Chemistry

1957

SovietRxiv

Abstract

Full Text

Chemistry

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Reactions of Diene Hydrocarbons with Nitroso Compounds

Addition of 1,3-Pentadiene to Nitrosobenzene

(Presented by Academician A. N. Nesmeyanov, 19 IV 1957)

It was shown earlier that conjugated diene hydrocarbons react with aromatic nitroso compounds according to the scheme of diene synthesis, with formation of derivatives of 3,6-dihydro-1,2-oxazine (^{1,2}).

The aim of the present work was to elucidate the structure of the product of the addition of 1,3-pentadiene to nitrosobenzene.

The diene-synthesis reaction involving conjugated dienes of unsymmetrical structure has been studied in a number of examples. Thus, in the reaction of 1,3-pentadiene with acrolein, acrylonitrile, methyl acrylate, methyl methacrylate, ethyl crotonate, and styrene, either *o*-isomers or mixtures of them with *m*-isomers, with a sharp predominance of the *o*-isomers, were obtained ($^{3-9}$). In the condensation of isoprene with acrolein, acrylonitrile, methyl acrylate, methyl vinyl ketone, chloromethyl vinyl ketone, and ethylenesulfochloride, *p*-isomers were obtained ($^{4,10-12}$). In the reaction of alkoxypiperylenes with acrolein, acrylonitrile, and methyl vinyl ketone, *p*-isomers are formed ($^{13-15}$). In the condensation of chloroprene and fluoroprene with methylacetylene ketone, *p*-isomers were obtained (^{16,17}). In the reaction of chloroprene with acrylic acid, the *p*-isomer was obtained (^{18}).

These data are in good agreement with the ionic mechanism of the diene-synthesis reaction, which consists in transfer of an electron from the diene to the dienophile with formation of an ionic complex. The second stage of the process is the rearrangement of the ionic complex with formation of a stable adduct (^{19,20}).

However, in a number of works results were obtained that contradict the ionic mechanism of the diene-synthesis reaction. Thus, in the reaction of butadiene-1,3-carbonic-1 acid with acrylic acid, Alder (^{21}) obtained the *o*-isomer. In the reaction of the acid chloride of butadiene-1,3-carbonic-1 acid with acrylic acid chloride, only the *o*-isomer was likewise obtained. On the basis of these data, Alder concluded that the diene-synthesis reaction has a cryptoradical mechanism. In the condensation of 1-(*p*-nitrophenyl)-butadiene-1,3 with acrylic acid and ethyl acrylate, Ropp and Coyner ([22]) obtained only *o*-isomers. In the reaction of 1-cyanobutadiene-1,3 with methyl acrylate and ethyl acrylate, Snyder and Pus ([23]) obtained *o*-isomers. The authors are inclined toward the conclusion, made by Alder, of a radical mechanism for the diene-synthesis reaction.

The question of the mechanism of the reaction of dienes with nitroso compounds has not yet been discussed. If the addition of 1,3-pentadiene to nitrosobenzene proceeds by an ionic mechanism, then the 6-substituted isomer Ia should be formed, possibly with an admixture of the 3-substituted isomer Ib.

To establish the structure of the product of the addition of 1,3-pentadiene to nitrosobenzene, the route chosen was that previously used in establishing

structure of the products of addition of dienes to aromatic nitroso compounds ([1,2]). On reduction of adducts Ia and Ib with zinc dust and acetic acid, the aminospirits IIa and IIb should be formed, which can be converted into the diacetyl derivatives IIIa and IIIb. On oxidation of diacetyl derivative IIIa with potassium permanganate, N-acetyl-N-phenylglycine IVa should be obtained, while oxidation of diacetyl derivative IIIb should give N-acetyl-N-phenylalanine IVb.

$$\begin{aligned} &\text{Ia} \longrightarrow \text{IIa} \longrightarrow \text{IIIa} \longrightarrow \text{IVa} \\ &\text{Ib} \longrightarrow \text{IIb} \longrightarrow \text{IIIb} \longrightarrow \text{IVb} \end{aligned}$$

Preparation of trans-pentadiene-1,3. Trans-pentadiene-1,3 was obtained by the following route: from crotonaldehyde and methylmagnesium bromide there was obtained penten-2-ol-4, which was dehydrated over magnesium sulfate at 300°. The hydrocarbon had the following constants: b.p. 41.5°/748 mm, d_4^{20} 0.6810, n_D^{20} 1.4321.

Preparation of the product of addition of trans-pentadiene-1,3 to nitrosobenzene and study of its structure. To an ice-cooled solution of 37.5 g (0.35 mole) of nitrosobenzene in 400 ml of chloroform there was added 27.3 g (0.4 mole) of pentadiene-1,3. The reaction mixture was left in ice for 48 hr, and then for 12 hr at room temperature. The chloroform was distilled off, and the residue was steam-distilled. The yellow oil that passed into the distillate was dissolved in chloroform, and the solution was dried with magnesium sulfate. The chloroform was distilled off, and the residue was fractionated in vacuo. There was obtained 44.1 g of an almost colorless liquid with the following constants: b.p. 94—95°/2 mm, d_4^{20} 1.0682, n_D^{20} 1.5614. $MR = 53.14$. Calculated for $C_{11}H_{13}ON$ 4F 51.95. EMR 1.19. Yield 72% of theory.

Found, %: C 75.50; 75.54; H 7.56; 7.56; N 8.43; 8.45
$C_{11}H_{13}ON$. Calculated, %: C 75.40; H 7.48; N 7.99

On reduction of 35 g (0.2 mole) of the addition product with zinc dust and glacial acetic acid, 25.5 g of an aminospirit of composition $C_{11}H_{15}ON$ was obtained, having the following constants: b.p. 155—156°/3 mm, d_4^{20} 1.0558, n_D^{20} 1.5702. $MR = 55.10$. Calculated for $C_{11}H_{15}ON$ 4F 54.06. EMR 1.04. Yield 71% of theory.

Found, %: C 74.57; 74.68; H 8.72; 8.82; N 8.00; 7.95
$C_{11}H_{15}ON$ Calculated, %: C 74.54; H 8.53; N 7.90

On acetylation of the amino alcohol with 22.2 g (0.125 mol) of acetic anhydride, 31.5 g of the diacetyl derivative of the amino alcohol of composition $C_{15}H_{19}O_3N$ was obtained, with the following constants: b.p. 153-154°/1 mm, d_4^{20} 1.0861, n_D^{20} 1.5199. $MR = 73.13$. Calculated for $C_{15}H_{19}O_3N$ 4F 72.66. Yield 95% of theory.

Found, %: C 68.85; 69.02; H 7.52; 7.32; N 5.40; 5.23
$C_{15}H_{19}O_3N$. Calculated, %: C 68.94; H 7.33; N 5.36

5.22 g (0.02 mol) of the diacetyl derivative was oxidized with potassium permanganate in acetone. From the oxidation products, 1.08 g of a mixture of acids with m.p. 135-148° was isolated. It was found that the mixture consisted of two substances, one of which was readily soluble in benzene, while the other was sparingly soluble. The mixture of acids was separated into two fractions. Fraction I, isolated from the benzene extract (0.81 g), had m.p. 130-133°. Fraction II, which did not dissolve in benzene (0.24 g), had m.p. 181-184°.

After three recrystallizations of the first fraction from water, N-acetyl-N-phenylalanine IV with m.p. 143-144° was obtained.

Found, %: C 63.49; 63.42; H 6.60; 6.45; N 6.77; 6.68
$C_{11}H_{13}O_3N$. Calculated, %: C 63.75; H 6.33; N 6.76

Literature data: m.p. 143° (24).

After three recrystallizations from water of the second fraction, N-acetyl-N-phenylglycine IVa with m.p. 190-192° was obtained. A mixed sample with N-acetyl-N-phenylglycine (m.p. 193-195°), obtained by acetylation of N-phenylglycine, melted at 192-194°.

Literature data: m.p. 190-191° (25); 194-195° (26); 194-195° (1).

From the above data it follows that the product of addition of trans-pentadiene-1,3 to nitrosobenzene consists of a mixture of 2-phenyl-6-methyl-3,6-dihydro-1,2-oxazine Ia and 2-phenyl-3-methyl-3,6-dihydro-1,2-oxazine I , with predominance of the latter isomer.

The result obtained contradicts the concept of an ionic mechanism for the diene-synthesis reaction and is in agreement with the assumption of a radical mechanism for this reaction.

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Received
12 IV 1957

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