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Orientation Studies in the Dibenzofuran Series

A. L. Jacoby
Iowa State College

D. M. Hayes
Iowa State College

P.R. Van Ess
Iowa State College

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and inhibitols cause no change subsequent to the end of the induction period, that they exert their effect solely by inhibiting the formation of the initial active moloxide, and that they are entirely destroyed before the start of rapid oxidation which characterizes the end of the induction period.

The mode of action of several different pro-oxidants is analyzed. Perbenzoic acid, and presumably other peracids, and Cu oleate decrease the induction period by virtue of their destruction of natural inhibitors.

BIOCHEMICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA.

ORIENTATION STUDIES IN THE DIBENZOFURAN SERIES

A. L. JACOBY, D. M. HAYES AND P. R. VAN EËSS

2-Hydroxydibenzofuran on bromination gives 1-bromo-2-hydroxydibenzofuran (m.p., 123.5°) and 2-hydroxy-3-bromo-dibenzofuran (m.p., 143-144°). The corresponding products but in a different ratio are obtained by the bromination of 2-methoxydibenzofuran. The allyl ether of 2-hydroxydibenzofuran rearranges to 1-allyl-2-hydroxydibenzofuran (m.p., 82.5°-83°), the methyl ether of which melts at 68°. Also, 2-hydroxydibenzofuran and benzenediazonium chloride couple to give 1-phenylazo-2-hydroxydibenzofuran. The 3-hydroxydibenzofuran couples to give 2-phenylazo-3-hydroxydibenzofuran (m.p., 166°), the structure of which was established by conversion to 2-bromo-3-hydroxydibenzofuran (m.p., 166°), the structure of which was established by conversion to 2-bromo-3-hydroxydibenzofuran (m.p., 115°-116°).

In bromination of the 4-hydroxy-, 4-methoxy- and 4-acetaminodibenzofuran bromine goes to the 1-position; and in coupling of the 4-hydroxy compound with benzenediazonium chloride the phenylazo group also goes to the 1-position (m.p., 175°). The Grignard reagent of 1-bromodibenzofuran (m.p., 67°-67.5°) (obtained by deamination of the 1-bromo-4-amino compound, m.p., 119°-120°) gives on oxidation 1-hydroxydibenzofuran (m.p., 140.5°) and on carbonation the dibenzofuran-1-carboxylic acid (m.p., 232°). Methyl dibenzofuran-1-carboxylate (m.p., 63°) on nitration gives methyl 7-nitro-dibenzofuran-1-carboxylate (m.p., 216°).

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.

DEPARTMENT OF CHEMISTRY,
IOWA STATE COLLEGE,
AMES, IOWA.

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.

DEPARTMENT OF CHEMISTRY,
IOWA STATE COLLEGE,
AMES, IOWA.

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.