

1936

The Friedel-Crafts Reaction with Furans

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Recommended Citation

McCorkle, M. and Turck, J. A. V. Jr. (1936) "The Friedel-Crafts Reaction with Furans," *Proceedings of the Iowa Academy of Science*, 43(1), 205-206.

Available at: <https://scholarworks.uni.edu/pias/vol43/iss1/50>

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Bromination of methyl dibenzofuran-4-carboxylate gives methyl 2-bromodibenzofuran-6-carboxylate (m.p., 166°-167°); and nitration gives heteronuclear substitution isomers, the nitro group going to the 2-position and to the 3-position to yield methyl 2-nitrodibenzofuran-6-carboxylate (m.p., 205.5°) and methyl 3-nitrodibenzofuran-6-carboxylate (m.p., 158°). Nitration of 4-methoxydibenzofuran gives 1-nitro-4-methoxydibenzofuran.

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EFFECTS OF CATALYSTS ON THE PREPARATION AND PROPERTIES OF ORGANOMETALLIC COMPOUNDS

M. LICHTENWALTER, J. C. BAILIE AND A. J. CARTER

It has been shown that the formation of RM compounds can be accelerated photochemically and by the use of varying quantities of selected reagents. Also, the rates of reaction between RM compounds and various reactants can be accelerated by small quantities of catalysts like cuprous chloride. For example, the time required for complete interaction of benzonitrile and phenylmagnesium bromide is reduced significantly by the addition of small amounts of compounds like cuprous chloride. It appears that these particular catalysts function by first forming very unstable organometallic compounds like phenylcopper, in the case mentioned. Then the phenylcopper decomposes to give copper and diphenyl, probably *via* free phenyl radicals which then set up chain reactions.

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THE FRIEDEL-CRAFTS REACTION WITH FURANS

M. McCORKLE AND J. A. V. TURCK, JR.

2-Furoic acid, aluminum chloride and substituted benzenes give 6-substituted-1-naphthoic acids. For example, with chlorobenzene the product is 6-chloro-1-naphthoic acid; with anisole, 6-methoxy-1-naphthoic acid; with toluene, 6-methyl-1-naphthoic acid.

Benzene, aluminum chloride and methyl 2-furoate give methyl α -naphthoate in 56 per cent yield.

Benzene, aluminum chloride and methyl 2-methyl-3-furoate give methyl 4-phenyl-4, 5-dihydro-2-methyl-3-furoate; and substituted benzenes and other aryl types give related products.

A very wide variety of branched and straight chained alkyl halides react with ethyl 5-bromo-2-furoate in the presence of aluminum chloride to give ethyl 4-*tert.*-butyl-5-bromo-2-furoate. However, *n*-amyl bromide (unlike *n*-C₅H₁₁Cl, *n*-C₅H₁₁I, and the other RX compounds) gives ethyl 5-*tert.*-butyl-2-furoate exclusively, unless a purer grade (resublimed) aluminum chloride is used in which case the ethyl 4-*tert.*-butyl-5-bromo-2-furoate is obtained.

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HYDROQUINONE MONOACETATE

H. S. ORCUTT

Alkyl monoesters of hydroquinone and pyrocatechol have not hitherto been prepared. Hydroquinone monoacetate has been obtained by the following series of reactions. Hydroquinone plus one molar equivalent of carbobenzoxy chloride gives hydroquinone monobenzyl carbonate. This compound is acetylated, and then hydrogenated in alcohol with Pd or Ni catalyst. Hydroquinone monoacetate, plates or needles from petroleum ether, M. P. 57-59°C., is obtained from the residue.

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MIXED DIACYL DERIVATIVES OF *O*-AMINOPHENOL CONTAINING AN ACYL DERIVED FROM A SULFONIC ACID

L. CHAS. RAIFORD AND J. REID SHELTON

In previous work in this Laboratory it was found that, in general, only one mixed diacyl derivative can be obtained from *o*-aminophenol, regardless of the order of introduction of these acyls, provided both are derived from carboxylic acids. In one