and ethyl chloroformate followed by treatment with sodium hydroxide.

The identical nature of these three compounds was shown by superimposable infrared spectra and no depression of the melting points on mixing.

Ethyl benzoylformate oxime. The oxime was prepared according to Gabriel[17] by the treatment of ethyl benzoylformate[18] with hydroxylamine hydrochloride and sodium carbonate in aqueous ethanol.

Benzoylformic acid oxime hydrazide. To a solution of 1.0 g. of ethyl benzoylformate oxime in 6 ml. of ethanol was added 1 ml. of hydrazine. The solution was refluxed for 10 min. and evaporated to approximately one third its volume. The addition of water afforded 1.0 g. of crude solid, m.p. 150–170°. An analytical sample was prepared by recrystallization from alcohol–carbon tetrachloride and alcohol–water, m.p. 164–172°.

Anal. Calcd. for $C_8H_9N_3O_2$: C, 53.62; H, 5.06; N, 23.45. Found: C, 53.81; H, 5.19; N, 23.45.

Benzoylformic acid oxime azide. To a solution of 0.1 g. of the above hydrazide in 4 ml. of acetic acid and 1 ml. of water was added dropwise a solution of 60 mg. of sodium nitrite in 1 ml. of water. An additional 2 ml. of water was added to yield 70 mg. of white solid, m.p. 110° vigorous dec. It was not purified due to its instability. The infrared spectrum of this compound showed an absorption band at *ca.* 2160 cm.$^{-1}$.

3-Phenyl-5-hydroxy-1,2,4-oxadiazole. (a) *By rearrangement of the azide.* Refluxing 60 mg. of the above azide, in 5 ml. of ethanol for 1 hr., adding water, and cooling afforded 30 mg. of white solid, m.p. 192–199°. Recrystallization from benzene raised the melting point to 197.0–200.5°.

(b) *From amidoxime.* The procedure of Falck[19] was used to obtain the oxadiazole from benzamidoxime.

Anal. Calcd. for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.23; H, 3.80; N, 17.22.

The identity of these two compounds is shown by identical infrared spectra and undepressed mixture melting point.

Ethyl phenylpyruvate oxime. The oxime was prepared by refluxing ethyl phenylpyruvate (from phenylpyruvic acid[20]) with hydroxylamine in ethanol for 3 hr. The preparation of the same substance by the action of nitrosylsulfuric acid on benzylacetoacetate ester is reported.[21]

Phenylpyruvic acid oxime hydrazide. To a solution of 5.0 g. (0.025 mole) of the above oxime in 25 ml. of ethanol was added 5 ml. of hydrazine. The solution was refluxed 15 min. and 50 ml. of water was added. Cooling afforded 2.3 g. (49%) of white needles, m.p. 138–143° dec. An analytical sample, m.p. 143–146°, was obtained by recrystallizations from benzene, ethanol-water, and chloroform–carbon tetrachloride.

Anal. Calcd. for $C_9H_{11}O_2N_3$: C, 55.95; H, 5.74; N, 21.75. Found: C, 55.96; H, 5.73; N, 21.78.

Phenylpyruvic acid oxime azide. To a solution of 1.2 g. of the above hydrazide in 50 ml. of 5% hydrochloric acid cooled in an ice bath was added dropwise 0.6 g. of sodium nitrite in 5 ml. of water. This yielded 1.0 g. of solid, m.p. 95° vig. dec., whose infrared spectrum had an absorption band at *ca.* 2160 cm.$^{-1}$. It was not purified due to its instability.

3-Benzyl-5-hydroxy-1,2,4-oxadiazole. (a) *By rearrangement of the azide.* Refluxing 1.0 g. of the above azide in 25 ml. of benzene for 30 min. caused the solution to darken. Evaporation left a dark residue which was recrystallized from water to give 0.4 g. of solid, m.p. 60–100°. Recrystallizations from carbon tetrachloride, water, and petroleum ether (b.p. 60–75°) with a trace of benzene gave an analytical sample, m.p. 112–115°.

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.41; H, 4.58; N, 15.94. Found: C, 61.36; H, 4.58; N, 15.90.

(b) *From amidoxime.* Phenylacetamidoxime[22] was converted to the oxadiazole[23] with ethyl chloroformate and base. Identical infrared spectra and undepressed mixture melting point showed these two samples to be the same compound.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Nitration of Unsaturated Alcohols[1]

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The nitration of several aliphatic alcohols containing carbon-carbon unsaturation has been accomplished using acetyl nitrate as the reagent. In specific cases, the normal nitration procedure could be modified to afford good yields but in most cases only 10 to 30% yields were obtained. These low yields are ascribed to subsequent addition of the elements of acetyl nitrate to the double bond with the formation of high boiling by-products. A number of new unsaturated nitrates, dibromoalcohols, and dibromoalcohol nitrates are described. The last can be obtained in good yields by both nitration of the dibromoalcohols and bromination of the unsaturated nitrates.

The most attractive method for the synthesis of molecules containing both nitrate ester functions and carbon-carbon unsaturation is the nitration of the corresponding unsaturated alcohol. A wide variety of general nitration media have been employed by different workers.[2,3] Most of these media, if not all, are composed of reagents which in

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addition to effecting hydroxyl nitration may also add to unsaturated systems. The successful nitrations of allyl alcohol,[4] both *cis*- and *trans*-2-buten-1,4-diol,[5] 2,2-bis(hydroxymethyl)-3-buten-1-ol,[6] and 2-(hydroxymethyl)-2-methyl-3-buten-1-ol[6] with absolute nitric acid in acetic anhydride (acetic acid was used as a diluent in the last two examples) suggested that this system might serve for the projected investigation. However, it was shown,[7-9] after the study reported herein was nearly complete, that acetyl nitrate, the effective nitrating reagent in this system, can add to olefinic linkages. The report by Bordwell and Garbisch[9] dealing with the addition of acetyl nitrate to aliphatic systems containing carbon-carbon double bonds was of particular value since it outlined the best addition conditions which were exactly the converse of our intention.

Since the eventual goal of our work was to study the polymerization of unsaturated substances containing nitrate ester groups, the unsaturated alcohols of greatest interest were those which contained a terminal or vinyl type carbon-carbon unsaturation. However, for completeness, several alcohols with internal unsaturation were also investigated. Nitration of the corresponding alcohols with acetyl nitrate (threefold excess at −30°) in acetic anhydride afforded the nitrates: 1-nitrato-4-pentene, 1-nitrato-5-hexene, 2-methyl-4-nitrato-1-pentene, 1-nitrato-2-butene, and 2-methyl-1-nitrato-2-propene. The yields of unsaturated nitrates obtained by this method, designated herein the standard method, ranged from 10 to 30%. These nitrates are all liquids and the last step in their preparation was distillation under reduced pressure. When the standard nitration method was employed, considerable nondistillable (bath temperature 75° at 0.1 mm. pressure) residues invariably resulted. These residues were viscous and on quantitative analysis always proved to contain more nitrogen than that required for hydroxyl nitration alone.

The reaction of silver nitrate dissolved in acetonitrile[10] with the corresponding unsaturated halogen derivatives gave 1-nitrato-4-pentene and 2-methyl-1-nitrato-2-propene in high yields (83 and 88%, respectively). Although these nitrates were isolated by distillation, as were the products from the standard nitration method, only negligible residues were formed.

These observations suggest that two factors may operate to reduce the yields in the standard nitration method. First, the acetyl nitrate may add to the double bond[7-9] to produce the high boiling acetoxy-nitronitrates. Second, these adducts may decompose on heating to produce radicals serving to initiate the polymerization of the unsaturated nitrates. In a single case, it was possible to isolate one of these adducts, 2-methyl-1-nitrato-2(or 3)-nitropropan-2(or 3)-ol acetate by subjecting the residue from the distillation of the unsaturated nitrate to higher temperature and greatly reduced pressure. Attempts to isolate similar adducts from the other residues by the same technique terminated in minor explosions or detonations.

Bordwell and Garbisch[9] state that acetyl nitrate fails to form on the addition of nitric acid (70%) to acetic anhydride at temperatures below −10°. This observation suggested that the solution of nitric acid in acetic anhydride formed in this way might effect hydroxyl nitration without the interference of double bond addition. However, experiments using this technique for the nitration of 2-methyl-2-propen-1-ol gave neither the unsaturated nitrate nor any adduct. Apparently, the alcohol survived this treatment without effect.

Although, as evidenced by the considerable heat of reaction, acetyl nitrate forms on the addition of absolute nitric acid to acetic anhydride at −30°, the nitrating mixture is more effective if it is prepared at 20 to 25° and then cooled to −30° prior to addition of the alcohol. Thus, 1-nitrato-2-butene was obtained in 30% yield by the standard method and in 65% yield when the nitrating solution was prepared at 25° (*caution*). The higher temperature may permit more nearly quantitative conversion of the nitric acid to the much more effective[9] nitrating agent acetyl nitrate. A similar increase in yield (25 to 50%) was observed when 2-methyl-2-propen-1-ol was nitrated with the mixture prepared at 25°.

After many experiments, the best method (65% yield) for the nitration of this last alcohol was evolved. This required the use of acetic acid as a diluent for the nitration system.[6] These various modifications appear to be rather specific for a given unsaturated alcohol since their application to the other alcohols studied did not meet with any improvement in yield over the standard method. None of the various methods permitted the preparation of 2-methyl-2-nitrato-3-butene from the corresponding alcohol. Perhaps this tertiary nitrate readily eliminates the elements of nitric acid to form isoprene.

In order to confirm the structures of these unsaturated nitrate derivatives, the original alcohols were brominated (50 to 70% yields) to obtain:

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1,2-dibromo-5-pentanol, 1,2-dibromo-6-hexanol, 1,2-dibromo-2-methyl-4-pentanol, 1,2-dibromo-2-methyl-3-propanol, 2,3-dibromo-1-propanol, and 1,2-dibromo-3-methyl-3-butanol; the second, third, and fourth compounds in the list are new. Since some of these dibromoalcohols tend to decompose during purification by distillation, conflicts appear in the literature on their physical properties[11] and this problem has not been resolved in our work.

Nitration of these dibromoalcohols by the standard nitration method afforded the new dibromonitrates: 1,2-dibromo-5-nitratopentane, 1,2-dibromo-6-nitratohexane, 2,3-dibromo-1-nitratopropane, 1,2-dibromo-2-methyl-3-nitratopropane, 1,2-dibromo-2-methyl-4-nitratopentane, and 1,2-dibromo-3-methyl-3-nitratobutane in yields of 67, 47, 56, 61, 86, and 50%, respectively. Identical samples of the first four were obtained by bromination of the corresponding unsaturated nitrates (79, 72, 87, and 88% yields, respectively).

EXPERIMENTAL

Materials and methods. The unsaturated alcohols, except 2-methyl-1-penten-4-ol, were commercial samples which were fractionated prior to use. Middle fractions with boiling point ranges of less than a degree were selected.

Prior to analysis of all the various products described below, the infrared spectra were checked to ensure their gross purity. The presence of the proper absorption peaks, following the assignments given by Bellamy,[12] as well as the absence of extraneous absorption peaks was employed for this purpose.

General bromination procedure. The unsaturated compound (0.1 mole) was dissolved in 100 ml. of dichloromethane (or carbon disulfide), stirred at −20° and 0.11 mole of bromine dissolved in 100 ml. of the same solvent was added dropwise. The resulting solution was extracted with 5% aqueous sodium hydroxide until colorless and with water until neutral. After drying with calcium sulfate, the solvent was removed under reduced pressure and the brominated product was purified by distillation under reduced pressure.

2,3-Dibromo-1-propanol. Pure material was isolated in 53% yield; b.p. 109° (20 mm.), $n_{\rm D}^{20}$ 1.5597. These values are in reasonable agreement with those cited for this substance.[13]

1,2-Dibromo-5-pentanol. This compound decomposed slightly during distillation under reduced pressure. A slightly impure sample was obtained; yield 69%, b.p. 107° (2 mm.), $n_{\rm D}^{20}$ 1.5417 (lit.,[11] b.p. 132–133° at 16 mm.).

1,2-Dibromo-6-hexanol. This new substance also decomposed slowly during distillation; yield 65%, b.p. 120° (2 mm.), $n_{\rm D}^{20}$ 1.5242.

1,2-Dibromo-3-methyl-3-butanol. A 62% yield of this substance was obtained; b.p. 103° (10 mm.), $n_{\rm D}^{20}$ 1.5302. This latter value agrees with the reported values[14,15] but the boiling points cited do not correlate exactly with each other or with our data.

1,2-Dibromo-2-methyl-4-pentanol. The required 2-methyl-1-penten-4-ol was prepared following Hudson and Schmerbaile.[16] Bromination gave the new, 1,2-dibromo-2-methyl-4-pentanol; yield 56%, b.p. 104° (5 mm.), $n_{\rm D}^{20}$ 1.5384.

1,2-Dibromo-2-methyl-3-propanol. Bromination of the unsaturated alcohol in carbon disulfide afforded this new compound; yield 50%, b.p. 104°, $n_{\rm D}^{20}$ 1.5453.

General nitration procedure. The absolute nitric acid employed was prepared by the reduced pressure distillation of colorless commercial reagent grade 70% nitric acid from an equal volume of concd. reagent grade sulfuric acid; b.p. 35–40° (30 mm.). All work was done behind explosion screens.

To 50 ml. of acetic anhydride, stirred and cooled at −30° in a flask covered with aluminum foil and protected from moisture, was added 12.6 ml. (0.3 mole) of absolute nitric acid. At the same temperature, 0.1 mole of the alcohol was added slowly. After stirring for a few minutes, the mixture was poured rapidly onto cracked ice. This and all subsequent processing in experiments with the unsaturated materials was conducted with a minimum exposure to light. The oily layer which formed was separated and washed with 5% sodium carbonate solution until neutral and then with water. With small volumes, the addition of either dichloromethane or ether facilitated these operations. The neutral material was dried with calcium sulfate (Drierite) and distilled under reduced pressure.

The reported nitrations, employing this method, of 2-propen-1-ol[4] and both *cis*- and *trans*-2-buten-1,4-diol[5] were successfully repeated in this laboratory. In the work described below, nearly all of the distillations produced large yields of viscous pot residues which were found to provide more complex infrared spectra and to contain more nitrogen than the desired product as determined by elemental analysis. Attempts were made to distill the pot residues obtained in most of the nitration experiments. The usual result was at least a fume-off if not an actual explosion.

Unless noted to the contrary, this general method was used for the nitration of the alcoholic substances.

2,3-Dibromo-1-nitratopropane. This new compound was prepared by two methods. Nitration of 2,3-dibromo-1-propanol and bromination of 1-nitrato-2-propene by the methods described afforded pure material of like constants and identical infrared spectra, in yields of 56 and 87%, respectively; b.p. 119° (20 mm.), $n_{\rm D}^{20}$ 1.5349.

Anal. Calcd. for $C_3H_5Br_2NO_3$: C, 13.90; H, 1.92; Br, 60.79; N, 5.33. Found: C, 14.04; H, 2.02; Br, 61.04; N, 5.55.

1,2-Dibromo-2-methyl-3-nitratopropane. Bromination of 2-methyl-1-nitrato-2-propene gave this new compound; yield 88%, b.p. 58° (0.4 mm.), $n_{\rm D}^{24}$ 1.5235. Identical constants and infrared spectra were obtained with a sample of this compound prepared by nitration of the dibromoalcohol; yield 61%.

Anal. Calcd. for $C_4H_7Br_2NO_3$: C, 17.35; H, 2.55; Br, 57.71; N, 5.06. Found: C, 17.35; H, 2.66; Br, 57.80; N, 5.11.

1,2-Dibromo-3-methyl-3-nitratobutane. This new compound was prepared from 1,2-dibromo-3-methyl-3-butanol by nitration; yield 50%, b.p. 106° (5 mm.), $n_{\rm D}^{20}$ 1.5222.

Anal. Calcd. for $C_5H_9Br_2NO_3$: C, 20.64; H, 3.12; N, 4.81; Br, 54.93. Found: C, 20.97; H, 3.21; N, 4.54; Br, 54.74.

1,2-Dibromo-2-methyl-4-nitratopentane. Nitration of the corresponding dibromoalcohol afforded this new compound; yield 86%, b.p. 120° (6 mm.), $n_{\rm D}^{20}$ 1.5155.

Anal. Calcd. for $C_6H_{11}Br_2NO_3$: C, 23.63; H, 3.64; Br, 52.40; N, 4.59. Found: C, 23.99; H, 3.87; Br, 52.23; N, 4.51.

1,2-Dibromo-5-nitratopentane. This new substance resulted from the nitration of the corresponding dibromoalcohol and the bromination (carbon disulfide) of the un-

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saturated nitrate; yields 67 and 79%, respectively, b.p. 109° (0.7 mm.), $n_{\rm D}^{20}$ 1.5263 ± 0.0004, infrared spectra identical.

Anal. Calcd. for $C_5H_9Br_2NO_3$: C, 20.64; H, 3.12; Br, 54.93; N, 4.81. Found: C, 20.77; H, 3.27; Br, 55.05; N, 4.94.

1,2-Dibromo-6-nitratohexane. Nitration of the dibromoalcohol and bromination of the unsaturated nitrate gave this new compound; yields 47 and 72%, respectively, b.p. 149° (5 mm.), $n_{\rm D}^{20}$ 1.5182 ± 0.0005, infrared spectra identical.

Anal. Calcd. for $C_6H_{11}Br_2NO_3$: C, 23.63; H, 3.64; Br, 52.40; N, 4.59. Found: C, 23.46; H, 3.91; Br, 52.77; N, 4.52.

1-Nitrato-4-pentene. This new nitrate was isolated in 20% yield; b.p. 27° (5 mm.), $n_{\rm D}^{20}$ 1.4321.

Anal. Calcd. for $C_5H_9NO_3$: C, 45.79; H, 6.91; N, 10.68. Found: C, 46.04; H, 7.06; N, 10.83.

A mixture of 1-bromo-4-pentene (25 g.) and 250 ml. of acetonitrile containing 90 g. of silver nitrate and 2 g. of hydroquinone was stirred for 56 hr. at room temperature. The insoluble material was removed by filtration and the filtrate was dissolved in ether and the solution was washed thoroughly with water. Drying over sodium sulfate and distillation (no residue) afforded 1-nitrato-4-pentene identical in boiling point, refractive index, and infrared spectra with the sample described above; yield 18 g. (83%).

1-Nitrato-5-hexene. An 11% yield of this new compound was obtained; b.p. 30° (0.1 mm.), $n_{\rm D}^{20}$ 1.4385.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.64; H, 7.64; N, 9.65. Found: C, 49.75; H, 7.60; N, 9.67.

2-Methyl-4-nitrato-1-pentene. This new, comparatively unstable nitrate was isolated in 19% yield; b.p. 26° (2 mm.), $n_{\rm D}^{20}$ 1.4308.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.64; H, 7.64; N, 9.65. Found: C, 49.67; H, 7.78; N, 9.56.

Attempted nitration of 2-methyl-3-buten-2-ol. Numerous attempts to prepare the nitrate of this alcohol by the method described above and by the various alternative methods discussed below were unsuccessful. Large pot residues were normally obtained and in the few cases where any distillate of product resulted, it shortly decomposed violently.

1-Nitrato-2-butene. Anhydrous acetic anhydride (60 ml.) was stirred at 25° while adding dropwise 21 ml. (0.5 mole) of absolute nitric acid (*caution*). The solution was cooled to −25° and 14.4 g. (0.2 mole) of 2-buten-1-ol was added dropwise. After 30 min. at −20°, the solution was poured into ice and water and the nitrate was isolated in the described manner; yield 15.2 g. (65%), b.p. 42° (18 mm.), $n_{\rm D}^{20}$ 1.4294. Employing the previously described nitration method, the yield was 30%.

Anal. Calcd. for $C_4H_8NO_3$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.24; H, 6.20; N, 12.19.

2-Methyl-1-nitrato-2-propene. A mixture of acetonitrile (250 ml.), silver nitrate (125 g.), and 2 g. of hydroquinone was stirred at 0° in the dark while adding 25 g. of 1-chloro-2-methyl-2-propene dropwise. The mixture was allowed to stir for 36 hr. without further cooling. After filtration, the filtrate was diluted with ether and the resulting solution was extracted with water, 2% aqueous sodium bisulfite, and again with water. Drying over sodium sulfate, evaporation of the ether, and distillation gave colorless 2-methyl-1-nitrato-2-propene; yield 88%, b.p. 37° (25 mm.), $n_{\rm D}^{24}$ 1.4229.

Anal. Calcd. for $C_4H_7NO_3$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.24; H, 6.10; N, 11.87.

Although the compound was prepared in this way for use as a reference compound in the studies described below, the data given represent significant improvements over those cited in the literature.[17]

Nitration of 2-methyl-2-propen-1-ol, employing the general method described previously, afforded the same nitrate in 25% yield. Almost no nitration was effected if the temperature was held at −55° during the course of the nitration process including the addition of the nitric acid to the acetic anhydride. Following the method of Kuhn and Duckworth,[6] which differs in that acetic acid is used to dilute the nitration system, there was likewise obtained low yields (25%) of unsaturated nitrate and considerable amounts of pot residue on distillation. In either process if the molar ratio of nitric acid to unsaturated alcohol was reduced to 1:1, only traces of unsaturated nitrate could be isolated; under these conditions no pot residue was obtained either.

Following an adaptation of the method of Bordwell and Garbisch,[9] 60 ml. of acetic anhydride was treated at 25° with 21 ml. (0.5 mole) of absolute nitric acid. The solution was cooled to −25° and 14.4 g. (0.2 mole) of 2-methyl-2-propen-1-ol was added dropwise. After 15 min. at −20°, the mixture was poured into ice and water and processed as described; yield 11.8 g. (50%), with only a trace of pot residue. When sulfuric acid (several drops) was added to this mixture before addition of the alcohol,[9] considerable amounts of pot residue and almost no unsaturated nitrate resulted. When the method of Bordwell and Garbisch,[9] employing a much larger ratio of acetic anhydride to 70% nitric acid, was used, no product of any kind was obtained; in these experiments various temperatures between −10 and 25° were employed for the addition of the nitric acid to the anhydride and in all cases the alcohol was added at −20°.

After these many experiments, the following method, comparable to that of Kuhn and Duckworth,[6] was found to give the best results. Acetic anhydride (28.3 ml., 0.3 mole) and acetic acid (57.2 ml., 1.0 mole) were stirred at 10° while adding 21 ml. (0.5 mole) of absolute nitric acid. This solution was cooled to −3° and 14.4 g. (0.2 mole) of 2-methyl-2-propen-1-ol was added slowly. After 15 min. at this temperature, the cooling bath was removed and the mixture was stirred until the temperature reached 10°. Then the solution was poured into ice and water and processed as described; yield 65%.

2-Methyl-1-nitrato-2(or 3)-nitropropan-2(or 3)-ol acetate. Following a modification of the method of Bordwell and Garbisch,[9] 37.8 g. of absolute nitric acid was added to 400 ml. of acetic anhydride stirred at 25°. The solution was cooled to −30° and 3 g. of concd. sulfuric acid was added. After 15 min., 21.6 g. of 2-methyl-2-propen-1-ol was added in one portion. The temperature rose rapidly to 23° and then subsided. After cooling to −35° and maintaining this temperature for 15 min., the mixture was poured into ice and water. Processing in the manner described under the general nitration procedure yielded a small amount of unsaturated nitrate and a pot residue which could be distilled in part. Redistillation afforded pure material; yield 3.5 g. (5%), b.p. 109–110° (1 mm.), $n_{\rm D}^{20}$ 1.4797.

Anal. Calcd. for $C_6H_{10}N_2O_7$: C, 32.44; H, 4.54; N, 12.61. Found: C, 32.67; H, 4.36; N, 12.89.

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