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Abstract

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SYNTHESIS AND CHEMISTRY OF NITROALLYL

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The only available method for obtaining nitroallyl—an interesting intermediate in the synthesis of polynitro compounds—is the exchange reaction of iodo- and bromoallyl with silver nitrite (V. Meyer reaction) ([1,2]). Reproduction of the reaction of acetylene with nitromethane, leading to the formation of nitroallyl, encounters considerable difficulties ([3]), and its synthesis by nitration of propylene with nitrogen pentoxide is experimentally difficult to carry out ([4]).

We unexpectedly found that, when iodo- and bromoallyl are nitrated with nitrogen tetroxide in ether at -20°, nitroallyl (I) is formed in good yield. The iodine and bromine nitrites arising here are converted into the more stable nitrogen tetroxide and molecular iodine (isolated during nitration of iodoallyl) and bromine. The latter, at the moment of its appearance, unlike iodine, brominates the starting bromoallyl, giving 1,2,3-tribromopropane (II). The appearance of 2-nitro-1,3-dibromopropane (III) can be explained by nitrohalogenation of bromoallyl with bromine nitrite.

When the reaction temperature is raised (in the case of iodo- and bromoallyl), the interaction of the nitroallyl formed with nitrogen tetroxide leads to the synthesis of 1,3-dinitropropanol-2 (IV), which may be regarded as a secondary nitration product.

$$O_2N + BrCH_2{-}CH{=}CH_2 + NO_2$$
$$\downarrow$$
$$O_2NBr + CH_2{=}CHCH_2NO_2 \quad (I)$$
$$\downarrow$$
$$O_2NBr \longrightarrow N_2O_4 + Br_2$$
$$\downarrow$$
$$[O_2NCH_2CHCH_2NO_2] \quad (IV^a)$$
$$ONO$$
$$\downarrow$$
$$O_2NCH_2CHCH_2NO_2 \quad (IV)$$
$$OH$$

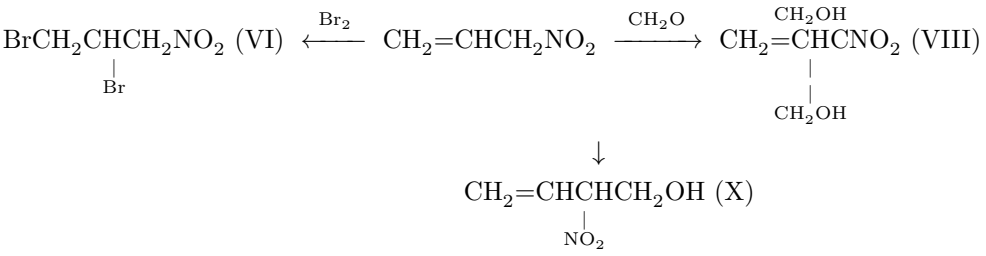
$BrCH_2CHCH_2Br$ (III), $BrCH_2CHBrCH_2Br$ (II)

In analogous conditions, chloroallyl, owing to the greater strength of the chlorine–carbon bond, does not exchange halogen for a nitro group and is not converted into nitroallyl, but forms only 1-nitro-3-chloropropanol-2 (V).

As a result of studying the chemical transformations of nitroallyl, substances were obtained that made it possible to confirm the structure of certain products of the reaction of bromo- and iodoallyl with nitrogen tetroxide. The absence of any appreciable mutual influence of the double bond and the nitro group ([5]) indicates that nitroallyl combines the properties of ethylene and nitroethane. Therefore, its nitration with nitrogen tetroxide ended in the synthesis of 1,3-dinitropropanol-2, isolated as a result of hydrolysis of the initially formed—

···of the nitrite being formed (IVa) and of the identical product IV; bromination gave the only possible 1-nitro-2,3-dibromopropane (VI), isomeric with III and therefore having the proposed structure; condensation with formaldehyde led to 2-nitro-2-methylolbuten-3-ol-1 (VII), characterized by the diacetate (VIII) and dibromide (IX).

By cleavage of the methylol group, VII was converted into 3-nitrobuten-1-ol-4 (X), in agreement with the data of Bulgarian investigators ([6])—the starting product for the synthesis of 2-nitrobutadiene-1,3.



The reaction described is the first example of the synthesis of nitro compounds by substitutive nitration of allylic halogen derivatives with nitrogen tetroxide. Its mechanism may apparently be explained by a conjugated allylic rearrangement involving allyl iodide or bromide and nitrogen tetroxide.

I. Preparation of nitroallyl by nitration of allyl bromide with nitrogen tetroxide. In a three-necked flask with ground joints, equipped with a stirrer with a glass piston seal, a calcium chloride tube, a low-temperature thermometer, and a dropping funnel with a cooling jacket, 26.2 ml (36 g–0.3 mole) of freshly distilled allyl bromide in 75 ml of dry ether are placed. Over 30 min, at a temperature not above −20° and with vigorous stirring, 18.3 ml (0.3 mole) of nitrogen tetroxide cooled to −40° in 10 ml of ether are added. After stirring for 4 hours at this temperature, the nitrogen oxides and ether are distilled off under the vacuum of a water-jet pump.

The nitration products (yield 48 g, 90% of theory) are washed several times with distilled water, dried over sodium sulfate, and subjected to distillation, first under the vacuum of a water-jet pump and then on an oil pump:

1st fraction: b.p. 65-66° (95 mm), is nitroallyl (I). Its b.p. 79-80° (180 mm), n_D^{20} 1.4270, d_4^{20} 1.056 (literature data: b.p. 80° (180 mm), n_D^{20} 1.4270, d_4^{20} 1.05). Yield 10 g, 35% of theory.

2nd fraction: b.p. 73-75° (3 mm). After washing with 10% sodium carbonate solution and redistillation, 1,2,3-tribromopropane (II) was isolated. Its b.p. 216° (754 mm), n_D^{18} 1.5840, d_4^{20} 1.4215 (literature data: b.p. 218-222° (760 mm), n_D^{17} 1.5835, d_4^{23} 1.43).

3rd fraction: b.p. 110° (3 mm). Redistillation gave 2-nitro-1,3-dibromopropane (II). n_D^{20} 1.5392, d_4^{20} 2.10, MR_D found 36.85, calculated 37.102; mol. wt.: found (ebullioscopically) 241, 225, calculated 246.9.

	Found, %:	C	14.37; 14.69;	H	1.91; 2.13;	N	5.66; 5.94
$C_3H_5O_2NBr_2$.	Calculated, %:	C	14.59;	H	2.04;	N	5.67

II. Preparation of nitroallyl by nitration of allyl iodide with nitrogen tetroxide. 16.8 g (0.1 mole) of freshly distilled allyl iodide, distilled in a stream

of carbon dioxide, in 25-40 ml of dry ether are nitrated at −20°, with vigorous stirring, with 6.1 ml (0.1 mole) of nitrogen tetroxide. Two to three minutes after the addition of the first portions of nitrogen tetroxide, iodine begins to separate and the reaction mass gradually acquires a dark-brown color. After being kept for 3 hours at −20°, the remaining nitrogen tetroxide and ether are distilled off under the vacuum of a water-jet pump, and the iodine is removed by filt···

treatment. The nitration products are washed with water, treated with metallic mercury to remove iodine, dried over sodium sulfate, and distilled.

The fraction at 78-80° (180 mm) is nitroallyl (I). Yield 35-40% of theoretical. The residue is a heavy brown liquid consisting of products of nitration of allyl iodide.

III. **Nitration of allyl chloride with nitrogen tetroxide.** To 24.2 ml (0.3 mole) of freshly distilled allyl chloride in 75 ml of dry ether, at a temperature not above −15°, 18.3 ml (0.3 mole) of cooled nitrogen tetroxide in 10 ml of ether are added over the course of an hour with vigorous stirring. After standing for 4 hours at this temperature, the residues of nitrogen tetroxide, ether, and unreacted allyl chloride are distilled off under the vacuum of a water-jet pump. After washing with distilled water, drying, and distillation of the nitration products (yield 80% of theoretical), at 103-105° (5 ml) a colorless liquid—product V—is obtained. n_D^{20} 1.485, d_4^{20} 1.450; molecular weight: found 137, calculated 139.5.

Found, %: N 10.51; 10.70

$C_3H_6O_3NCl$. Calculated, %: N 10.03

IV. **1,3-Dinitropropan-2-ol (IV).** To 8.7 g (0.1 mole) of nitroallyl in 50 ml of dry ether, at −15° and with vigorous stirring over the course of half an hour, a cooled solution of 6.1 ml (0.1 mole) of nitrogen tetroxide in 10 ml of dry ether is added. After stirring for 4 hours at −10 to −15° and removing the ether under the vacuum of a water-jet pump, the precipitated crystals are separated by filtration from the liquid product, washed with small portions of cooled chloroform. 1,3-Dinitropropan-2-ol (IV) has m.p. 73-74° (from ethyl acetate), yield 5.2 g, 35% of theoretical. Molecular weight: found by Rast 135, 142, calculated 150.

Found, %: C 24.79; 24.84; H 4.32; 4.11; N 18.80; 18.66

$C_3H_6O_5N_2$. Calculated, %: C 24.0; H 4.00; N 18.66

V. **1-Nitro-2,3-dibromopropane (VI).** 8.3 ml (0.1 mole) of nitroallyl in 25 ml of dry chloroform, with stirring and cooling to 10°, was brominated with 5.1 ml of bromine (0.2 mole). After decolorization of the reaction mass, the chloroform was removed and 1-nitro-2,3-dibromopropane was distilled at 115° (3 ml). Yield 23 g, 94% of theoretical. n_D^{20} 1.5451, d_D^{20} 2.10; MR_D calculated 37.102, found 37.34.

Found, %: C 14.84; 14.74; H 1.89; 2.09; N 5.85; 5.90

$C_3H_5O_2NBr_2$. Calculated, %: C 14.57; H 2.04; N 5.67

VI. **2-Nitro-2-methylolbuten-3-ol-1 (VII).** To a mixture of 8.7 g (0.1 mole) of freshly distilled nitroallyl and 16.5 g (0.22 mole) of 40% formalin solution, 50 mg of potash are added with stirring. After 20 min, owing to the heat of reaction, the temperature rapidly rose to 70°. After cooling to 35°, the reaction mass is stirred for another 6 hours. The reaction product is extracted twice with ether; the ethereal extracts are washed several times with saturated sodium chloride solution and dried over ignited sodium sulfate. The residue—an oily liquid—crystallized after standing for two days in a vacuum desiccator. 2-Nitro-2-methylolbuten-3-ol-1—colorless crystals, m.p. 45° (from chloroform), yield 12.5 g, 80% of theoretical.

Found, %: N 9.41; 9.45

$C_5H_9O_4N_3$. Calculated, %: N 9.50

VII. **Acetate of 2-nitro-2-acetoxymethylbuten-3-ol-1 (VIII).** 1.47 g (0.01 mole) of 2-nitro-2-methylolbuten-3-ol-1 is heated for 4 hours with 2.6 g (0.025 mole) of acetic anhydride, the reaction mass is poured

poured into water, washed several times with dilute potash solution and with water, extracted with ether, and the ether solution was washed with water and dried over sodium sulfate. The diacetate was a light-yellow liquid, n_D^{20} 1.4610.

Found, %:	N 6.43; 6.35
$C_9H_{13}O_6N$. Calculated, %:	N 6.06

VIII. 2-Nitro-3,4-dibromo-2-methylbutanol-1 (IX). With stirring and irradiation by an infrared lamp, a solution of 0.875 g of 2-nitro-2-methylbuten-3-ol-1 and 0.8 g of bromine in 20 ml of dry chloroform was decolorized after 5 h. The thick mass, after removal of the chloroform and treatment with benzene, was recrystallized from dichloroethane, m.p. 92°.

Found, %:	C 20.39; 19.38; H 2.68; 2.61; Br 51.34; 52.27
$C_5H_9Br_2O_2N$. Calculated, %:	C 20.49; H 3.09; Br 54.54

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