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).

tionated by means of a Glinsky column. Permanganate oxidation of the *o*-tolylcarbinol fraction, in accordance with the procedure employed with benzylmagnesium chloride and formaldehyde,[1a] gave *o*-toluic acid, the identification of which was completed by a mixed melting point determination.

The experiment was checked.

Summary

It has been shown that benzyl-lithium, like benzylmagnesium chloride, undergoes a nuclear allylic rearrangement with formaldehyde.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

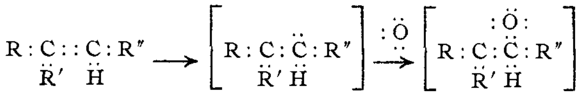
The Structure of the Acids Obtained by the Oxidation of Triisobutylene. I. The Beta Acid of Conant and Wheland[1]

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN

Since the formula suggested tentatively by Conant and Wheland[1] for the beta acid, $C_{12}H_{24}O_2$, m. p. 129°, obtained by the oxidation of triisobutylene would involve a rearrangement entirely at variance with known rearrangements as well as contrary to the modern conceptions of such processes, we decided to study the structure of this acid. We find that the beta acid is methyl-*tert*-butylneopentylacetic acid.

The separation of the acids was accomplished by the fractional distillation of their acid chlorides through an effective column under diminished pressure.[2] The beta chloride was degraded to the corresponding amine by the sodium azide procedure of Naegeli.[3] The amine with nitrous acid gave a tertiary alcohol which was converted to its chloride by hydrochloric acid and was proved to be identical with methyl-*tert*-butylneopentylcarbinol synthesized from methylmagnesium chloride and *tert*-butyl neopentyl ketone.

The formation of the beta acid from 2,2,4,6,6-pentamethylheptene-3[4] probably involves the addition of a neutral oxygen atom (with its six valence electrons) to the electron pair in the activated ethylene bond.



$$R:\underset{\ddot{R}'}{C}::\underset{\ddot{H}}{C}:R'' \longrightarrow \left[R:\underset{\ddot{R}'}{C}:\underset{H}{\ddot{C}}:R''\right] \xrightarrow[\cdot\cdot]{:\ddot{O}} \left[R:\underset{\ddot{R}'}{C}:\underset{H}{\overset{:\ddot{O}:}{\ddot{C}}}:R''\right]$$

R, R', and R'' = neopentyl, methyl and *tert*-butyl, respectively.

The carbon with the open sextet then attracts the electron pair and R'', thus forming an aldehyde which, under the oxidizing conditions, is changed to a tri-substituted acetic acid. If the process followed other courses, ketonic products would be formed. Such products are actually formed with the alpha and beta acids in the oxidation of triisobutylene. They are being studied in this Laboratory.

The structure now proved for the beta acid was tentatively assigned by Conant and Wheland to the alpha acid, $C_{12}H_{24}O_2$, m. p. 89°. Preliminary studies show that the alpha acid corresponds to neither formula suggested by these authors for the two acids obtained from triisobutylene. By means of the mechanism used in the present paper to explain the formation of the beta acid, the formula of the alpha acid and its formation from 2-neopentyl-4,4-dimethylpentene-1[4] become obvious. These will be published later.

Experimental

Oxidation of Triisobutylene.—At first the acids were prepared by N. H. Hale by the oxidation of crude triisobutylene according to Butlerow.[5] The rest was prepared by the following method. A solution of 2 kg. (6.7 moles) of sodium dichromate in 2 liters of 50% acetic acid was placed in a 12-liter flask equipped with dropping funnel, reflux condenser and stirrer. To this was added 1680 g. (10 moles) of the lower-boiling fractions of triisobutylene, separated by M. R. Fenske and his co-workers in this Laboratory, b. p. 175.6° (738 mm., Cottrell), n^{20}_{D} 1.4300. The mixture was stirred vigorously and 1600 cc. of sulfuric acid was added dropwise over a period of four days, with the temperature not above 60°. The reaction mixture was steam distilled from the same flask, and the oil layer of the distillate was set aside for future investigation. The lower layer was siphoned from the hot residue and the remaining oil layer, after washing with 200 cc. of hot water, was distilled to 120° (22 mm.) through column K, 44 × 1.4 cm., 9.6 theoretical plates, glass helix packing.[6] The distillate was combined with

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[1] Conant and Wheland, THIS JOURNAL, **55**, 2499 (1933).

[2] *Cf.* Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

[3] Naegeli, *Helv. Chim. Acta*, **15**, 49 (1932).

[4] McCubbin, THIS JOURNAL, **53**, 356 (1931), confirmed by C. D. Wilson of this Laboratory.

[5] Butlerow, *Ber.*, **12**, 1482 (1879).

[6] Wilson, Parker and Laughlin, THIS JOURNAL **55**, 2795 (1933).