8. The I effects discussed in the preceding sections are greater the longer the chain or the more branched the alkyl. Thus on a constant enol basis the order of rates of acid alcoholysis for a series of diacetylmethane derivatives is: *i*-C_3H_7, *n*-C_4H_9, *n*-C_3H_7, C_2H_5, $C_6H_5CH_2$. This is also the order of polarity (+I). The cyclohexyl group has a +I effect like the alkyl groups and so has a similar effect, very different from the ±T of the phenyl group.

9. Monoacylglutaric esters underwent acid alcoholysis more rapidly than the corresponding succinates.[5] This is presumably due to the greater −I of the —CH_2COOEt in the succinate as compared to the —CH_3CH_2COOEt in the glutarate.

10. Acetyl trimethylacetylglutaric ester was more resistant to alcoholysis than the acetyl *n*-butyrylglutaric ester for the stronger +I effect of the *t*-butyl group decreased the rate of cleavage. The ratio of the cleavage products was more favorable to acetyl cleavage in the case of the normal compound, the actual amount of the acetyl cleavage being almost the same. This is due to the +I effect of the branched chain slowing the cleavage adjacent to that group but having only a slight slowing effect on the cleavage at the other end.

11. The proportion of acetyl cleavage was lower for the diacylglutarates than for the diacylsuccinates. The comparison is between the addition reactions (1) to the acetyl carbonyl carbon, and (2) to the other acyl carbonyl carbon. (1) is a faster reaction than (2); therefore if the product is removed faster, the disturbing influence will be greatest on the equilibrium which is maintained most slowly (2), thus the concentration of the addition product in this case is lowered and the reaction slowed relative to the competing reaction. Therefore the succinic ester which cleaves faster should have the greater percentage of acetyl cleavage.

Summary

Mechanisms have been suggested for the alcoholysis of 1,3-dicarbonyl compounds in acid and basic solutions. The polarization and the polarizability of different groups have been discussed in relation to the suggested mechanism. A correlation of the experimental work on the alcoholysis of 1,3-dicarbonyl compounds in this Laboratory has been made upon the basis of these concepts.

MADISON, WISCONSIN RECEIVED NOVEMBER 1, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Aromaticities. IV. Furyl-Alkali Compounds[1]

BY HENRY GILMAN AND FRITZ BREUER[2]

Introduction

The pronounced tendency of furan to undergo α-nuclear substitution reactions[3] has been advanced as one of a number of reactions in support of the thesis that furan has super-aromatic properties. The facility of such substitution is not confined to the use of acidic reagents, for it is now shown that furan undergoes nuclear substitution by metals under conditions where benzene, a typical aromatic compound, is unaffected.

Schorigin[4] showed that simple saturated aliphatic hydrocarbons underwent no reaction with sodium and that ethylsodium reacted with benzene to give phenylsodium and ethane. Inasmuch as both ethylsodium and phenylsodium react with furan to give 2-furylsodium, the order of decreasing ease of substitution by sodium is: $C_4H_4O > C_6H_6 > C_2H_6$. This order of relative aromaticities is also shown by other studies such as the electronegativities of the radicals as determined by hydrogen chloride scission of organolead compounds and the ionization constants of the corresponding carboxylic acids. The correlation of organo-alkali formation (by replacement of hydrogen by sodium or potassium) with negativity series has not been settled. For example, triphenylmethane with potassium gives triphenylmethylpotassium [$(C_6H_5)_3CK$] under conditions where benzene undergoes no reaction.[5] On such a basis, the triphenylmethyl radical may be considered more negative than the phenyl radical. However, this reaction has been interpreted

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[1] The preceding paper in this series, THIS JOURNAL, **56**, 464 (1934).

[2] Austro-American Exchange Fellow.

[3] Gilman and Wright, *Chem. Reviews*, **11**, 323 (1932).

[4] Schorigin, *Ber.*, **41**, 2711, 2723 (1908); **43**, 1938 (1910).

[5] Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930).

differently.[6] Entirely apart from the various interpretations of reactions of this type it is significant for our immediate purposes that the lateral hydrogen in triphenylmethane, and in related compounds, readily lends itself to diverse substitution reactions; and that in a direct comparison of the replacement of nuclear hydrogen by metals, furan exceeds benzene in ease of substitution.

It is quite obvious that there may be real interpretational difficulties, in the present reaction, when one considers compounds other than such parent types as methane, benzene, thiophene and furan. Fundamentally, the replacement of hydrogen by a metal is a reaction of relative acidities. The acidity of lateral hydrogen appears, however, to be influenced markedly by the so-called aromaticity of the nucleus to which the lateral hydrogen is attached.

Reaction with 2-Methylfuran.—The following over-all reaction takes place between 2-methylfuran and ethyl-, phenyl- and benzylsodium, followed by carbonation and hydrolysis

$$\text{2-}CH_3C_4H_3O + RNa \longrightarrow RH + \text{2,5-}CH_3C_4H_2ONa \xrightarrow{CO_2} \text{2,5-}CH_3C_4H_2OCOOH \quad \text{(I)}$$

The formation in this manner of 5-methyl-2-furoic acid indicates nuclear substitution of an α-hydrogen by sodium, with the probability of preliminary addition. Actually, however, there are reasons for interpreting this reaction as one involving lateral substitution. Schorigin[4] has shown that methylbenzenes react with ethylsodium to give benzylsodium types which on carbonation yield phenylacetic acids

$$C_6H_5CH_3 \xrightarrow{C_2H_5Na} C_6H_5CH_2Na \xrightarrow{CO_2} C_6H_5CH_2COOH \quad \text{(II)}$$

On the basis of this general[7] reaction he formulated the empirical rule that the carboxyl group is introduced (subsequent to carbonation) in a position such that the resulting acid has the lowest melting point of all possible isomers. 2-Furylacetic acid would have been expected because it melts at 68° whereas the 5-methyl-2-furoic acid actually isolated melts at 109°. No 2-furylacetic acid was isolated, but because of its instability it would not be surprising if some had formed and then decomposed under the experimental conditions.

The modified allylic rearrangement postulated here finds support in 2-furylmethyl rearrangements observed by Johnson[8] and by Reichstein.[9] Furthermore, a rearrangement of this type has been noted in the carbonation of cinnamylmagnesium chloride;[10] and the following paper shows that organo-alkali compounds undergo allylic rearrangements like those observed with organomagnesium compounds.

The recent interesting and highly suggestive studies by Kischner[11] on tautomeric modifications of 2-methylfuran offer another interpretation for the formation of 5-methyl-2-furoic acid.[12]

It is significant that 2-methylthiophene also reacts with benzylsodium to give an organosodium compound which on carbonation yields 5-methyl-2-thenoic acid.

If 2-furylmethylsodium and 2-thienylmethylsodium are the first compounds formed from 2-methylfuran and 2-methylthiophene, respectively, with benzylsodium, then it may be concluded that furan and thiophene are more aromatic than benzene.

Relative Aromaticities of Furan and Thiophene.—It has been shown on the basis of the scission of organolead compounds, that furan is more aromatic than benzene and that furan also appears to be more aromatic than thiophene. The present results on attempts to determine the relative aromaticities of furan and thiophene do not lend themselves to unequivocal interpretation. Furan reacts with 2-thienylsodium to give 2-furylsodium, for the mixture on carbonation yields 2-furoic acid and *no* thenoic acid. This, of itself, indicates the greater aromaticity of furan. However, thiophene with 2-furylsodium gives, after carbonation, 2-thenoic acid which may or may not contain any 2-furoic acid. Because the method of mixed melting points is unreliable with a mixture of 2-thenoic and 2-furoic acids, and because there is not available at this time an analytical procedure for determining the presence of small amounts of 2-furoic acid in 2-thenoic acid, we do not know whether 2-furoic acid was admixed in small quantities with the 2-thenoic acid. However, the quantitative analysis of the 2-thenoic acid belies any significant contamina-

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[6] Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

[7] With toluene and ethylsodium, formed from diethylzinc and sodium, he isolated a mixture of phenylacetic and *p*-toluic acids. Such mixtures were not reported with the other hydrocarbons.

[8] Runge, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930).

[9] Reichstein, *Ber.*, **63**, 749 (1930).

[10] Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927).

[11] Kischner, *J. Gen. Chem.*, (U. S. S. R.) **1**, 1212 (1931); *C. A.* **26**, 5299 (1932).

[12] Additional general mechanisms for furan substitutions are contained in Ref. 3.

tion with 2-furoic acid. Accordingly, one may conclude from these experiments that furan is at least as aromatic as thiophene and probably more aromatic than its sulfur analog. The recent experiments on the nitration of 2-furyl 2-thienyl ketone show furan to be more aromatic than thiophene.[1]

Furan and 2-Methylfuran with Alkali Metals.—Benzene undergoes no substitution reaction with sodium or potassium,[13] although reaction has been reported with rubidium and cesium to give, for example, phenylcesium.[14] Furan has been reported as undergoing no reaction with sodium or potassium.[15] In view of the greater general reactivity of an α-furan hydrogen when compared with a hydrogen of benzene, it seemed reasonable to expect replacement of an α-hydrogen by potassium. This was confirmed by the preparation of 2-furylpotassium when furan was brought into reaction with liquid sodium-potassium alloy or potassium metal. 2-Methylfuran also underwent reaction with the alloy and with potassium to give 5-methyl-2-furoic acid subsequent to carbonation. No reaction was observed, under our conditions, with lithium, sodium, 4% sodium amalgam, sodamide and sodium hydroxide at temperatures from 60 to 100°. The reaction with potassium was highly complex and apparently complete in the sense that the furan was used up. Ring scission also probably occurred accompanied by the removal of oxygen to give butadiene types. This reaction is under investigation.

Acidity of Furan.—Studies by Wooster and Mitchell,[5] Ziegler,[16] and Conant and Wheland[17] on metathetical reactions between organoalkali compounds and hydrocarbons

$$\mathrm{RH} + \mathrm{R'\,Metal} \rightleftharpoons \mathrm{R\,Metal} + \mathrm{R'H} \quad \text{(III)}$$

have shown that it is possible to arrange the very weak acids (hydrocarbons) in a series of acid strengths on the basis of reaction with the salts (organometallic compounds). For example, inasmuch as ethylsodium with benzene gives ethane and phenylsodium, it may be concluded that benzene is a stronger acid than ethane. It was considered desirable to place approximately furan in such a series, particularly since a representative number of very weak acids has been arranged recently.[17] We have observed that triphenylmethylsodium reacts with furan to give 2-furylsodium, and that 2-furylsodium underwent a highly limited reaction with triphenylmethane to give a faint reddish color, but no triphenylacetic acid was isolated after carbonation. These results show furan to be a stronger acid than triphenylmethane. From the reaction between phenylacetenylsodium and furan only phenylpropiolic acid was isolated, and this indicates that furan is a weaker acid than phenylacetylene. The order of increasing acid strength is, therefore

$$(C_6H_5)_3CH > C_4H_4O > C_6H_5C{\equiv}CH$$

It might be mentioned that in Conant's[17] series of acids of increasing strength, phenylacetylene is relatively of high acid strength, ranking eleven in the twelve compounds studied, and that triphenylmethane occupies the fifth position. No study was made to determine how much more strongly acidic furan is than triphenylmethane.

Apropos the reaction of alkali metals with benzene it appears not at all unlikely that all hydrogen-containing organic compounds are acidic in the sense that they might undergo replacement of hydrogen by an alkali metal. For example, Marcus[18] reports that cesium slowly decomposes saturated aliphatic hydrocarbons at room temperatures. This warrants confirmation in view of the preparation of the ethylcesium-diethylzinc complex by v. Grosse.[19] Possibly the separate findings are not in conflict because of a "stabilizing" effect of the diethylzinc. In any event, there remains the future possibility of using the most active alkali metal, Element 87, to classify roughly saturated aliphatic hydrocarbons in a series of relative acidities.[20]

Experimental Part

Furan and RNa Compounds. General Procedures.—The organosodium compounds were prepared prior to reaction with furan or prepared from the organomercury compound and sodium in the presence of furan. The latter procedure is more convenient and the presence of sodium has no apparent deleterious effect inasmuch as it does not react, under the experimental conditions, with furan or 2-methylfuran. *n*-Hexane or the furans brought into reaction were used as the media, the reactions being

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[13] Schlenk and Mayer, *Ber.*, **46**, 4060 (1913).

[14] Hackspill, *Ann. chim. phys.*, [8] **28**, 653 (1913).

[15] Limpricht, *Ann.*, **165**, 282 (1873).

[16] Ziegler, Crössmann, Kleiner and Schäfer, *ibid.*, **473**, 1 (1929); Ziegler and Bähr, *Ber.*, **61**, 253 (1928).

[17] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[18] Marcus, p. 946 of Vol. IV of the second edition of Houben "Die Methoden der organischen Chemie."

[19] V. Grosse, *Ber.*, **59**, 2646 (1926).

[20] From a theoretical point of view it is interesting to reflect that Element 87 might be sufficiently reactive so that no typical organoalkali compound would result because of a progressive replacement of hydrogen by the metal resulting ultimately in the formation of carbide.

carried out in modified Schlenk tubes. Prior to carbonation, which was generally effected by solid carbon dioxide,[21] the excess furan was removed by distillation and replaced by *n*-hexane. Then any unused alkali metal was either destroyed by the careful addition of wet ether, or preferably removed by the addition of mercury in order to avoid secondary reductions by hydrogen from the wet ether. The suspension of salts was poured upon ice, and the resulting alkaline solution extracted with ether to remove non-acidic products. The temperature was not allowed to exceed 5° during acidification of the alkaline hydrolysate by sulfuric acid. The acids were recovered by a combination of salting out and ether extraction, and then generally purified by sublimation. All operations, prior to hydrolysis, were carried out in dry, inert atmospheres and the reagents were carefully purified prior to use.

Diethylmercury (2.58 g. or 0.01 mole), 150 cc. of furan and an excess of freshly cut sodium chips were heated at 60° for three days with occasional shaking. The organosodium compound was dark brown in color and resembled a preparation of ethylsodium in petroleum ether. Several experiments were carried out and the yield of 2-furoic acid, calculated on the basis of diethylmercury, varied from 15 to 25%.

Reaction was effected in a corresponding manner between furan, diphenylmercury (0.01 mole) and sodium to give yields of 5–15% of 2-furoic acid. Mixed melting point determinations of 2-furoic and benzoic acids showed that benzoic acid could have been present only in very small quantities, if, indeed, any were present.

The same ratio of reactants (as with phenylsodium) was used in experiments with dibenzylmercury, and a very satisfactory yield (58%) of 2-furoic acid was obtained. Again, mixed melting points showed that but very small quantities, if any, of phenylacetic acid could have been contained in the product. In one experiment, a small amount of acidic material melting at 120–121° was isolated. This was not identified, but it was shown not to be 3-furoic acid which melts at about the same temperature.

2-Methylfuran and 2-Methylthiophene with RNa Compounds.—Noticeable warming was observed on mixing 32 g. (0.4 mole) of 2-methylfuran, 5 g. (0.02 mole) of diethylmercury and sodium. The formation of organoalkali compound was immediate, and the reactants were heated for ten hours at 60°. During acidification, subsequent to carbonation, gas evolution was noted and this together with an odor remindful of phenylacetic acid might be taken as indications of the formation of some of the unstable 2-furylacetic acid. A small quantity of 5-methyl-2-furoic acid was isolated.

From a corresponding reaction between 0.62 mole of 2-methylfuran and 0.02 mole of phenylsodium, there was isolated 7.5% of 5-methyl-2-furoic acid.

The reaction with 2-methylthiophene (0.026 mole) was carried out with 0.1 mole of dibenzylmercury in 80 cc. of *n*-heptane over a period of 144 hours and at a temperature of 60°. The yield of 5-methyl-2-thenoic acid, melting at 135–136°, was 21%. *Neutral equivalent* (micro): calcd., 142.1; found, 138.4.

Furan and 2-Thienylsodium. Thiophene and 2-Furylsodium.—A mixture of one mole of furan, 2.3 g. (0.006 mole) of 2,2′-dithienylmercury and sodium was heated at 60° for fifty-two hours. During acidification, a distinct odor of hydrogen sulfide was noted,[22] and there was also a significant quantity of decomposition products. The yield of 2-furoic acid was 20%, and delicate qualitative tests for sulfur[23] indicated the absence of 2-thenoic acid.

A mixture of 20 g. (0.24 mole) of thiophene, 3.37 g. (0.01 mole) of 2,2′-difurylmercury[24] and sodium was heated at 60° for twelve hours. The metal became heavily coated, and because eight hours of vigorous shaking did not remove the covering, the tube was heated at 90° for a short time to melt the sodium, and then at 60° for an additional twelve hours. The yield of 2-thenoic acid was in excess of 16%, part being lost by accident. The 2-thenoic acid was analyzed by micro methods.

Anal. Calcd. for $C_5H_4O_2S$: C, 46.84; H, 3.15; S, 24.99. Found: C, 47.07; H, 3.28; S, 25.05.

Furan with Triphenylmethylsodium and Phenylacetenylsodium.—A mixture of triphenylmethylsodium (prepared from 0.01 mole of triphenylchloromethane) and one mole of furan was heated at 60° for seventy-three hours. A small quantity of 2-furoic acid was isolated in addition to a large quantity of triphenylmethane. From triphenylmethane (purified by treatment with zinc and glacial acetic acid) and 2-furylsodium, there was isolated subsequent to carbonation, 2-furoic acid but no triphenylacetic acid. The faint reddish color observed in this reaction was like that noted when triphenylmethane was shaken for a long time with sodium amalgam (70% by weight). This latter experiment is significant because the 2-furylsodium was prepared from sodium and 2,2′-difurylmercury. It is interesting to note that the color test[25] with triphenylmethylsodium appears to be less intense than that noted with some other organosodium compounds.

From 0.018 mole of phenylacetenylsodium and furan heated at 60° for eleven days there was obtained a 68% yield of phenylpropiolic acid. Inasmuch as traces of admixed 2-furoic acid have an appreciable effect on the mixed melting point, it is reasonable to conclude that no furoic acid was present.

Furan and 2-Methylfuran with Sodium–Potassium Alloy.—Reaction set in promptly between furan (34 g. or 0.5 mole) and the liquid sodium–potassium alloy. After intermittent shaking over a five-day period, carbonation yielded 0.02 g. of furoic acid and 1.3 g. of an as yet unidentified oil from the ether extract of the alkaline hydrolysate.

In a similar experiment using 11.5 g. (0.22 mole) of 2-methylfuran, a trace of 5-methyl-2-furoic acid was isolated and identified by the method of mixed melting points.

Preparation of 2-Furylsodium from 2,2′-Difurylmercury.—The reaction between 2,2′-difurylmercury[24] and sodium was carried out in *n*-hexane, cyclohexane and ether as media, and the quantity of dark brown solid formed was less than that observed generally in the preparation of ethylsodium or phenylsodium. Carbonation at atmos-

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[21] This Journal, **55**, 1258 (1933).

[22] Scheibler, *Ber.*, **48**, 1821 (1915); **49**, 2596 (1916); Steinkopf, *Ann.*, **428**, 151 (1921).

[23] Emich-Schneider, "Microchemical Laboratory Manual," John Wiley and Sons, New York, 1932.

[24] Gilman and Wright, This Journal, **55**, 3302 (1933).

[25] *Ibid.*, **47**, 2002 (1925).

pheric pressure is slow, as observed by the color test, and the yields of 2-furoic acid varied between 20 and 26%. It is interesting to note that 2-furylsodium is insoluble in ether[26] and also relatively stable in this medium as may be inferred by the distinct color test obtained after one week. In a sense, this latter observation is not surprising for furan itself is an ether and if there were any marked tendency of 2-furylsodium to cleave ethers it is altogether likely that the organosodium compound would decompose in any or no media.

The authors are grateful to Mr. M. Lousinian for liberal supplies of furan and to the Miner Laboratories and the Quaker Oats Co., for some starting compounds.

Summary

1. The formation of 2-furylsodium from furan and phenylsodium, and of 2-furylpotassium from potassium and sodium–potassium alloy under conditions where benzene undergoes no substitution of hydrogen by potassium are offered as additional evidence for the super-aromatic nature of furan.

2. The allylic rearrangement characteristic of some furfuryl systems may be responsible for the formation of 5-methyl-2-furoic acid from 2-methylfuran and RNa compounds, followed by carbonation. 2-Methylthiophene undergoes a like reaction giving 5-methyl-2-thenoic acid.

3. The approximate acidity of furan, established by interaction with organosodium compounds, is less than that of phenylacetylene and greater than that of triphenylmethane.

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[26] Di-2-furylmagnesium prepared in like manner, by R. H. Kirby, from di-2-furylmercury and magnesium in ether, is soluble in ether.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Allylic Rearrangement of Benzyl-lithium

BY HENRY GILMAN AND FRITZ BREUER

Introduction

The literature now contains numerous illustrations of allylic rearrangements involving Grignard reagents.[1] These are of three kinds: (1) aliphatic systems; (2) aliphatic–aromatic systems where rearrangement is lateral; and (3) aliphatic–aromatic systems where rearrangement is nuclear. The most important type of the last mentioned rearrangement was first reported by Tiffeneau and Delange.[2] They observed that benzylmagnesium chloride and formaldehyde gave *o*-tolylcarbinol and not the expected β-phenylethyl alcohol. Since that time numerous other reactants have been observed to give allylic rearrangements with a variety of benzylmagnesium chloride types.[1]

In connection with a related possible allylic rearrangement of 2-furfurylsodium (or 5-methyl-2-furylsodium) to give 5-methyl-2-furoic acid (see preceding paper), it was desirable to learn whether such nuclear allylic rearrangements occurred with organo-alkali compounds. Accordingly, benzyl-lithium was treated with formaldehyde, and it has been shown that such rearrangement does occur to give *o*-tolylcarbinol. Simple lateral, allylic rearrangements of organopotassium compounds have been recorded.[3] By analogy, therefore, one might expect that benzyl-alkali compounds other than benzyl-lithium would show nuclear allylic rearrangements with a reactant like formaldehyde. This may or may not be the case, and it is significant that triphenylmethylsodium and formaldehyde react normally to give triphenylethanol.[4]

Experimental Part

Gaseous formaldehyde, mixed with nitrogen, was added over the surface of an ice-cooled ether solution of 0.4 mole of benzyl-lithium contained in a three-necked flask provided with a mercury sealed stirrer and a condenser. Turbidity and decolorization soon occurred, and at the end of one-half hour a negative color test[5] showed that the benzyl-lithium was used up. Hydrolysis was effected by iced, dilute hydrochloric acid, and the dried ethereal solution was then carefully frac-

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[1] Discussion of mechanisms and ample literature references are contained in two recent papers: (a) Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); (b) Austin and Johnson, *ibid.*, **54**, 647 (1932). See also, Young and Prater, *ibid.*, **54**, 404 (1932); Johnson, *ibid.*, **55**, 3029 (1933).

[2] Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

[3] Ziegler, Crössmann and Schäfer, *Ann.*, **473**, 11, 13 (1929); Ziegler and Schäfer, *ibid.*, **479**, 154, 164, 165 (1930); Schlenk and Bergmann, *ibid.*, **463**, 6 (1928); **479**, 64, 79 (1930); Bergmann, *Ber.*, **63**, 2593 (1930).

[4] Schlenk and Ochs, *Ber.*, **49**, 610 (1916).

[5] THIS JOURNAL, **47**, 2002 (1925).