (11) for the compound made by the usual Duff procedure.

2,3-Dimethoxy-5-methylbenzonitrile. 2,3-Dimethoxy-5-methylbenzaldoxime (44 g.), prepared from the above material by successive methylation and treatment with hydroxylamine hydrochloride according to Manske and Ledingham (11), was converted to the nitrile by the method described for 2,3-dimethoxy-5-bromobenzonitrile. The addition of ice was necessary to bring about solidification of the crude product. Distillation *in vacuo* gave 32.6 g. (81.5% yield) of a colorless liquid, b.p. 128-130° (1 mm.), which solidified; m.p. 35-36°. Recrystallization of the solid from low-boiling petroleum ether gave needles; m.p. 36-37°.

Anal. Calc'd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26.
Found: C, 67.96; H, 6.43.

Reaction of 2,3-dimethoxy-5-methylbenzonitrile and ethylmagnesium bromide. Treatment of 12 g. of the distilled nitrile with the Grignard reagent in the usual way gave a neutral fraction weighing 8.1 g. and an imine portion weighing 4.0 g. The neutral portion was distilled *in vacuo* (1 mm.). The first fraction (6.3 g., b.p. 108-110°) solidified; m.p. 41-43°. The yield of 2-ethyl-3-methoxy-5-methylbenzonitrile was 52%. The nitrile separated from low-boiling petroleum ether in white needles; m.p. 42.5-43.5°.

Anal. Calc'd for $C_{11}H_{13}NO$: C, 75.39; H, 7.48.
Found: C, 75.31; H, 7.48.

The second fraction of the distillate (0.8 g., b.p. 113-116°) did not crystallize when seeded with either the above nitrile or the starting material. It was probably a ketone or mixture of ketones resulting from hydrolysis of imines before their separation from the reaction mixture.

The imine fraction failed to form a crystalline hydrochloride. It was hydrolyzed by brief warming with dilute hydrochloric acid, and the oily ketones were isolated by ether extraction. Two fractionations at reduced pressure gave 2.5 g. of a light yellow liquid boiling at 100-102° (1 mm.); n^{20}_{D} 1.5251. The forerun and residue were negligible. Analysis showed that the oil had a composition corresponding to a mixture of about equal parts of 2,3-dimethoxy-5-methylpropiophenone and 2-ethyl-3-methoxy-5-methylpropiophenone. Another attempt to fractionate this oil by distillation *in vacuo* gave no apparent separation.

Anal. Calc'd for $C_{12}H_{16}O_3$: C, 69.20: H, 7.75.
for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80.
Found: C, 72.44; H, 8.14.

An attempt to form the oxime gave an oil which could not be induced to crystallize.

Reaction of piperonylonitrile and ethylmagnesium bromide. The Grignard reagent acted on 9.85 g. of the nitrile (12) in the usual manner to give 2.3 g. of practically pure starting material in the neutral fraction and 9.4 g. of solid yellow imine. The crude imine melted at 36-38° and gave a white hydrochloride; m.p. 143-144°. It proved too easily hydrolyzed to be analyzed, and 3 g. of the imine was accordingly converted to the ketone by treatment with warm acid. This compound weighed 2.5 g. and melted at 38-39°, the reported melting point of 3,4-methylenedioxypropiophenone (13). The phenylhydrazone, reported to melt at 97° (14), was prepared but melted at 106-107°. However, the melting points of the semicarbazone, m.p. 185-187°, and the oxime, m.p. 103-104°, agreed well with the reported values of 187-188° (15) and 104° (16), respectively.

Reaction of veratronitrile and ethylmagnesium bromide. Veratronitrile (10 g.) (17) and the Grignard reagent reacted in the usual fashion to form 5.2 g. of yellow imine; m.p. 55-57°, 2.7 g. of the nitrile being recovered. Treatment of the imine with hydrogen chloride gave a gummy precipitate, which, however, could be converted to the ketone by hydrolysis. Two grams of the imine yielded 1.1 g.; m.p. 58-59°, agreeing with the recorded melting point (60°) of 3,4-dimethoxypropiophenone (18). The phenylhydrazone melted at 107-109°. The value in the literature is 108-110° (18).

Reaction of 2,3-methylenedioxybenzonitrile and ethylmagnesium bromide. This nitrile (8.5 g.) (19) reacted with the Grignard reagent to give 1.4 g. of neutral material and 8.1 g. of an imine. The neutral material proved to be identical with the ketone described below. The imine, pressed free of oil, melted at 26–28°. It formed an easily hydrolyzed hydrochloride melting at about 330°, with decomposition. From 0.3 g. of the imine was obtained 0.2 g. of the ketone; m.p. 59–61° before purification. During distillation of a larger sample of this material an interesting transition was noted. At 135–140° (1 mm.) it distilled as a yellow oil which gradually formed thick transparent needles. When cooled they changed rapidly into a white opaque form; m.p. 59–61°. Recrystallization from a mixture of high- and low-boiling petroleum ethers gave white needles of 2,3-methylenedioxypropiophenone; m.p. 63.5–64.5°.

Anal. Calc'd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66.
Found: C, 67.83; H, 5.90.

2,3-Methylenedioxypropiophenone oxime, after recrystallization from dilute ethanol, formed white needles; m.p. 112–113°.

Anal. Calc'd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74.
Found: C, 62.15; H, 6.02.

2,3-Ethylenedioxybenzoic acid. The procedure was similar to that employed by Perkin and Trikojus for the methylenedioxy compound (19). A mixture of 44 g. of 2,3-dihydroxybenzoic acid, 46.5 g. of potassium hydroxide, 23.7 ml. of ethylene bromide, 250 ml. of water, and 107 ml. of 95% ethanol was heated under reflux in an oxygen-free atmosphere for twenty hours. The mixture was poured into 1 liter of an ice-hydrochloric acid mixture, and the precipitated acid collected and dried. The crude acid weighed 19.5 g. (38% yield) and gave no blue color with ferric chloride solution, indicating the absence of appreciable amounts of the dihydroxy acid. Purification was attended by excessive loss. Recrystallization from dilute acetic acid gave small white crystals; m.p. 195.5–196.5°.

Anal. Calc'd for $C_9H_8O_4$: C, 60.01; H, 4.47.
Found: C, 59.86; H, 4.70.

2,3-Ethylenedioxybenzoyl chloride. This compound, prepared in nearly quantitative yield by use of pure thionyl chloride, boiled at 107–108° (1 mm.). Although carefully recrystallized from high-boiling petroleum ether which had been dried over sodium, the white needles (m.p. 69.5–70.5°) gave analytical results indicating partial hydrolysis.

Anal. Calc'd for $C_9H_7ClO_3$: C, 54.43; H, 3.55.
Found: C, 55.61; H, 3.73.

2,3-Ethylenedioxybenzamide. The crude acid (17 g.) was converted to the acid chloride as indicated above, and the chloride was distilled at reduced pressure and dissolved in 100 ml. of benzene. This solution was added during the course of an hour to 200 ml. of concentrated ammonia water cooled in an ice-bath. The amide precipitated and was collected on a filter. By concentrating the mother liquor and again cooling, a total of 13.0 g. (77% yield based on crude acid) was obtained. Efficient cooling during the reaction is essential. Recrystallization of the amide from a mixture of benzene and high-boiling petroleum ether gave white crystals; m.p. 133–134°.

Anal. Calc'd for $C_9H_9NO_3$: C, 60.29; H, 5.07.
Found: C, 60.43; H, 4.98.

2,3-Ethylenedioxybenzonitrile. The crude amide (13.4 g.) was heated under reflux with 50 ml. of purified thionyl chloride for six hours. After the excess reagent had been removed at the aspirator, 11.0 g. (91% yield) of the nitrile distilled at 127–129° (1 mm.) as a yellow oil. When recrystallized from a mixture of high- and low-boiling petroleum ethers, it formed white needles melting at 51.5–52°.

Anal. Calc'd for $C_9H_7NO_2$: C, 67.08; H, 4.38.
Found: C, 67.19; H, 4.21.

Reaction of 2,3-ethylenedioxybenzonitrile and ethylmagnesium bromide. The reaction of 8 g. of the nitrile with the Grignard reagent gave 5.3 g. of neutral material melting at 54–56° and 2.9 g. of an imine. The neutral fraction proved to be identical with the ketone described below. No crystalline hydrochloride could be obtained from the imine but it was readily hydrolyzed to the ketone by warming with dilute acid. This compound melted at 55–56° without purification and distilled at 115–116° (1 mm.). 2,3-Ethylenedioxypropiophenone formed broad white needles from low-boiling petroleum ether; m.p. 57.5–58.0°.

Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30.
Found: C, 68.87; H, 6.32.

2,3-Ethylenedioxypropiophenone oxime was obtained in a form melting at 124–125° but changed on recrystallization from dilute ethanol to a more stable modification; m.p. 113–114°.

Anal. Calc'd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.33.
Found: C, 63.89; H, 6.36.

SUMMARY

Replacement of the 2-methoxyl group in 2-methoxybenzonitriles by the action of Grignard reagents has been observed only with those derivatives which have a second alkoxyl group in position 3. Two new examples have been discovered.

The reaction of ethylmagnesium bromide with 2-methoxybenzonitrile, 2,5-dimethoxybenzonitrile, 2,6-dimethoxybenzonitrile, veratronitrile, piperonylonitrile, 2,3-methylenedioxybenzonitrile, and 2,3-ethylenedioxybenzonitrile has been found to produce only 1,2 addition products as contrasted to the formation of 2-ethyl-3-methoxybenzonitrile from 2,3-dimethoxybenzonitrile.

URBANA, ILL.

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