CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR D. N. KURSANOV and M. E. VOL’ PIN

1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR D. N. KURSANOV and M. E. VOL' PIN

A NEW ROUTE TO TROPYLIUM AND METHYLTROPYLIUM COMPOUNDS

At the present time, two fundamentally different routes are known for the formation of the seven-membered aromatic tropylium system (I).

I II III

Derling and Knox (1) first obtained tropylium bromide (I; $X = \mathrm{Br}$) by splitting off HBr from dibromocycloheptadiene. It was subsequently established (2) that, by the same method, although in very low yield (0.8%), salts of carboxytropylium (II, $R = \mathrm{COOH}$) can be obtained. Another method, recently developed by Doering and Pettit (3), is based on the facile isomerization of the norcaradiene system into the tropylium system. Thus, in the Curtius rearrangement of norcaradienecarboxylic acid azide (III), tropylium isocyanate was obtained, and from the azide of methyl-norcaradienecarboxylic acid—the methyltropylium salt (II, $R = \mathrm{CH_3}$).

Meanwhile, it was undoubtedly of interest to demonstrate the possibility of a direct transition from the cycloheptatriene (tropylidene) system (IV), with three double bonds, to the aromatic tropylium system. As a result of the removal, by some means, from the $\mathrm{CH_2}$ group of cycloheptatriene of a hydrogen atom together with an electron pair, and with the accompanying transition of the seventh carbon atom from the state of sp^3-hybridization to the state of sp^2-hybridization, there should arise the possibility of cyclic conjugation of all six π-electrons of the double bonds, leading to the formation of the aromatic tropylium system. Such a transition would be a kind of analogue of the corresponding conversion of cyclopentadiene into the cyclopentadienyl anion under the action of alkali metals and strong bases. However, in contrast to cyclopentadiene, where a proton is removed, from cycloheptatriene hydrogen must be abstracted with an electron pair (hydride ion):

$$\text{cyclopentadiene} \xrightarrow{(-\mathrm{H}^+)} \text{cyclopentadienyl anion} \quad ; \quad \mathrm{IV} \xrightarrow{(-\mathrm{H}^-)} \text{tropylium cation}$$

In both cases a nonbenzenoid aromatic system with 6π electrons is formed.

In searching for routes for such a direct conversion of cycloheptatriene into tropylium salts, we studied the action on cycloheptatriene of a series of electrophilic reagents—strong acids, oxidizing agents, halogen derivatives, etc. Many of these substances react vigorously with the double bonds of cycloheptatriene, which greatly impedes the course of the tropylium-forming reaction.

Under the action of concentrated sulfuric acid on cycloheptatriene, an exothermic reaction occurs, accompanied by resinification. One

however, alongside this, oxidation of tropilidene takes place with the formation of appreciable amounts of tropylium salt (18% yield):

$$C_7H_8 + 2H_2SO_4 \rightarrow C_7H_7^+ + HSO_4^- + 2H_2O + SO_2$$

The formation of the aromatic carbonium ion—tropylium—under the action of concentrated H_2SO_4 on cycloheptatriene is analogous to the formation of aliphatic carbonium ions under the action of concentrated H_2SO_4 on saturated hydrocarbons containing a tertiary carbon atom. This analogy is an indirect confirmation of the carbonium mechanism of deuterium exchange and other reactions proposed in the latter case ([4]).

As in the case of saturated hydrocarbons, acids that do not possess oxidizing properties—concentrated phosphoric acid and hydrochloric acid—do not cause the conversion of cycloheptatriene into tropylium either in the cold or on heating. Concentrated nitric acid reacts very vigorously with cycloheptatriene; in this case small amounts of tropylium are formed.

A study of the action of other oxidizing agents on cycloheptatriene confirmed that, upon oxidation in an acidic medium, cycloheptatriene is converted to a greater or lesser extent into tropylium. Thus CrO_3 in glacial acetic acid converts up to 14% of cycloheptatriene into tropylium. When tropilidene is boiled with SeO_2 in aqueous dioxane in the presence of sulfuric acid, about 7% of tropylium salt is formed.

Such strong electrophilic reagents as boron fluoride and aluminum chloride might react with cycloheptatriene, converting it into tropylium according to the scheme:

$$C_7H_8 + BF_3 \rightarrow C_7H_7^+ + [HBF_3]^-$$

However, BF_3 and $AlCl_3$ react so energetically with double bonds that, although the reaction forming the tropylium salt does occur, it does so only to a small extent. On heating tropilidene with boron trifluoride etherate, about 2% of tropylium salt is formed along with a large amount of polymer. About 18% of tropylium salt is formed in the interaction of tropilidene with anhydrous aluminum chloride.

It could be expected that halide compounds of elements with variable valence would be capable of removing a pair of electrons from cycloheptatriene, converting it into tropylium. It indeed proved that phosphorus pentachloride reacts extremely readily with cycloheptatriene. In this process tropylium chloride is formed, while phosphorus pentachloride is reduced to the trichloride:

$$C_7H_8 + PCl_5 \rightarrow C_7H_7^+ + HCl + PCl_3 + Cl^-$$

The reaction proceeds in practically quantitative yield at room temperature and is accompanied neither by resinification nor by any other side processes.

The discovered reaction of cycloheptatriene with phosphorus pentachloride may serve as a good preparative method for obtaining tropylium salts and its derivatives. The advantages of this method are the high yield of tropylium, mild conditions, and simplicity of carrying out the reaction. An excess of PCl_5, conducting the reaction without heating and in an inert solvent, favors an increase in the yield of tropylium chloride. The tropylium formed is best isolated not in the form of the unstable and very hygroscopic tropylium chloride, but by converting it into the sparingly soluble perchlorate, chloroplatinate ([5]), or iodide.

The developed method was also applied to the preparation of methyltropylium salts (II, $R = CH_3$). The reaction of methylcycloheptatriene with phosphorus pentachloride

phosphorus proceeded very rapidly and smoothly in the cold. Methyltropylium chloride was obtained and converted into the sparingly soluble methyltropylium chloroplatinate. At the same time, an attempt to obtain a methyltropylium salt by the method of Doering and Knox (1) led only to the formation of resinification products. The preparation of other substituted tropyliums by this method is being studied.

As was to be expected, phosphorus trichloride, in contrast to phosphorus pentachloride, does not convert cycloheptatriene into tropylium. This reaction also does not occur with phosphorus tribromide. Phosphorus pentabromide readily dissociates under ordinary conditions; therefore, in reaction with it cycloheptatriene readily adds bromine without formation of bromotropylium.

Analogously to the reaction with phosphorus pentachloride, cycloheptatriene reacts with sulfuryl chloride:

$$C_7H_8 + SO_2Cl_2 \rightarrow C_7H_7^+ + Cl^- + SO_2 + HCl$$

In this case up to 25% of tropylium salt is formed; however, the reaction is accompanied by appreciable resinification. Thionyl chloride does not react with cycloheptatriene.

Thus it has been shown that, under the action on cycloheptatriene of various electrophilic reagents (H_2SO_4, HNO_3, CrO_3, BF_3, $AlCl_3$, SeO_2, SO_2Cl_2, PCl_5), a pair of electrons and a hydrogen atom are removed from cycloheptatriene, converting it into the aromatic tropylium system. The reaction of cycloheptatriene (and its derivatives) with phosphorus pentachloride may serve as a preparative method for obtaining tropylium derivatives.

Experimental Part

The starting cycloheptatriene was obtained by the photochemical reaction of benzene with diazomethane (6). After distillation on a column of 40 theoretical plates, a fraction was isolated with b.p. 116.3-117.0°/744 mm, n_D^{20} 1.5228, containing 95% cycloheptatriene and 5% toluene.

Reaction with sulfuric acid. 0.08 g of cycloheptatriene was added, with cooling and shaking, to 2 ml of concentrated sulfuric acid. The red solution was left for 10 days at room temperature, then carefully diluted twofold with water under cooling. On addition of chloroplatinic acid, tropylium chloroplatinate precipitated from the solution. The precipitate was filtered off, washed with alcohol, and dried. Yield of tropylium chloroplatinate: 0.048 g (18% of theory).

In experiments with CrO_4, BF_3, $AlCl_3$, HNO_3, SeO_2, and SO_2Cl_2, the tropylium salt formed was isolated analogously in the form of the chloroplatinate.

Reaction with phosphorus pentachloride. Into a flask equipped with a stirrer and a reflux condenser protected by a calcium chloride tube were placed 4.1 g (~0.02 mole) of PCl_5 and 40 ml of CCl_4, and, with stirring, 0.91 g (0.0098 mole) of cycloheptatriene in 10 ml of CCl_4 was added. A copious white precipitate began to separate immediately. The reaction mixture was stirred for about an hour and then boiled for 15 min. After cooling, the precipitate was rapidly suction-filtered on a funnel, washed with CCl_4, and treated under cooling with 4 ml of water (vigorous reaction). The reaction flask and funnel were rinsed with a small amount of alcohol. The resulting aqueous-alcoholic solution (the CCl_4 layer at the bottom does not interfere with further operations) was treated with a slight excess of 30% $HClO_4$. A copious precipitate of tropylium perchlorate immediately separated; after cooling, it was filtered off and washed with cold alcohol. The perchlorate, without recrystallization, was sufficiently pure for further work. Yield of tropylium perchlorate: 1.49 g (80% of theory). From the filtrate, by addition of H_2PtCl_6, tropylium was additionally precipitated as the chloroplatinate; yield 0.30 g (10%). The total yield of tropylium is 90%. In carrying out the same

of the reaction without heating, with stirring for 2.5 hours and standing overnight; the yield of tropylium reaches 98%.

In special experiments for identification, the tropylium chloride formed in the reaction was isolated—a hygroscopic substance readily soluble in water; after recrystallization from nitromethane, m.p. 97°. According to literature data (^1), m.p. 102°. Aqueous solutions give a positive reaction for Cl^- (test with $AgNO_3$) and for the tropylium ion—the formation of precipitates with $HClO_4$,

H_2PtCl_6, $NaB(C_6H_5)_4$ (⁀6).

Found, %: C 28.26; 28.38; H 2.61; 2.49; Pt 33.21; 32.98
$C_{14}H_{14}PtCl_6$. Calculated, %: C 28.49; H 2.39; Pt 33.08

Methylcycloheptatriene, the starting material for obtaining methyltropylium, was synthesized by the photochemical reaction of toluene with diazomethane. By column distillation a fraction was isolated (b.p. 138.2–139.0°/730 mm, n_D^{20} 1.5114) containing about 70% methylcycloheptatriene. The reaction of methylcycloheptatriene with PCl_5 was carried out analogously to that described above. After standing for 1 hour at room temperature, the precipitate was filtered off and the methyltropylium formed was converted into the chloroplatinate—a yellow precipitate, sparingly soluble in water and even less soluble in alcohol; it darkens at a temperature of ~140°. Yield ~50%.

Found, %: C 31.27; 31.22; H 3.20; 3.24; Pt 30.89; 30.75
$C_{16}H_{18}PtCl_6$. Calculated, %: C 31.08; H 2.93; Pt 31.58

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
16 X 1956

CITED LITERATURE

⁀1 W. E. Doering, L. H. Knox, J. Am. Chem. Soc., **76**, 3203 (1954).
⁀2 A. W. Johnson, A. Langemann, M. Tishler, J. Chem. Soc., **1955**, 1622.
⁀3 M. J. S. Dewar, R. Pettit, J. Chem. Soc., **1956**, 2021.
⁀4 D. N. Kursanov, V. V. Voevodskii, Usp. khim., **23**, No. 6, 645 (1954).
⁀5 M. E. Vol' pin, S. I. Zhdanov, D. N. Kursanov, DAN, **112**, No. 2 (1957).
⁀6 W. E. Doering, L. H. Knox, J. Am. Chem. Soc., **75**, 297 (1953).