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Abstract

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ON THE INTERACTION OF BENZYLPYRIDINIUM CHLORIDE WITH CYCLOPENTADIENYLLITHIUM

In the present work the interaction of cyclopentadienyllithium (I) with benzylpyridinium chloride (II) was studied.

It might have been expected that benzylpyridinium chloride would benzylate the cyclopentadiene ring. However, instead of the expected benzyl-substituted cyclopentadienes, a substance (III) was isolated which, on the basis of analytical data and molecular-weight determination, had the formula $C_{17}H_{15}N$.

The isolated substance III consists of air-stable, golden-yellow crystals, readily soluble in acetone, nitrobenzene, chloroform, and pyridine, less soluble in dioxane, alcohol, and benzene, and insoluble in water, ether, petroleum ether, and carbon tetrachloride.

At temperatures above 180°, compound III decomposes without melting. The substance dissolves in dilute acids and is precipitated again from the solution upon treatment with alkalis. In order to determine the structure of the substance obtained, we carried out its catalytic hydrogenation over Pt black in alcohol and glacial acetic acid at atmospheric pressure ([1]). It turned out that one mole of III absorbs five moles of hydrogen, indicating the presence of five double bonds in the molecule of the substance under investigation. Determination of the iodine number leads to the same conclusion.

Upon hydrogenation, an amine (IV) was obtained, which was then converted into the chloroplatinate and the methiodide, the analyses of which corresponded to the formulas $C_{17}H_{25}N \cdot {}^{1}/_{2}H_2PtCl_6$ and $C_{18}H_{28}NJ$.

It is known from the literature ([2]) that the action of alkaline reagents on pyridinium salts often causes cleavage of the pyridine ring at the nitrogen–carbon bond.

To clarify the question of whether the pyridine ring was preserved in III, we attempted to acylate amine IV. The presence of tertiary nitrogen in amine IV would indicate preservation of the pyridine ring in substance III, whereas the presence of secondary nitrogen would indicate opening of the pyridine ring. The structural formulas IIIa, III , III , III

Figure 1: structural formulas IIIa, III , III , III

experiment showed that amine IV is tertiary, which points to the preservation of the pyridine ring in molecule III.

The data presented raise for discussion the following possible structural formulas for substance III.

In this connection it was of interest to obtain experimental confirmation of the polarity of the molecule of substance III. For this purpose the di-

dipole moment of III. The measurement of the dipole moment, at our request, was carried out by A. N. Shidlovskaya in the laboratory of Prof. Ya. K. Syrkin, Corresponding Member of the Academy of Sciences of the USSR, to whom we express our deep gratitude. It turned out that the dipole moment of substance III has an exceptionally high value for an organic compound, equal to 9.7 D.

This value of the dipole moment is in sharp disagreement with the fulvene structure and confirms the polar nature of our substance, which, according to the nomenclature proposed by Wittig, should be called benzylpyridinium cyclopentadienylide.

Thanks to the work of Wittig (^3), it is known that, under the action of phenyllithium on quaternary ammonium salts, bipolar ions—“ylides”—are formed. Thus, for example, in the interaction of tetramethylammonium bromide with phenyllithium, methylide is formed:

$$[(CH_3)_3NCH_3]^{\oplus}Br^{\ominus}+C_6H_5Li \longrightarrow [(CH_3)_3N{-}CH_2{-}H]^{\oplus}\ C_6H_5^{\ominus} \longrightarrow (CH_3)_3N^{\oplus}{-}CH_2^{\ominus}+LiBr+C_6H_6$$

However, from the work of Schlenk (^4) it is also known that, in reactions of quaternary ammonium salts with potassium- and sodium-organic compounds, salt-like compounds are formed in which the positively charged ammonium group is ionically bound to a negatively charged hydrocarbon residue. Such compounds include triphenylmethyltetramethylammonium, benzyltetramethylammonium, etc.

$$(C_6H_5)_3C^{\ominus}\ N^{\oplus}(CH_3)_4; \qquad C_6H_5CH_2^{\ominus}\ N^{\oplus}(CH_3)_4;$$

Comparing the different cases of formation of Schlenk’ s quaternary salts and ylides, Wittig came to the conclusion that the stability of Schlenk salts depends on the mobility of the hydrogen atoms in the radicals bound to the positively charged nitrogen atom, and also on the proton-acceptor capacity of the anion. In those cases where the cation of the quaternary salt contains a mobile α-hydrogen atom and the anion is a strong proton acceptor, cleavage of the quaternary salt occurs with formation of an ylide.

In the case studied by us, in the interaction of benzylpyridinium chloride with cyclopentadienyllithium, a quaternary ammonium salt of the Schlenk-salt type is probably first formed.

$$[C_6H_5-CH_2-N^{\oplus}(C_5H_5N)]\,Cl^{\ominus}+C_6H_5Li \longrightarrow \{[C_6H_5-CH_2-N^{\oplus}(C_5H_5)]\,[C_5H_5^{\ominus}]\}+LiCl$$

Next, the stable cyclopentadienyl anion alkylates the positions of lowest electron density of the pyridine ring (α- and γ-positions):

$$\{[C_6H_5CH_2-N^{\oplus}(C_5H_5)]\,[C_5H_5^{\ominus}]\} \longrightarrow C_6H_5CH_2{-}N(C_5H_5)(C_5H_6) \xrightarrow{-2H} C_6H_5CH_2{-}N^{\oplus}(C_5H_4)(C_5H_5^{\ominus})$$

Then two hydrogen atoms are eliminated* (as follows from the analytical data for substance III), with formation of the energetically more favorable bipolar compound with a stable cyclopentadienyl anion (^5).

* We did not detect the evolution of hydrogen, probably because of side oxidation-reduction processes.

Recently, a number of reports have appeared in the literature on bipolar compounds containing a negatively charged cyclopentadienyl residue. Such compounds include triphenylphosphonium cyclopentadienylide (6), pyridinium cyclopentadienylide (7), and diazocyclopentadiene (8). Unstable fluorenylides of ammonium (3,9) and sulfonium (10) had previously been discovered.

In general form they may be represented as:

$$A^{\oplus}-C_5H_5^{\ominus}$$

where *A* is an atom in the onium state.

$$(-N^{\oplus}-, -P^{\oplus}-, -S^{\oplus}-)$$

In most cases these are brightly colored crystalline substances. Some of them melt at high temperature, while others decompose without melting. They are soluble in polar solvents and insoluble in nonpolar ones. Under the action of dilute acids they dissolve, and upon alkalization they precipitate again. With alkyl halides ($CH_3J, C_6H_5CH_2Br$, etc.) they form salts.

Usually such bipolar compounds are obtained from onium salts by the action on them of bases which, by removing a proton from the onium compound, make possible the formation of a bipolar ion. In all bipolar compounds of this group the positively charged onium atom is always directly bonded to the anion of cyclopentadienyl, as is seen in the example of pyridinium cyclopentadienylide

$$C_5H_5N^{\oplus}-C_5H_5^{\ominus}$$

The benzylpyridinium cyclopentadienylide obtained by us possesses all the above-mentioned properties of bipolar ions. However, in contrast to the previously described bipolar ions of this type, our substance III is the first representative of stable bipolar ions in which there is no direct bond between the positively charged nitrogen atom and the carbon of the negatively charged cyclopentadienyl nucleus.

Experimental Part

1. Preparation of cyclopentadienyllithium. To 29.18 g of butyllithium, prepared by the method of Gilman (11), 33.10 g of cyclopentadiene was added dropwise with stirring. The reaction was carried out while cooling the reaction flask with ice water. After addition of the cyclopentadiene, stirring was continued for another two hours at room temperature. To determine the yield, C_5H_5Li was converted into bis-cyclopentadienylcarboxylic acid (12). The yield of C_5H_5Li was 71.9%.

2. Preparation of benzylpyridinium cyclopentadienylide. In a round-bottomed three-necked flask equipped with a stirrer and reflux condenser were placed 102.9 g of benzylpyridinium chloride, ground in a dry chamber, prepared by condensation of benzyl chloride with pyridine, and 150 ml of absolute ether. To the ethereal suspension of benzylpyridinium chloride, with vigorous stirring, was added a suspension of cyclopentadienyllithium in ether. The mixture was stirred for 20 hours at room temperature, after which the reaction products were treated with water. A precipitate formed, from which, by crystallization from benzene, was obtained

6.55 g of substance III was isolated. From the ether layer a further 12.14 g of III was obtained. The total yield was 24.5% of the cyclopentadienyllithium taken into the reaction*.

Mol. wt. 232.0 (cryoscopically, from nitrobenzene); for $C_{17}H_{15}N$, calculated 233.3.

Found, %: C 87.51; 87.43; H 6.47; 6.28; N 5.95; 5.89
$C_{17}H_{15}N$. Calculated, %: C 87.52; H 6.48; N 6.01.

3. Investigation of the structure and properties of $C_{17}H_{15}N$.

a. Determination of the iodine number for $C_{17}H_{15}N$. The determination was carried out in chloroform solution. The iodine number values found were 327.1; 321.2. Calculated for five double bonds: 342.5.

b. Hydrogenation of $C_{17}H_{15}N$. Hydrogenation of the product of the interaction of benzylpyridinium chloride and cyclopentadienyllithium was carried out over Pt black in alcohol and glacial acetic acid at atmospheric pressure.

	Sample weight, g	Amount of hydrogen absorbed, ml	Amount of hydrogen calculated for 5 double bonds
Alcohol	0.5019	232	241
Glacial acetic acid	0.5631	259	270

c. Analysis of salts of the hydrogenated amine. Chloroplatinate $C_{17}H_{25}N \cdot \frac{1}{2}H_2PtCl_6$ (m.p. 140°) found, % Pt 21.93; 21.82; calculated 21.77. Iodomethylate $C_{18}H_{28}NJ$ (m.p. 160-170°) found, % J 32.82; 33.00; calculated 32.94.

d. Acylation of the hydrogenated amine. Acylation of the hydrogenated amine was carried out in the form of its hydrochloride with acetic anhydride in pyridine medium [13]. Acetic anhydride taken for acylation: 0.3101 g; 0.2446 g; recovered: 0.3106 g; 0.2415 g; % error 0.5-1.2. Thus, the acylation data indicate that the hydrogenated amine is tertiary.

e. Determination of the dipole moment of $C_{17}H_{15}N$. The dipole moment, determined by the method of Smyth [14], is $\mu = 9.7D$ (in benzene). The error of the determination is 2-3%, since the measurements were carried out in a highly diluted solution, owing to the low solubility of the substance. The magnitude of the dipole moment of the compound $C_{17}H_{15}N$ proved to be considerably higher than the dipole moments of ordinary organic compounds.

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* Compound I can likewise be obtained by the interaction of benzylpyridinium chloride with cyclopentadienylpotassium [12].

Note: Figure translations are in progress. See original paper for figures.

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