241. *Addition of Dinitrogen Tetroxide to Olefins. Part II. Ethylene.*

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Ethylene can be nitrated with liquid or dissolved dinitrogen tetroxide, preferably with addition of gaseous oxygen, to give high overall yields, *i.e.*, 70—80% on ethylene, of pure separated products. The reaction must be controlled below room temperature. Ethylene reacts much more slowly than the higher olefins, and best results are given by absorbing 0·4 mol. of ethylene per mol. of tetroxide during approximately 10 hours. It has been established that addition follows only two paths : (i) as two nitro-groups to give 1 : 2-*dinitroethane*, and (ii) as one nitro-group and one nitrite group to give the *nitrite* of 2-nitroethanol. This ester is extremely unstable, especially in the last stages of removing excess of dinitrogen tetroxide from the reaction product, and is best converted into the nitro-alcohol by reaction with methanol at an early stage in separation. On cooling, the methanol solution deposits solid 1 : 2-dinitroethane, m. p. 39—40°, in 35—40% yield, and nitroethanol and its nitrate (formed in the main reaction by oxidation of part of the nitrite) are separated by water–benzene extraction, each in 12—20% yield. Some of the properties and derivatives of the three products are described, and 1 : 2-dinitroethane is adequately characterised for the first time.

WORK on the nitration of olefins with dinitrogen tetroxide began with ethylene, and most of the general problems of olefin nitration were solved in its investigation, though it eventually proved to be the least tractable of the olefins, the addition reaction being much slower and the initial products less stable than with higher homologues. The literature on the nitration of ethylene with oxides of nitrogen is somewhat conflicting and describes various single products without accounting for the bulk of the reactants. Semenoff (*Jahresber.*, 1864, 480; *Z. Chem. Pharm.*, 1864, **7**, 129) made careful examination of the reaction between dry ethylene and dry tetroxide (made by heating dry lead nitrate) in the gas phase at 60—70°, in the liquid phase, and in ethereal solution, and in the last case was able to crystallise from the solution a white solid, m. p. 37·5°, which he called " ethylene dinitrite." The present work clearly shows that the solid was in fact 1 : 2-*dinitroethane*, m. p. 39—40° when pure, and that it represents only about half of the product from liquid-phase reaction. The remainder gives rise to 2-nitroethanol and its nitrate by the treatment outlined in the preceding paper. Although these are not new substances (Wieland and Sakellarios, *Ber.*, 1920, **53**, 201; McKie, *J.*, 1927, 962) they have not been previously obtained by nitration of ethylene with the tetroxide or " nitrous gases."

Demjanow (*Ann. Inst. Agron. Moscow*, 1894, **4**, 155) obtained " ethylene nitrosite," m. p. 116—117°, from the reaction between ethylene and " nitrous fumes " in ether. Sidorenko (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1585), who repeated this preparation, stated that examination of residual products in the ether was dangerous since they invariably exploded during concentration of the solution. The reaction between ethylene and dinitrogen trioxide in ether and other inert solvents to give " ethylene nitrosite," for use as a secondary charge in blasting caps and primers, has been patented (Marshall, U.S.P. 1,473,825, 1921). Harris and Siegel (*J. Amer. Chem. Soc.*, 1941, **63**, 2520) found no reaction between ethylene and gaseous tetroxide in the dark at room temperature, but under the influence of ultra-violet light ethylene oxide and acetaldehyde were formed.

The present work shows, in confirmation of Semenoff's results, that reaction in the vapour phase does occur and that 1 : 2-dintroethane can be isolated from the products. Even at 100°, this can be formed, but above 150° a chain oxidation reaction sets in and may become explosive. Liquid-phase reaction, using either pure tetroxide or a solution, is much more satisfactory in that it leads to simpler products in high total yield; by the methods here described the recoveries of pure products are 35—40% of 1 : 2-dinitroethane, 12—20% of 2-nitroethanol and 12—20% of 2-nitroethyl nitrate, all based on ethylene absorbed. The 1 : 2-dinitroethane obtained and characterised beyond doubt is quite different from the greenish-yellow oil, b. p. 94—96°/5 mm., prepared by Ipatov (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 297) by reaction between silver nitrite and ethylene iodide.

Nitration Procedure.—The reaction is carried out by passing dry ethylene into pure liquid or dissolved dinitrogen tetroxide, cooled by a bath at 0°. Reaction is quite slow compared with that of other olefins, and at least 10 hours are required for the optimum absorption of ethylene, which is found to be 0·4 mol. per mol. of tetroxide. With higher proportions of ethylene, the yield of nitrated products per mol. of ethylene diminishes. The initial addition products are 1 : 2-dinitroethane (I) and 2-nitroethyl nitrite (II), while a portion of the latter is oxidised to the nitrate (III) by the tetroxide which in turn gives rise to trioxide :

$$\underset{\text{(I.)}}{NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2} \xleftarrow{N_2O_4} CH_2{:}CH_2 \xrightarrow{N_2O_4} \underset{\text{(II.)}}{NO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2} \xrightarrow{N_2O_4} \underset{\text{(III.)}}{NO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2} + N_2O_3$$

Side reactions due to trioxide can be avoided by passing oxygen into the reaction mixture during ethylene absorption, usually at about 20—30% of the ethylene rate. As well as keeping the tetroxide fully oxidised, the use of oxygen produces a more stable nitration product. Analysis of the gases leaving the reaction vessel shows that very little oxidation of ethylene to oxides of carbon occurs. Yields are not increased by addition of dehydrating agents, *e.g.*, sulphuric acid, phosphoric oxide, or anhydrous copper sulphate, although moisture appears to have a deleterious effect through formation of the trioxide.

The ethylene is preferably introduced through a sintered-glass plate. Although the speed of absorption is increased with a spinning gas distributor, the nitration rate is hardly affected. In small-scale experiments considerable absorption of products occurs in the sintered plate, which should be extracted with methanol for good recoveries. Benzene, carbon tetrachloride, ethyl ether, and dioxan have been studied as reaction solvents, and the same three products obtained in each case. When oxygen is not used, the ether class of solvents decreases the proportion of nitrate formed by moderating the oxidising character of the tetroxide. This observation is in line with the rôle of ether or ester solvents in the nitration of propylene and the butylenes where such solvents appear to be essential for dinitroparaffin formation.

Separation Procedure.—After completion of absorption to the optimum molar ratio, excess of tetroxide is removed by a current of dry air, nitrogen, or carbon dioxide, or by evaporation under reduced pressure, and is recovered by condensation as solid in receivers cooled to −70°. Care should be taken to keep the crude nitration product cold, *i.e.*, at about 0°, in the final stages of removal of tetroxide since the nitro-nitrite is very unstable when free from tetroxide or solvent. Although batches exceeding 1 kg. of crude product have been satisfactorily handled in this manner, it is preferable to evaporate continuously from a warm falling film in the manner applied to other olefins and described in the previous paper (see British Patent Application No. 17,160/45). This avoids the risk of accumulating a large volume of unstable product and permits it to fall dropwise into cold methyl alcohol where the 2-nitroethyl nitrite is immediately converted into the stable 2-nitroethanol, methyl nitrite being evolved: $NO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2 + CH_3{\cdot}OH \longrightarrow OH{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2 + CH_3{\cdot}O{\cdot}NO$. This mechanism has been confirmed by (i) condensing and identifying the methyl nitrite formed, (ii) proving that the quantity of nitrite in the crude oil corresponds to the amount of nitro-alcohol formed, (iii) isolating somewhat impure nitroethyl nitrite by very careful fractional distillation of the crude oil, (iv) preparing nitroethyl nitrite from nitroethanol and converting it back into nitroethanol by treatment with methyl alcohol. It has been shown, in addition, that the nitrite is slowly oxidised to the nitrate ester by liquid tetroxide and oxygen.

About 1½—2 vols. of methyl alcohol per vol. of crude oil are used and the solution, which now contains dinitroethane, nitroethanol, and nitroethyl nitrate is cooled with stirring in a bath of solid carbon dioxide–methanol. Crystalline 1 : 2-dinitroethane is deposited, and filtered off for recrystallisation from methanol or benzene. The separation is assisted by the presence of the nitroethanol, which prevents deposition of the nitrate and consequent interference with the crystallisation of 1 : 2-dinitroethane. Methyl alcohol is evaporated from the filtrate under reduced pressure, leaving a mixture of nitroethanol and nitroethyl nitrate containing a small quantity of dissolved dinitroethane. This mixture is best separated by stirring with benzene and water; the nitrate and the dinitroethane pass into the benzene, and the nitroethanol into the water for later extraction with ether. After removal of the solvents, the nitroethyl nitrate and nitroethanol are purified by fractional distillation under high vacuum. The crude products attack the skin and direct contact should be avoided; dinitroethane and nitroethyl nitrate also give rise, when crude, to highly lachrymatory nitroethylene, and hence the separation stages involved should be carried out in an efficient fume cupboard, which also affords safe release of the toxic methyl nitrite formed by alcohol treatment.

Yields.—The total yield of pure products accounts for at least 70% of the ethylene and 80% of the tetroxide. In the example described later, the amounts of the three pure products isolated correspond to the following percentages on the reagents consumed :

	Yield % on C_2H_4.	Yield % on N_2O_4.
1 : 2-Dinitroethane	36·9 (38·7)	41·5 (43·6)
2-Nitroethanol	16·4 (20·5)	18·4 (23·0)
2-Nitroethyl nitrate	20·2 (28·0)	22·8 (31·5)
Totals	73·5 (87·2)	82·7 (98·1)

Parallel experiments applying the entire separation procedure to synthetic mixtures indicate losses of the order of 5%, 20%, and 28%, respectively, for the three components, and the figures in parentheses are corrected percentages for the untreated product mixture. These are sufficiently close to quantitative values to indicate that, under the given reaction conditions, addition of dinitrogen tetroxide to ethylene takes only the two courses mentioned on p. 1097, other modes, *e.g.*, dinitrite or nitroso-nitrate addition, not occurring to any significant extent.

It is noteworthy that the oxygen absorbed is usually equivalent to the nitroethyl nitrate formed; referring to the example given later, 32·5 g. of oxygen were absorbed, whereas 30·8 g. are required for the oxidation of the nitroethyl nitrite (*via* the tetroxide) to the 261·7 g. of nitroethyl nitrate isolated. Also of interest is the observation that 1 : 2-dinitroethane is obtained by reaction of ethylene and tetroxide in the vapour phase at approximately 100°. As might be expected, the yields of nitroethanol and nitroethyl nitrate are low under these conditions.

Properties and Reactions.—Some of the physical and explosive properties and chemical reactions of the products are described below. It is hoped to deal more fully with the reactions of dinitroparaffins, nitro-alcohols, and the nitrates in later publications.

1 : 2-*Dinitroethane.*—This is a white crystalline solid, m. p. 39—40° after recrystallisation from methanol or benzene; it distils under high vacuum to give a clear colourless liquid, b. p. 88°/*ca.* 1 mm. Molten 1 : 2-dinitroethane is easily supercooled and may be kept liquid even at 0°; shaking, scratching, or seeding causes immediate solidification with evolution of heat. The solid slowly decomposes on storage, turning yellow, becoming liquid, and finally decomposing after several weeks with the production of nitrous fumes, some nitroethylene, and a tarry liquid residue. It readily loses nitrous acid in the presence of alkali: $NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2 + NaOH \longrightarrow NaNO_2 + H_2O + CH_2{:}CH{\cdot}NO_2 \longrightarrow$ polymer. Even very weak bases promote this reaction, which may be carried out with ammonia, the carbonates and bicarbonates of the alkali and alkaline-earth metals, urea, and some heavy-metal oxides such as zinc oxide. "Pyrex" containers are therefore preferable to ordinary soda-glass bottles for storage. The dispersion of a small amount of aromatic sulphonic acid in the melt greatly increases the stability of 1 : 2-dinitroethane, and samples containing 0·5% of the 1 : 5-disulphonic acids of either naphthalene or anthraquinone have been stored both at room temperature and at 50° for a year without appreciable change.

1 : 2-Dinitroethane is a powerful explosive, showing a power of 91·1% blasting gelatin in the mortar test.

It is insensitive to friction and impact, but is also very insensitive to initiation. It has been characterised by reduction to ethylenediamine and by mineral acid hydrolysis to hydroxylamine and oxalic acid.

2-*Nitroethanol*.—When pure, this is a colourless mobile liquid, b. p. 63°/*ca.* 0·5 mm., 102°/*ca.* 11 mm., $d_{4^\circ}^{20^\circ}$ 1·296, $n_D^{20^\circ}$ 1·443. It is somewhat hygroscopic. Although stable to storage and distillation when pure, care is essential in distilling impure samples at the beginning and end of distillation. It has an explosive power of 61·1% blasting gelatin and is very insensitive to friction, impact, and initiation.

2-Nitroethanol can be dehydrated to give monomeric nitroethylene which, however, instantly polymerises in the presence of a trace of alkali. It has been reduced to ethanolamine and has been further characterised through its esters and trityl ether and by comparison with 2-nitroethanol prepared by Wieland and Sakellarios's method (*loc. cit.*).

2-Nitroethyl nitrate, when pure, is a colourless mobile liquid, b. p. 74°/*ca.* 1 mm., $d_{4^\circ}^{20^\circ}$ 1·446, $n_D^{20^\circ}$ 1·455. It can be distilled under high vacuum, withstands heating in a vacuum at 100° for more than 20 hours, and has been stored at room temperature for more than two years without appreciable deterioration. It is a powerful explosive, giving values of 102% blasting gelatin in the mortar test when mixed with 7% soluble blasting gun-cotton. It is very insensitive to friction and impact, but can be detonated to high velocity. Like dinitroethane, it is converted by molar quantities of alkali into polymeric nitroethylene: $NO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2 + NaOH \longrightarrow NaNO_3 + H_2O + CH_2{:}CH{\cdot}NO_2 \longrightarrow$ polymer. It has been hydrolysed to nitroethanol and nitric acid and is further characterised by comparison with nitroethyl nitrate prepared according to Wieland and Sakellarios (*loc. cit.*).

EXPERIMENTAL.

Reagents.—Crude liquid dinitrogen tetroxide was obtained by refrigeration of gas from an ammonia-oxidation plant and rigorously purified by fractional distillation in a stream of oxygen at 30° to eliminate lower oxides and dissolved nitric acid. Nitric acid spray and moisture were removed from the vapour by passage through silica gel and phosphoric oxide. The pure substance was condensed as a clear white solid in receivers cooled to −70° by solid carbon dioxide–methanol. The receiver outlets were fitted with phosphoric oxide and calcium chloride drying tubes to prevent ingress of atmospheric moisture. Liquid tetroxide was obtained on allowing it to warm to room temperature and was stored in closed pressure bottles of glass or stainless steel.

Ordinary commercial ethylene and oxygen, both of sufficiently high purity, were taken from cylinders and dried by passage through calcium chloride before being mixed and delivered to the reaction vessel.

Nitration Apparatus and Method.—Standard batch preparations were made with a quantity of 3 l. of liquid tetroxide (about 4500 g.) contained in a round-bottomed 5-l. "Pyrex" flask cooled by a bath at 0°. Ethylene at 30 l./hr. and oxygen at 8 l./hr. were measured through rotary gas-meters, the volumes being corrected to atmospheric pressure by reference to manometers attached to the gas lines. After being dried and mixed, the gases were passed for 10½ hours into the liquid tetroxide through a sintered-glass spoon. Exit gases from the reaction flask were passed through receivers at −70° to trap the tetroxide, the volume then measured by rotary gas-meters, and the composition determined by gas analysis. Ground glass joints were used throughout and, where flexibility was necessary, *e.g.*, in the connection between reaction flask and tetroxide traps, joints were of the ball-and-socket type.

Out of 347·9 l. of ethylene passed, 228·5 l. were absorbed, the corresponding figures for oxygen being 81·3 and 24·4 l., respectively, all volumes being corrected to 20° and 760 mm. The amounts absorbed were in close agreement with the difference between the initial weight of tetroxide and the combined weight of the final reaction mixture and the tetroxide trapped.

Excess of tetroxide was removed from the reaction mixture by bubbling with dry air, and recovered by cooling to −70°; special care was taken to keep the mixture cool with a bath at 0° during the last stages of its removal. The residual pale yellow oil weighed 1153 g., which, reckoned completely as $C_2H_4O_4N_2$, represented an almost theoretical yield of crude oil on the ethylene absorbed.

Separation and Purification of Products.—The crude oil, which showed slow gas evolution, was added to 2 l. of methyl alcohol with stirring and cooling in a bath of solid carbon dioxide–methyl alcohol. On filtration, 408·4 g. of solid 1 : 2-*dinitroethane* were obtained. A further 13 g. were deposited from a second cooling. The yield on ethylene absorbed was 36·9%, and on tetroxide consumed 41·5%. Analysis after recrystallisation from methyl alcohol gave C, 20·1; H, 3·5; N, 23·2 ($C_2H_4O_4N_2$ requires C, 20·0; H, 3·3; N, 23·3%).

Methyl alcohol was distilled from the filtered solution, first at 15 mm. and finally at 1 mm. and 40°, leaving 613 g. (440 ml.) of a stable oil. This was subjected to double solvent washing by stirring with a mixture of 2·2 l. of benzene and 2·2 l. of water for a total period of 4 hours. Nitroethanol, which is practically insoluble in benzene, passed wholly into the water layer, and the nitroethyl nitrate into the benzene layer. Were it nor for the presence of small amounts of nitric acid, simple separation of the two layers would have sufficed, but this impurity necessitated intermittent withdrawal of the water layer for partial neutralisation so as to minimise solution of nitroethyl nitrate in the aqueous layer. Almost complete separation of the two components was achieved in this manner, with a final neutralisation of the aqueous layer before taking it off.

The aqueous layer was extracted continuously with ether for 48 hours, the ethereal extract dried (Na_2SO_4), and the ether distilled off at reduced pressure. The crude nitroethanol was fractionally distilled at *ca.* 1 mm. to give 142·2 g. of 2-nitroethanol and 13·1 g. of residue. The yield on ethylene was 16·4%, and on tetroxide 18·4%. Analysis after vacuum redistillation was C, 26·3; H, 5·6; N, 15·5 (Calc. for $C_2H_5O_3N$: C, 26·4; H, 5·5; N, 15·4%).

The benzene layer was dried and the benzene distilled off. The resulting oil was fractionally distilled at *ca.* 1 mm. to give 261·7 g. of 2-nitroethyl nitrate and 56·0 g. of residue, consisting partly of nitrate and partly of dinitroethane which are not included in the yields, but gave 14·3 g. dinitroethane on freezing in a large volume of methanol. The yield of nitroethyl nitrate on ethylene was 20·2% and on tetroxide 22·8%. Analysis after redistillation gave C, 20·7; H, 3·0; N, 17·9 (Calc. for $C_2H_4O_5N_2$: C, 20·6; H, 2·9; N, 17·7%).

Vacuum distillations of crude nitroethanol and crude nitroethyl nitrate required particular care, *i.e.*, slow rate of boiling, use of a dry carbon dioxide leak in place of the usual air leak, and occasional rapid cooling of the boiler with a solid carbon dioxide–methanol mixture kept at hand for use whenever gas evolution was marked. Redistillation of once-distilled materials, was, on the other hand, quite smooth and without difficulty.

Preparation of Derivatives.—Reduction of 1 : 2-dinitroethane to ethylenediamine was carried out in glacial acetic acid by using Adams's platinum catalyst and hydrogen at 80—100 atm. At concentrations above 2·6 g. of dinitroethane per 100 ml. of acetic acid, yields tended to be low apparently through interaction of amine and primary nitro-group, despite the use of an acid solvent. In one experiment 0·269 g. of dinitroethane in 45 ml. of glacial acetic acid was reduced at 90 atm. in the presence of 0·022 g. of catalyst. The acetic acid was then saturated with dry hydrogen chloride and distilled off, leaving ethylenediamine dihydrochloride which was washed with ethyl alcohol; yield 0·261 g., 87·6% (Found : C, 18·1; H, 7·4; N, 20·2; Cl, 54·5. Calc. for $C_2H_{10}N_2Cl_2$: C, 18·0; H, 7·5; N, 21·0; Cl, 53·4%).

Hydrolysis of 1 : 2-dinitroethane was best carried out by heating it with mineral acids other than nitric in a sealed tube at 150°. Hydrochloric, sulphuric, phosphoric, and even sulphonic acids could be used, but the highest yields were given by concentrated hydrochloric acid and 13 mins.' heating : the best method was to heat 0·301 g. of dinitroethane with 4·5 ml. of the acid, cool the mixture, and dilute it with 200 ml. of distilled water for analysis. One portion of the solution was boiled with at least 100% excess of ferric salt, air being excluded, and the ferrous ion titrated with standard dichromate, using an internal indicator, to give the hydroxylamine content. The result was confirmed on another portion by precipitating the hydroxylamine as copper salicylaldoxime complex (Ephraim, *Ber.*, 1930, **63**, 1928), regenerating hydroxylamine from the complex by boiling it with sulphuric acid, and estimating it as before. The estimated yield was 90·8% on the basis of 2 mols. of hydroxylamine per mol. dinitroethane. Oxalic acid was determined on a third portion by neutralising it with ammonia, precipitating calcium oxalate, and titrating with N/10-permanganate. Despite the heating to 150°, the yield was 47·3%.

Esters and Trityl Ether of 1-*Nitroethanol*.—The acetate, benzoate, and *p*-nitrobenzoate were prepared by reaction with the acid chlorides. Properties were as follows : Acetate, liquid, b.p. 70°/<1 mm. (Found : C, 36·3; H, 5·5; N, 10·8. Calc. : C, 36·1; H, 5·3; N, 10·5%); benzoate, m. p. 42—44°; p-*nitrobenzoate*, m. p. 100° after recrystallisation from ethyl alcohol (Found : C, 44·9; H, 3·4; N, 11·7. $C_9H_8O_6N_2$ requires C, 45·0; H, 3·3; N, 11·7%).

The *trityl ether* was prepared by refluxing 2 g. of 2-nitroethanol with 6·1 g. of triphenylmethyl chloride in 40 ml. of benzene for 11 hours. Part of the benzene was removed, the solution cooled, and 4·9 g. of crystals filtered off. After three recrystallisations from benzene, the ether had m. p. 162—164° (Found : C, 74·6; H, 5·8; N, 4·6. $C_{21}H_{19}O_3N$ requires C, 75·6; H, 5·7; N, 4·2%); the mixed m. p. with the ether (m. p. 160—162°) prepared from synthetic 2-nitroethanol was 160—162°.

Reduction of 2-nitroethanol to ethanolamine could be carried out in glacial acetic acid as for dinitroethane. Reduction in ethyl alcohol, however, permitted the preparation of more distinctive derivatives, *e.g.*, the picrate : 2·79 g. in 25 ml. of absolute alcohol were reduced at 100 atm. in the presence of 0·201 g. of Adams's catalyst for 5 hours, the catalyst filtered off, 6·8 g. of picric acid added, and the solution warmed and filtered; on standing overnight, 3·95 g. (44·4%) of the picrate were obtained; recrystallisation gave m. p. 157—159°, whereas the picrate obtained in identical manner from synthetic 2-nitroethanol (Wieland and Sakellarios, *loc. cit.*) had m. p. 157—160° and this was also the mixed m. p.

Polymeric nitroethylene from 2-*nitroethanol nitrate*. Both 1 : 2-dinitroethane and nitroethyl nitrate gave polymeric nitroethylene in good yield on reaction with alkali; *e.g.*, 10 g. of the nitrate were dissolved in 100 ml. of methanol and added with brisk stirring during 3 minutes to 6·7 g. of ammonium hydrogen carbonate dissolved in 100 ml. of water. The lachrymatory nitroethylene monomer first formed rapidly polymerised and, after 30 minutes' stirring, the polymer was filtered off, washed with dilute hydrochloric acid and water, and dried in a vacuum over phosphoric acid; yield 5·1 g. (84%) [Found : C, 32·9; H, 4·2; N, 19·1. Calc. for $(C_2H_3O_2N)_n$: C, 33·1; H, 4·2; N, 18·9%].

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