CHEMISTRY

Yu. A. ARBUZOV and L. K. LYSANCHUK

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

Yu. A. ARBUZOV and L. K. LYSANCHUK

REACTIONS OF DIENE HYDROCARBONS WITH NITROSO COMPOUNDS

ADDITION OF ISOPRENE AND 2-METHOXYBUTADIENE-1,3 TO NITROSOBENZENE

(Presented by Academician A. N. Nesmeyanov, February 13, 1962)

It had previously been found that conjugated diene hydrocarbons react with aromatic nitroso compounds according to the scheme of diene synthesis, with formation of substituted derivatives of 3,6-dihydro-1,2-oxazine (^1). In the present work we investigated the condensation of nitrosobenzene with isoprene and 2-methoxybutadiene-1,3.

The reaction of dienophiles of unsymmetrical structure with dienes having a substituent in position 2 has been studied in a number of examples. Thus, in the condensation of isoprene with acrolein, acrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone, chloromethyl vinyl ketone, and ethylenesulfochloride ($^{2-}$6), in the reaction of alkoxyprenes with acrolein, acrylonitrile, methyl vinyl ketone, and methyl ethynyl ketone (^2, ^3, $^{7-}$9), and in the reaction of haloprenes with acrylic acid and methyl ethynyl ketone (^3, $^{10-}$12), either *p*-isomers, or mixtures of them with *m*-isomers with a sharp predominance of the *p*-isomers, were obtained. The reaction of dienes having a substituent in position 2 with aromatic nitroso compounds has been studied very little. In 1954 Kojima (^13) obtained the product of addition of isoprene to nitrosobenzene. In 1953 Wichterle and Kolinsky (^14) carried out the addition of chloroprene to nitrosobenzene. In both cases the structures of the adducts were not established.

As follows from the above, in the addition of 2-substituted dienes to unsymmetrical dienophiles the order of addition agrees well with the direction of polarization of both the diene component and the dienophile. We therefore expected that in the reaction of isoprene with nitrosobenzene either 2-phenyl-4-methyl-3,6-dihydro-1,2-oxazine (Ia), or a mixture of it with 2-phenyl-5-methyl-3,6-dihydro-1,2-oxazine (Ib), would be formed, with predominance of the first isomer.

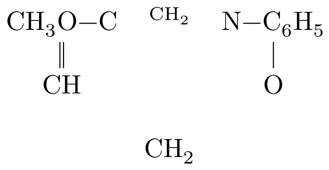
To establish the structure of the product of addition of isoprene to nitrosobenzene, we chose the following route. On reduction of adducts Ia and Ib with zinc dust and acetic acid, the amino alcohols IIa and IIb (^15) should be formed. Catalytic reduction of amino alcohol IIa should give 2-methylbutanol-4 (IIIa) and aniline (IV), whereas reduction of amino alcohol IIb should form

2-methylbutanol-1 (IIIb) and aniline (IV) (^16).

$$\underset{\text{(Ia)}}{CH_3-C(=CH)-CH_2-N(C_6H_5)-O} \longrightarrow \underset{\text{(IIa)}}{CH_3-C(=CH)-CH_2-NH-C_6H_5} \quad OH \longrightarrow CH_3-CH$$

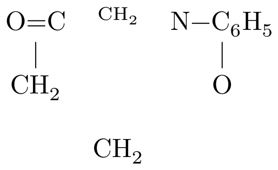
$$\underset{\text{(Ib)}}{CH_2-CH=C(CH_3)-CH_2-N(C_6H_5)-O} \longrightarrow \underset{\text{(IIb)}}{CH_2-CH=C(CH_3)-CH_2-NH-C_6H_5} \quad OH \longrightarrow CH_3-C$$

On reduction of the adduct with zinc dust and acetic acid, an aminosyirt of composition $C_{11}H_{15}ON$ was obtained, which was subjected to catalytic hydrogenation. From the reaction products aniline and 2-methylbutanol-4 were isolated; for identification the latter was converted into crystalline 3,5-dinitrobenzoate. Thus, as expected, the product of addition of isoprene to nitrosobenzene has structure Ia. On the basis of literature data on the analogous behavior of isoprene and alkoxypropenes in the diene-synthesis reaction, it should be considered that the product of addition of 2-methoxybutadiene-1,3 to nitrosobenzene has the structure of 2-phenyl-4-methoxy-3,6-dihydro-1,2-oxazine (V). This addition product is a cyclic simple vinyl ether, which should be readily hydrolyzed by acids with formation of the corresponding keto derivative. By the action on the adduct of hydrochloric acid 2,4-dinitrophenylhydrazine and hydrochloric acid semicarbazide in aqueous-alcoholic solution we obtained



$$\begin{array}{ccc} CH_3O-C & {\scriptstyle CH_2} & N-C_6H_5 \\ \| & & | \\ CH & & O \\ & CH_2 & \end{array}$$

(V)



$$\begin{array}{ccc} O=C & {\scriptstyle CH_2} & N-C_6H_5 \\ | & & | \\ CH_2 & & O \\ & CH_2 & \end{array}$$

(VI)

2,4-dinitrophenylhydrazone and semicarbazone. As a result of hydrolysis of the semicarbazone with dilute sulfuric acid, a crystalline keto derivative was obtained, to which we assign structure VI.

Experimental Part

2-Phenyl-4-methyl-3,6-dihydro-1,2-oxazine. Experiment 1. To an ice-cooled solution of 32.1 g (0.3 mole) of nitrosobenzene in 300 ml of chloroform, 27.2 g (0.4 mole) of isoprene (b.p. 32.5–33° at 747 mm) was added. The flask with the mixture was left in ice. After a day the initially green solution had acquired a reddish-brown color. The chloroform was then distilled off, and the residue was steam-distilled. The orange oil that passed into the distillate was dissolved in 200 ml of ether, and the solution was dried over sodium sulfate.

This gave 15.0 g (28% of theory) of the adduct, an orange liquid with b.p. 113-115° at 1 mm, d_4^{20} 1.0715, n_D^{20} 1.5680. MR 53.50. Calculated 51.95. EMR 1.55.

Found, %: C 75.46, 75.59; H 7.55, 7.52; N 8.29, 8.27
$C_{11}H_{13}ON$. Calculated, %: C 75.40; H 7.48; N 7.99

Experiment 2. An ice-cooled solution of 48.2 g (0.45 mole) of nitrosobenzene in 400 ml of chloroform was mixed with 34 g (0.5 mole) of isoprene, and the mixture was left in ice for 24 hours. The chloroform was then distilled off, and the residue was extracted with 250 ml of petroleum ether. The petroleum ether was distilled off, and the residue was fractionated in vacuo at 1 mm. Two substances were isolated: 1) b.p. 113-115°, n_D^{20} 1.5677 (23.1 g); 2) b.p. 160-161° (7.0 g).

The substance with b.p. 113-115°/1 mm is 2-phenyl-4-methyl-3,6-dihydro-1,2-oxazine. Yield 29% of theory. The substance boiling at 160-161°/1 mm soon crystallized. After recrystallization from methanol, m.p. 35-36°. A mixed test with azoxybenzene (m.p. 35.5-36°) melted without depression.*

Reduction of 2-phenyl-4-methyl-3,6-dihydro-1,2-oxazine to 4-phenylamino-3-methylbuten-2-ol-1. A solution of 17.5 g (0.1 mole) of 2-phenyl-4-methyl-3,6-dihydro-1,2-oxazine in 200 ml of glacial acetic acid. Twenty grams of zinc dust was added, the flask was stoppered and shaken vigorously for 10 min. Then a further 20 g of zinc dust was added and the flask was shaken for 15 min. The mixture was diluted with 200 ml of water, and 200 g of caustic soda was added gradually. The mixture was then steam-distilled to remove substances volatile with steam. The contents of the distillation flask were then filtered while hot, the filtrate was cooled and extracted with benzene. The benzene extract was washed with water, the benzene was distilled off, and the residue was distilled in vacuo. There was isolated 11.5 g of a substance with b.p. 167-169° at 8 mm, which was 4-phenylamino-3-methylbuten-2-ol-1. Yield 65% of theory. After redistillation the amino alcohol had b.p. 149-150° at 1 mm, d_4^{20} 1.0614, n_D^{20} 1.5765. MR 55.30. Calculated 54.06. EMR 1.24.

Found, %: C 74.63, 74.43; H 8.72, 8.67
$C_{11}H_{15}ON$. Calculated, %: C 74.54; H 8.53

Catalytic reduction of 4-phenylamino-3-methylbuten-2-ol-1. 10.6 g (0.06 mole) of 4-phenylamino-3-methylbuten-2-ol-1 was dissolved in 70 ml of

---

* In the literature, cases are described of the formation of azoxybenzene in the reaction of nitrosobenzene with substances containing methylene or methyl groups activated by a neighboring double bond (safrole [17], apiol, asarone [18], rubber [19]).

absolute ether and reduced at room temperature and ordinary pressure in the presence of 1 g of platinized charcoal (10% Pt). The reduction was complete after 6 h. 2160 ml of hydrogen (0°, 760 mm) was absorbed. The catalyst was filtered off, the ether was distilled off, and the residue was fractionated. 2-Methylbutanol-4 and aniline were isolated.

2-Methylbutanol-4 (2 g) had b.p. 128–129° at 724 mm, d_4^{20} 0.8151, n_D^{20} 1.4044. Literature data (20): b.p. 132.0° at 760 mm, d_4^{15} 0.813, n_D^{15} 1.4085. For identification, 2-methylbutanol-4 was converted into the 3,5-dinitrobenzoate: m.p. 58–59°. After recrystallization from petroleum ether, 1.1 g of 2-methylbutanol-4 3,5-dinitrobenzoate was obtained, m.p. 61–62°. A mixed sample with the 3,5-dinitrobenzoate (m.p. 61–62°) prepared from pure 2-methylbutanol-4 melted without depression. Literature data (21): m.p. 61–62°.

Aniline (1.5 g) had b.p. 81–82° at 12 mm, d_D^{20} 1.0168, n_D^{20} 1.5854. Aniline was identified as acetanilide: m.p. 113–114°.

2-Phenyl-4 (or 5)-methoxy-3,6-dihydro-1,2-oxazine. To a solution, cooled to 0°, of 69.6 g (0.65 mole) of nitrosobenzene in 600 ml of chloroform was added 63.1 g (0.75 mole) of 2-methoxybutadiene-1,3 (prepared by Petrov' s method (22); b.p. 74.0-74.5° at 749 mm, d_4^{20} 0.8304, n_D^{20} 1.4420). The flask with the mixture was left in ice. After 24 h the reaction mixture was a reddish-brown transparent solution. The chloroform was distilled off in vacuo, and the residue was extracted in the cold with isopentane (2 · 250 ml). The isopentane was distilled off, and the residue was distilled in vacuo. 63.8 g (51% of theory) of the adduct was obtained as a red-orange liquid: b.p. 124–125° at 2 mm, d_4^{20} 1.1430, n_D^{20} 1.5711. MR 54.97. Calculated 53.60. EMR 1.37.

Found, %: C 69.46, 69.57; H 6.93, 7.01; N 7.94, 7.98
$C_{11}H_{13}O_2N$. Calculated, %: C 69.09; H 6.85; N 7.33

2,4-Dinitrophenylhydrazone of 2-phenyl-4 (or 5)-ketotetrahydro-1,2-oxazine. To a hot solution of 1 g of hydrochloric-acid 2,4-dinitrophenylhydrazine in 50 ml of 95% ethanol were added 1 ml of conc. hydrochloric acid and a solution of 1 g of the adduct in 10 ml of ethanol. The mixture was heated to boiling and left for 12 h. After recrystallization from a chloroform–methanol mixture (1:1), 1 g of 2,4-dinitrophenylhydrazone was obtained, m.p. 197–198°.

Found, %: C 53.79, 53.83; H 4.20, 4.22; N 19.71, 19.63
$C_{16}H_{15}O_5N_5$. Calculated, %: C 53.78; H 4.23; N 19.60

Semicarbazone of 2-phenyl-4 (or 5)-ketotetrahydro-1,2-oxazine. To a solution of 4 g of semicarbazide hydrochloride in a mixture of 15 ml of methanol and 15 ml of water, 3 g of the adduct was added, and the mixture was stirred until the oil disappeared (about 10 hr). The resulting finely crystalline precipitate was filtered off, washed with water and methanol, and dried. This gave 2.4 g of semicarbazone with mp 173-176°. After recrystallization from methanol, mp 185-185.5°.

Found, %: C 56.80, 56.84; H 5.96, 5.99; N 24.04, 24.09
$C_{11}H_{14}O_2N_4$. Calculated, %: C 56.40; H 6.02; N 23.92

2-Phenyl-4 (or 5)-ketotetrahydro-1,2-oxazine. A mixture of 0.7 g of semicarbazone, 15 ml of benzene, 15 ml of petroleum ether, and 20 ml of 10% sulfuric acid was stirred at room temperature until complete dissolution of the semicarbazone (about 24 hr). The organic layer was separated and washed with a 5% solution of soda and with water. The solvent was distilled off, and the residue was evaporated several times with petroleum ether. This gave 0.23 g of a substance with mp 36-37°. After recrystallization from a mixture of petroleum ether and diethyl ether (10 : 1), mp 36.5-37.5°. Shiny scaly crystals.

Found, %: C 67.42, 67.47; H 6.07, 6.26; N 8.47, 8.31
$C_{10}H_{11}O_2N$. Calculated, %: C 67.78; H 6.26; N 7.91

Moscow State University
named after M. V. Lomonosov

Received
2 XII 1961

REFERENCES

1. Yu. A. Arbuzov, T. A. Pisha, DAN, **116**, 71 (1957).
2. A. A. Petrov, A. F. Sapozhnikova, ZhOKh, **18**, 424 (1948).
3. I. N. Nazarov, A. I. Kuznetsova, N. V. Kuznetsov, ZhOKh, **25**, 88 (1955); Yu. A. Titov, A. I. Kuznetsova, Izv. AN SSSR, OKhN, **1960**, 1815.
4. K. Alder, W. Vogt, Lieb. Ann., **564**, 109 (1949).
5. Yu. A. Arbuzov, B. L. Dyatkin, DAN, **111**, 1249 (1956).
6. H. R. Snyder, H. V. Anderson, D. P. Hallada, J. Am. Chem. Soc., **73**, 3258 (1951).
7. A. A. Petrov, ZhOKh, **11**, 661 (1941); **17**, 538 (1947).
8. A. A. Petrov, M. G. Vladimirova, ZhOKh, **17**, 1543 (1947).
9. E. A. Braude, E. R. H. Jones, F. Sondheimer, J. B. Toogood, J. Chem. Soc., **1949**, 607.

10. A. A. Petrov, N. P. Sopov, ZhOKh, **17**, 1295 (1947).

11. A. A. Petrov, A. V. Tumanova, ZhOKh, **26**, 2744 (1956).

12. J. S. Meek, W. P. Trapp, J. Am. Chem. Soc., **74**, 2686 (1952).

13. S. Kojima, Chem. Abstr., **49**, 10966 (1955).

14. O. Wichterle, M. Kolinsky, Chem. Listy, **47**, 1787 (1953); Collect. Trav. Chim. Tchécosl., **19**, 493 (1954).

15. Yu. A. Arbuzov, DAN, **60**, 993 (1948).

16. Yu. A. Arbuzov, DAN, **76**, 681 (1951).

17. A. Angeli, L. Alessandri, R. Pegna, Zbl., **2**, 302 (1910).

18. L. Alessandri, Zbl., **1915**, **1**, 1210; **1922**, **3**, 259.

19. G. Bruni, E. Geiger, Zbl., **1928**, **1**, 52.

20. N. A. Lange, *Handbook of Chemistry*, 3rd ed., 1961, pp. 406, 1280.

21. T. Reichstein, Helv. Chim. Acta, **9**, 799 (1926).

22. A. A. Petrov, ZhOKh, **19**, 1046 (1949).

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