Save for *o*-xylene the three xylenes are attacked on the methyl groups exclusively. Alkylation of the mono-products gives the corresponding methylhexylbenzene. Carbonation of the dimetalated compounds gives the corresponding phenylene diacetic acids. *o*-Xylene undergoes some nuclear metalation, presumably after one sodium atom has been introduced in the methyl group. Alkylation and metalation of the xylenes occurs with more difficulty than the corresponding reaction of toluene.

The products of dimetalation of benzene and toluene are meta substituted exclusively. A reasonable interpretation of this result is that the mono-metalated product is a salt and acts as an ion-pair with the sodium ion so close to the anion that it exerts a meta directing influence, *i. e.*, the cation dominates the position taken by a substituent in the anion. This opinion is shown to be consistent with other experimental facts and with current theories.

The substitution, disproportionation, and metathetical reactions which amylsodium and like reagents undergo with various other compounds are discussed from the viewpoint of the findings in the orientation study, *viz.*, that an organosodium compound may act as an ion-pair with the metal ion having the leading role, if any preference is to be considered. The reactions are shown to be consistent with such a view. A comparison with electrophilic reagents is possible.

The difficulty of alkylating or metalating the three xylenes and *o*-xylene in particular is correlated with the general retarding effects of alkyl groups on metalation. These results may likewise be interpreted in the light of an ion-pair mechanism with the sodium ion having an equal or more dominant role.

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Condensations by Sodium. XXVII. Furylene Disodium. Comments on the Aromatic Properties of Furan

BY AVERY A. MORTON AND G. HAROLD PATTERSON

While endeavoring to prepare furylsodium by the action of amylsodium on excess furan, we discovered, after pouring the mixture on solid carbon dioxide, that an appreciable quantity of α,α'-furandicarboxylic acid was present. Furan had obviously been metalated twice. Although no attempt was made to find conditions for optimum yields as was done in the case of benzene and toluene,[1] the generally greater ease of substitution in furan as compared with benzene suggests that the process is capable of giving large amounts of material in one step.

Since the sodium ion has a strong meta-directing influence,[1] this result constitutes one more of the failures of such groups[2] in general to exert any influence in the furan nucleus. Since it is reasonable to assume that the properties which cause sodium to be meta-directing in the benzene nucleus are inherent in the metal, it is logical to look for a reason why this influence is set aside when the same type of reaction is carried out in another system. Now a meta-directing group can fail to operate even in an aromatic system, chiefly when opposed by an ortho–para directing force such as an ether (methoxy) group. It is, therefore, necessary to look only to the ether group in furan to observe a cause for the failure of meta-directing groups in general to function in this heterocyclic system.

A transfer of the seat of activity from a point outside to one inside the ring is by no means an unusual occurrence. The C=N system in pyridine has the properties of an ammono aldehyde[3]; the imide (ammono phenol[3]) function in pyrroles[4] and in indoles[5] serves as an imino phenolic group and participates with varying degrees of success in such reactions as the Kolbe or Reimer synthesis; the amidine function is evident in imidazoles. Even in such a resonating molecule as benzene the additive character of the double bonds is not entirely suppressed. Finally, in the case of furan itself, the ether function still has, to an advanced degree in fact, the property of easy

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[1] Morton, Little and Strong, THIS JOURNAL, **65**, 1339 (1943).

[2] Kohler, Westheimer and Tishler, *ibid.*, **58**, 264 (1936).

[3] Franklin and Bergstrom, *Chem. Rev.*, **16**, 305 (1935).

[4] Ciamician, *Monatsh.*, **1**, 624 (1880); Ciamician and Silber *Ber.*, **17**, 1437 (1884).

[5] Ellinger, *ibid.*, **39**, 2515 (1902).

hydrolysis by acids in spite of the fact that it is part of a ring. The retention and enhancement, therefore, of some of the other properties, such as labilizing the ortho hydrogen atom, would not be unexpected.

The logical consequence of this view, of course, is that furan does not derive its special property of ease of substitution from a relationship to any aromatic system so much as from the presence of an activating ether linkage. However stimulating the expression "superaromatic" has proven to be, it nevertheless implies as a basis the opinion that furan is merely a carbon ring with oxygen replacing two methine groups. A suitable comparison, if one is to be made, should be with a molecule, such as anisole in which the all-important ether link is present. Or if the position inside the ring has, by mere proximity to the alpha position, permitted the effect to be magnified, the comparison might be made with a benzene ring carrying two alkoxy substituents such as the dimethyl ether of resorcinol. The greater ease of substitution, the ready mercuration, the mild catalytic agents needed in the Friedel–Crafts synthesis, are thereby understandable. So also is the loss of meta-directing power on the part of nitro, sodium and other substituents.

It should be mentioned also that the other major failure of the superaromatic concept, *viz.*, the absence of a true phenolic effect and occurrence instead of an enol–keto (or imino-ketimine[6]) relationship, is better accommodated to this new angle. For it is a well-established fact that the presence of hydroxyl groups in an aromatic system, as in resorcinol or phloroglucinol, induces many reactions[7] such as oxime formation or the introduction of methyl groups by means of methyl iodide and sodium methylate which are identical with the behavior of keto–enol systems. Such results are realized also with the methyl ethers of these compounds as long of course as the necessary one hydroxyl group is present. It is clearly evident, therefore, that the introduction of more and more hydroxyl or alkoxyl groups into a ring system induces a shift from the true phenolic to one of an enol–keto relationship. The behavior of the hydroxyl group in furan would therefore represent merely the extreme end of a change the trend of which was already well marked.

The purpose of these comments is not of course to affirm that anisole or like compound is the parent type for the chemistry of furan for that heterocyclic compound has also interesting additive properties like those of a diene. Rather it is to suggest that where it becomes necessary or desirable to make a comparison the great ease of substitution, the predominant α-substitution, and the keto–enol properties of hydroxy furan, are all more closely connected to a powerful ether effect, a "superalkoxy" influence as it were, than to a "superaromatic" effect and that this exhibition is merely in accord with the pronounced activity of the furan ether linkage in other lines such as the unusual ease of hydrolysis.

Experiments

Sodium sand was first prepared from 17.3 g. (0.75 g. atom) of sodium in *n*-octane solution in the high speed stirring apparatus as described before.[1] Furan (51 g. or 0.75 mole) was added rapidly and the mixture stirred vigorously at −15° for one hour. No reaction was apparent. Amyl chloride (26.69 or 0.25 mole) in 30 ml. of octane was then added at 0° over a one-hour period. The mixture was stirred for an hour longer and then warmed at a moderate stirring speed to 64°. It was cooled and then carbonated by pouring on solid carbon dioxide. The unreacted sodium metal was removed by adding water. The brick-red aqueous layer was acidified with hydrochloric acid, saturated with salt and extracted repeatedly with small portions of ether, ethyl acetate and *t*-butyl alcohol in an attempt to remove all the color from the aqueous layer. The extracts were evaporated, the combined residues methylated with diazomethane and the ester fractionated at 16–17 mm. Methyl furoate, boiling over the range from 70–95°, was obtained in a yield of 8.6 g. or 27% calculated on the amyl chloride originally used. Dimethyl furan-2,5-dicarboxylate was obtained above 140° in a yield of 1.5 g. or 6.5% (amyl chloride basis) or about 19% based on the furan products isolated. The tarry residue which probably resulted from ring opening (amylsodium attacks ether linkages) amounted to 0.5 g. The diester, after being recrystallized twice from methanol and once from aqueous acetone, melted at 107.2–108.2° and showed no depression in melting point when mixed with an authentic sample that melted at 107–108°. Crystallographic analysis and melting point (121–122.5°) of the anilide derivatives also showed that the material obtained from the reaction was identical with the authentic sample. The saponification equivalent showed an abnormal consumption of alkali as if the ring had opened, but the same result was noted also with the authentic diester.

Summary

Amylsodium readily introduces a second sodium atom in the furan. 2,5-Furandicarboxylic acid is obtained by carbonation.

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(6) Rinkes, *Rec. trav. chim.*, **51**, 349 (1932); Gilman and Wright, *ibid.*, **53**, 13 (1934); Stevenson and Johnson, THIS JOURNAL, **59**, 2525 (1937).

(7) Pollak and Gans, *Monatsh.*, **23**, 949 (1908); Spitzer, *ibid.*, **11**, 104 (1890); Herzig and Erthal, *ibid.*, **31**, 827 (1910); Kaserer, *ibid.*, **23**, 587 (1902).

Absence of the powerful meta-directing influence of the sodium ion in the furan nucleus suggests that it is overcome by a strong ortho-directing influence such as an ether linkage inside the ring.

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Polarographically Controlled Syntheses, with Particular Reference to Organic Chemistry

BY JAMES J. LINGANE, C. GARDNER SWAIN AND MELVIN FIELDS[1]

Electrolytic preparative methods, particularly in the field of organic chemistry, have not been exploited to the extent that their inherent advantages would seem to warrant. This is chiefly attributable to the difficulties of predicting, by the classical procedures, optimum conditions of electrolysis, and the consequent necessity of performing an inordinately large number of laborious trial-and-error experiments to establish even approximately correct conditions. The highly empirical character of the organic electrochemical preparative literature is well reflected in the almost universal custom of specifying current density as a variable of purportedly great importance, although actually it has only minor significance unless other factors, such as cell design and resistance, exact solution composition, temperature, *et cetera*, are also specified. This practice has long tended to obscure the fundamental fact that the electrode potential, and not current density, is the *conditio sine qua non* which more often than not determines the success or failure of electrolytic methods; the current density cannot be adjusted arbitrarily to produce a desired rate of electrolysis without regard to the electrode potential. The importance of the electrode potential has, of course, long been recognized, but a preliminary determination of its optimum value in any given case has been difficult and often practically impossible by classical procedures, except for those rather rare instances which involve reversible oxidation-reduction reactions accessible to the ordinary potentiometric methods.[2]

The purpose of the present paper is to demonstrate the extent to which electrolytic preparative procedures can be rationalized and improved by using the polarographic method of electrolysis[3] as a pilot technique to establish optimum electrolysis conditions before actual preparative work is undertaken. The term "polarographic synthesis" is suggested to describe this new technique.

From a preliminary polarographic investigation of a projected starting material under widely diverse conditions of solution composition, *p*H, temperature, *et cetera*, the feasibility of, and optimum conditions for, a large-scale electrolytic preparation with practically quantitative yield usually can be determined readily, regardless of whether or not the electrode reaction is reversible. Since the polarographic method need not be limited to the dropping mercury electrode, but can also be applied to solid microelectrodes,[3] it may also serve to determine the most satisfactory electrode material for a given reaction; this should prove to be especially advantageous in investigating selective oxidation reactions at a large platinum anode of alcohols, acids (Kolbe synthesis), hydrocarbon side chains (controlled stepwise degradations), etc. Furthermore, information obtained in a preliminary polarographic investigation should be a valuable aid in solving the frequent and often difficult problem of selecting the proper "chemical" reducing or oxidizing agent for effecting a desired reaction, particularly in those cases where the reduction or oxidation proceeds through several stages.

The present study is concerned chiefly with the application of the proposed method to the preparation of 9-(*o*-iodophenyl)-dihydroacridine by reduction of 9-(*o*-iodophenyl)-acridine according to

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(1) National Scholar, Harvard University, 1942–43.

(2) For a comprehensive review of the organic electrochemical preparative literature, see S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., New York, N. Y., 1936.

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.