44. *Rubber, Polyisoprenes, and Allied Compounds. Part VII. Action of Nitric Oxide thereon.*

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The reaction of nitric oxide with the olefins *cyclo*hexene, 1-methyl*cyclo*hexene, dihydromyrcene, and rubber presents characteristics of a free-radical, chain reaction. In the products the molecular ratio of combined oxygen to nitrogen is considerably in excess of 1 : 1, the nitrogen atom being generally directly linked to carbon. In many instances definite nitro-compounds have been isolated, and a considerable part of the attack appears to proceed at the ethylenic carbon atoms, either by substitution or addition of NO_2 and N_2O_3 groups. The precise reaction mechanism is obscure.

ALTHOUGH the reactions of nitrogen dioxide, dinitrogen trioxide, and nitrosyl chloride with olefins have been studied extensively, the action of nitric oxide has received but little attention and it has in fact been stated (Sidgwick, " The Organic Chemistry of Nitrogen," 1937, p. 213) that it does not combine with a normal ethylenic linkage. Nitric oxide is, however, of well-established utility in the study of free-radical reactions, which it can promote, retard, or inhibit in virtue of its property of starting reaction chains, or stopping them by combination with other free radicals.

General Characteristics of the Reaction of Nitric Oxide with Olefins.—Characteristics of a free-radical mechanism were exhibited. For instance, when a solution of rubber, dihydromyrcene, 1-methyl*cyclo*hexene, or *cyclo*hexene was shaken in contact with nitric oxide there was generally an induction period of 15—30 minutes, depending on the intensity of the prevailing light, before any sign of reaction became evident. Then the solution acquired a pronounced green colour, absorption of nitric oxide commenced, and some heat was evolved. The induction period was not confined to the initial starting of the reaction, for if the reaction was stopped by removing the nitric oxide from the system and then, after a short interval, nitric oxide was readmitted, an induction period was again observed before reaction recommenced. Under the conditions employed, the reaction ceased owing to admixture by nitrogen produced in the reaction. When provision was made for removing the nitrogen, no difficulty was experienced in carrying the reaction as far as was desired, and it became obvious that absorption of nitric oxide could proceed far beyond one molecular proportion per double bond, and that the volume of nitrogen formed was generally between a third and a quarter of the volume of nitric oxide which had been absorbed at any given stage of the reaction. The formation of nitrogen in reactions of nitric oxide with free radicals (but not with olefins) has been reported by Nauta and Mulder (*Rec. Trav. chim.*, 1939, **58**, 1070) and by Sonneborn and Wiselogle (*J. Amer. Chem. Soc.*, 1942, **64**, 860), who attributed its formation to decomposition of an intermediate hyponitrite.

Obviously the reaction of nitric oxide with olefins does not proceed by any simple attachment of nitric oxide itself to the unsaturated molecule, and it is not surprising that a variety of products was isolated containing nitrogen in various states of combination with oxygen.

Reaction with Rubber.—Gorgas's observation (*Ber.*, 1930, **63**, 2700) that an insoluble nitrogenous product was precipitated by the action of nitric oxide on a rubber solution has been confirmed. This occurred at a stage represented by the absorption of approximately 1 mol. of nitric oxide per C_5H_8 unit, and the composition of the product corresponded with the introduction into half of the available C_5H_8 units of groups containing nitrogen and oxygen in the ratio 1 : 2 to 1 : 2·7, varying from one preparation to another. At a somewhat earlier stage the product could be separated into two components of approximate compositions $C_{10}H_{15}O_2N$ and $C_{10}H_{15}O_3N$. In the early stages of reaction there was considerable reduction of molecular size, by an obscure mechanism which required the absorption of a proportion of nitric oxide appreciably greater than the proportion of oxygen required to bring about a comparable reduction in molecular size (Farmer and Sundralingam, J., 1943, 125).

Reaction with Simpler Olefins allied to Rubber.—Dihydromyrcene and 1-methyl*cyclo*hexene yielded products which appeared to contain substituent nitro-groups, together with substances of rather lower oxygen : nitrogen ratio. In the formation of the former products the unsaturation was considerably affected, being much lower than that calculated for simple nitro-substituted olefins.

*cyclo*Hexene yielded the following products : (1) the already known crystalline *cyclo*hexene *pseudo*-nitrosite * (Baeyer, *Annalen*, 1894, **278**, 110; Wieland, *ibid.*, 1921, **424**, 71), (ii) a mixture of isomeric nitro*cyclo*hexenes containing a considerable proportion of 1-nitro*cyclo*hexene, and (iii) an unstable, non-distillable, viscous oil constituting the major product. Partial separation of the isomeric nitro*cyclo*hexenes yielded a fairly pure sample of the 1-nitro-isomer but the other isomer, in all probability 3-nitro*cyclo*hexene, could not be isolated in a pure state since it underwent considerable decomposition in the presence of alkali (cf. the instability of α-methylene-substituted halogen; preceding paper). The constitution of the 1-nitro*cyclo*hexene was established by oxidation to adipic acid and by reduction to *cyclo*hexanoneoxime, the latter reaction probably proceeding through the intermediate *cyclo*hexenylhydroxylamine (cf. the reduction of nitro*cyclo*hexane to *cyclo*hexylhydroxylamine), or possibly by direct 1 : 4-addition of hydrogen to the C:C·N:O system. As was expected from the presence on the ethylenic carbon atom of a strongly polar group, capable of forming a conjugated system with the ethylenic linkage, addition of iodine chloride to the $>C=C<$ bond was almost completely inhibited, but the additive capacity for hydrogen established the presence of the ethylenic linkage. Spectrographic examination by Dr. H. P. Koch, for which the authors' thanks are due, has confirmed the presence of considerable conjugation in the 1-nitro*cyclo*hexene component of the mixture (Fig. 1). The other nitro*cyclo*hexene which was present exhibited a much more satisfactory additive capacity for iodine chloride. The constitution of the major non-volatile reaction product has not been established; it was a unimolecular substance exhibiting no additive capacity for iodine chloride, with groups containing oxygen and nitrogen in a ratio slightly in excess of 2 : 1 added or substituted at the original ethylenic linkage of the *cyclo*hexene; treatment with alkali gave a crystalline product of higher nitrogen content than the original oil, suggesting the presence of stable carbon–nitrogen linkages.

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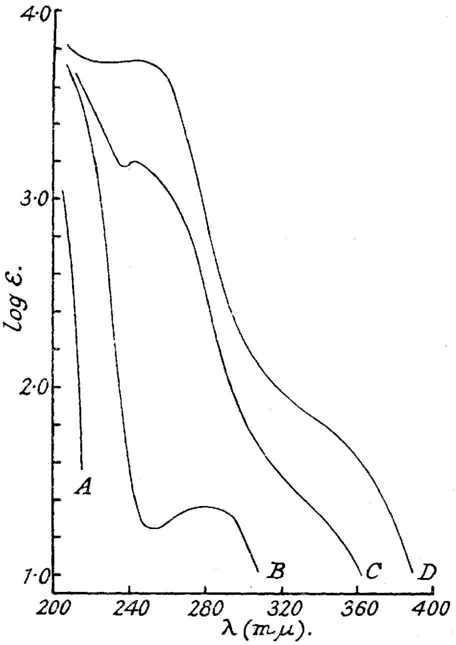
* The bimolecular structure proposed by Wieland has been confirmed by *X*-ray examination (p. 123).

The principal characteristics of the reaction under consideration are therefore: (1) Various products are formed; all contain nitrogen directly linked to carbon, and the nitrogen is combined with oxygen in the proportion **1 : 2**, **2 : 3**, or **1 : 3**; several of the products are identical with those known to be formed by the action of higher oxides of nitrogen on the corresponding olefin. (2) At least 1 mol. of nitrogen is formed for every 4 mols. of nitric oxide reacting. (3) When substitutive reaction is taken into account, the H : C ratio is substantially preserved. (4) The ethylenic carbon atoms are extensively involved in substitutive and additive reactions. (5) The reaction is inhibited by alcohol or acetic acid.

FIG. 1.



A.—*cyclo*Hexene.
B.—Nitro*cyclo*hexane.
C.—Mixture of isomeric nitro*cyclo*hexenes.
D.—1-Nitro*cyclo*hexene (mainly).

Since most of the reaction products are precisely those obtained by the action of higher oxides of nitrogen or of nitrous acid, it is likely that reaction proceeds by conversion of the nitric oxide into a higher state of oxidation, probably by a free-radical chain mechanism involving the hydrocarbon. The attack at the ethylenic carbon atoms may be closely related to the preferential attack of free halogen radicals at these carbon atoms (preceding paper). Any such reaction must occur in the liquid phase, since brown fumes in the gas phase were not observed; the presence of nitrous acid or, more probably, dinitrogen trioxide in the liquid phase was, however, detected by Sonneborn and Wiselogle's procedure (*loc. cit.*) during the course of the reaction. If nitrous acid itself is formed, it must become involved in a course of reaction other than the usual formation of ψ-nitroles with those secondary nitro-groups already present. The formation of some of the reaction products is satisfied by overall reactions of the type represented by the equations

$$(a)\quad RH + 4NO = RNO_2 + N_2 + HNO_2 \text{ or}$$
$$2RH + 8NO = 2RNO_2 + 2N_2 + N_2O_3 + H_2O$$

$$(b)\quad >C{:}C< + N_2O_3 = >C(NO)\cdot\overset{|}{\underset{|}{C}}(NO_2)$$

$$(c)\quad 2RH + 10NO = 2RNO_3 + 3N_2 + 2HNO_2 \text{ or}$$
$$2RH + 10NO = 2RNO_3 + 3N_2 + N_2O_3 + H_2O.$$

EXPERIMENTAL.

(Microanalyses were carried out by Dr. W. T. Chambers and Miss H. Rhodes.)

Reactions were conducted either in a glass globe or in a small flask fitted with a sintered-glass distributor through which gas could be passed, first from reservoir *A* into reservoir *B* (Fig. 2), and then back into *A* by manipulation of the stopcocks and application of nitrogen pressure to the reservoirs. The apparatus was first swept out with purified nitrogen, then evacuated until the solvent had boiled vigorously for a few minutes under the reduced pressure, refilled with nitrogen, re-evacuated, and finally filled with nitric oxide obtained from sodium nitrite, potassium ferrocyanide, and acetic acid. The gas remaining at the conclusion of an experiment was displaced into a measuring system and, after removal of any nitric oxide with aqueous potassium permanganate, the volume of residual nitrogen was measured.

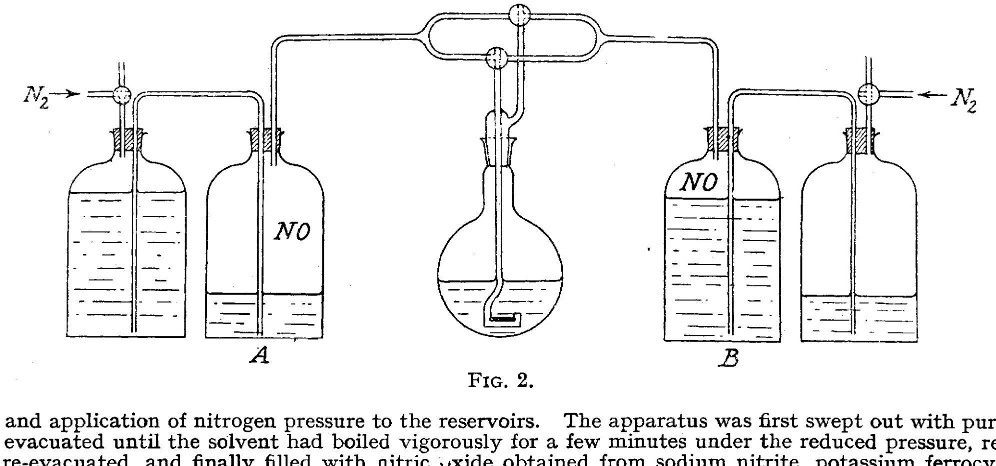


FIG. 2.

Experiments with Rubber.—The hydrocarbon (sol rubber, 5 g.) was dissolved in carbon tetrachloride (300 c.c.); reaction required 30—120 mins. The results are in the table.

*Experiments with Dihydromyrcene and 1-Methyl*cyclo*hexene.*—Dihydromyrcene (15·6 g.) in carbon tetrachloride (150 c.c.) was shaken with nitric oxide (1888 c.c., N.T.P.) in the glass globe during 8 hours in diffused sunlight. The residual gas (588 c.c.) contained a little nitric oxide (38 c.c.), whence the nitric oxide consumed and the nitrogen formed were equivalent to 0·73 mol. and 0·22 mol. respectively per mol. of dihydromyrcene. A little yellow resin was precipitated. The yellow supernatant solution yielded on distillation unreacted dihydromyrcene (10·8 g.), a liquid fraction, b. p. 66—70°/0·001 mm. (0·6 g.), and considerable residue (4·1 g. Found: C, 55·55; H, 8·5; N, 11·6%; *I.V.*, *Reaction of Nitric Oxide with Rubber.*

NO consumed, mols per C_5H_8 unit.	N_2 formed, mols. per mol. NO.	Analysis of product, %.					Solubility of product.
		C.	H.	N.	O.	*I.V.*	
0·13	—	84·2	11·3	—	—	—	Soluble
0·15	0·28	83·9	11·3	1·65	3·2	—	,, *
0·19	0·23	83·15	11·1	—	—	—	,,
0·48	0·25	76·0	10·15	4·2	9·65	262	,, †
0·94	0·24 ‡	—	—	—	—	—	,,
0·95	0·29	68·7	9·05	6·0	16·25	220	Partly insol.
ca. 1·0	—	63·25	8·45	7·85	20·3	—	Insol.
ca. 0·9	—	68·0	8·9	6·95	16·15 §	—	Insol. part, 74% of product
		60·7	7·85	6·85	24·6 ‖	—	Soluble part, 26% of product
1·35	0·29 ‡	—	—	—	—	—	Insol.

* Intrinsic viscosity 0·74 in benzene + 15% methanol; mol. wt. 74,000 (original mol. wt. 238,000).

† Intrinsic viscosity 0·57 in benzene; mol. wt. 33,000 (original mol. wt. 220,000).

‡ In these experiments the absence of carbon dioxide in the residual gas was demonstrated by passage of the latter through a weighed CO_2-absorption tube.

§ Empirical formula $C_{10}H_{15·6}(NO_2)_{0·9}$.

‖ Empirical formula $C_{10}H_{15·4}NO_3$.

79, corresponding to $C_{10}H_{18}O_{3·3}N_{1·8}$). The liquid fraction was probably a *nitrodihydromyrcene* [Found: C, 65·6; H, 9·4; N, 7·7; *I.V.*, 156. $C_{10}H_{17}O_2N$ requires C, 65·5; H, 9·35; N, 7·65%; *I.V.*, 277 $(|\overline{_2})$, 139 $(|\overline{_1})$].

1-Methyl*cyclo*hexene similarly yielded a liquid product, b. p. 50°/0·01 mm., probably a *nitromethyl*cyclo*hexene* (Found: C, 59·3; H, 8·0; N, 10·0; *I.V.*, 73. $C_7H_{11}O_2N$ requires C, 59·55; H, 7·85; N, 9·9%; *I.V.*, 180), and some viscous residue.

Reaction with cyclo*Hexene.*—Nitric oxide equivalent to 1·6 mols. per mol. of *cyclo*hexene was consumed during 15 hours in a dull light, with formation of 0·44 mol. of nitrogen; a white, crystalline solid separated continuously from the commencement of the reaction. This (2·44 g.) was filtered off and the filtrate yielded on distillation a pale yellow liquid, b. p. 33—46°/0·01 mm. (*ca.* 6 g.), and considerable residue (14·4 g.).

Crystalline solid. This was *cyclo*hexene *ψ*-nitrosite, m. p. 153° (decomp.) from benzene, mixed m. p. with authentic specimen 153° (decomp.) (Found: C, 45·55; H, 6·35; N, 17·5; *I.V.*, 0. Calc. for $C_6H_{10}N_2O_3$: C, 45·55; H, 6·35; N, 17·75%); recrystallisation from chloroform–alcohol separated it into triclinic needles, m. p. 153° (decomp.), $d_{4°}^{20°}$ 1·389, and monoclinic prisms. m. p. 153° (decomp.), $d_{4°}^{20°}$ 1·378.

Note on crystal structure of cyclo*hexene nitrosites* (by G. A. JEFFREY). The triclinic needles had cell dimensions $a = 7·19$ A., $b = 10·20$ A., $c = 5·15$ A., $\alpha = 90°$, $\gamma = 98°$, $\beta = 104·5°$, whence the calculated density for $2(C_6H_{10}N_2O_3)$ was 1·35. The space group may be *P*1 with an asymmetric dimeric molecule, or *P*1 with two monomers or one centrosymmetric dimer. These dimensions, particularly the short *c* axis, impose certain limitations on the choice of possible configurations for this compound. About 3·3 A. being allowed as the nearest approach of atoms in adjacent molecules between which there are only ordinary van der Waals forces, it follows that the width of the molecules along any line parallel to the *c* axis must not exceed about 2·2 A. For the monomeric nitrosite there are a number of configurations to consider depending upon the positions of the NO_2 and NOH groups and the shape of the ring. Two such arrangements, one with a Sachse boat-shaped ring and the other with the chair-shaped ring, would give the necessary flat molecules, but neither of these could be packed into the unit cell without a much closer association than 3 A. between atoms of adjacent molecules. The triclinic form must therefore be dimeric.

The monoclinic prisms had cell dimensions $a = 11·44$ A., $b = 12·28$ A., $c = 11·06$ A., $\beta = 101° 21'$, whence the density calculated for 4 dimeric or 8 monomeric molecules in the cell was 1·36. The space-group was $P2_1/c$. Although the cell dimensions give little guide to the molecular shape, there is scarcely sufficient room to accommodate eight monomeric molecules and four dimers seems the more likely.

Consideration of the configurations for the dimeric molecules is complicated by uncertainty of the true nature of the associating link (cf. Sidgwick, *op. cit.*, p. 214). For the triclinic form, only a molecule with the C–N (nitro) bonds approximately in the plane of the ring is consistent with the short axis, and for the monoclinic prisms a stereoisomeric arrangement with the nitro-group projecting out of the plane is possible.

Liquid product. This appeared to be a mixture of isomeric nitro*cyclo*hexenes (Found: C, 56·6; H, 7·15; N, 11·3; *I.V.*, 75. Calc. for $C_6H_9O_2N$: C, 56·7; H, 7·15; N, 11·0%; *I.V.*, 200), the presence of the nitro-group being indicated by the following facts: (1) Close resemblance to authentic nitro*cyclo*hexenes prepared by two different methods (see below). (2) The blue colour characterising a secondary nitro-group was observed on treatment with nitrous acid. (3) The active hydrogen content (*ca.* 0·1%), which probably arose from partial isomerisation of the nitro-group, was much too low to permit of the presence of a hydroxyl group. (4) No derivatives characterising a carbonyl or a hydroxyl group could be obtained. (5) cyclo*Hexyl nitrite* (Found: C, 56·2; H, 8·8; N, 10·8. $C_6H_{11}O_2N$ requires C, 55·75; H, 8·6; N, 10·8%), prepared by the action of nitrous acid on *cyclo*hexanol, had a considerably lower b. p. (<30°/13 mm., 41°/20 mm.) than the liquid under consideration. (6) Reduction with zinc dust in acetic acid gave a 30% yield of *cyclo*hexanone-oxime, m. p. 75—79°, mixed m. p. with authentic specimen (m. p. 84—85°) 79—81° (Found: C, 63·1; H, 9·65; N, 12·3. Calc. for $C_6H_{11}ON$: C, 63·2; H, 9·7; N, 12·3%). Reduction of nitro*cyclo*hexane under the same conditions yielded cyclo*hexylhydroxylamine*, m. p. 137° (Found: C, 62·6; H, 11·4; N, 12·1. $C_6H_{13}ON$ requires C, 62·55; H, 11·4; N, 12·15%), which was sparingly soluble in water (solution feebly alkaline). (7) Hydrogen uptake was 7 atoms per mol. with Adams's catalyst, 8 atoms per mol. with Raney nickel. (8) The ultra-violet absorption spectrum (curve *C*, Fig. 1) established the presence of considerable conjugation. (9) To 3·4 g. of the liquid, stirred with 2N-sodium hydroxide (14 c.c.), was added a 3% solution of potassium permanganate (315 c.c.) at 0—20°; the yield (1·3 g.) of adipic acid, m. p. 151°, mixed m. p. 151° (Found: C, 49·5; H. 6·95; equiv., 73. Calc. for $C_6H_{10}O_4$: C, 49·3; H, 6·9%; equiv., 73), established the presence of at least 40% of 1-nitro*cyclo*hexene in the sample. (10) 1-Nitro*cyclo*hexene was partly separated from the accompanying isomer by shaking with cold N-sodium hydroxide, in which 1-nitro*cyclo*hexene was known to be insoluble, and then extracted with ether. The alkali-insoluble portion had b. p. 35—36°/0·01 mm., and 1·0 g. gave 0·8 g. of adipic acid (equivalent to 0·7 g. of nitro*cyclo*hexene) on oxidation as above; (Found: C. 56·65; H, 7·3; N, 10·7%; *I.V.*, 23). (For ultra-violet absorption spectrum see curve *D*, Fig. 1.) The alkali-soluble portion, b. p. 30—42°/0·01 mm., had undergone partial hydrolysis * [Found: C, 61·2; H, 7·7; N, 8·5; *I.V.*, 119. Calc. for mixture of 75% $C_6H_9·NO_2$ and 25% $C_6H_9·OH$ (?): C, 60·9; H, 7·7; N, 8·5%; *I.V.*, 215].

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* A high order of reactivity of groups substituted at the 3-position of *cyclo*hexene has already been observed in halogen-substitution products (preceding paper).

Examination of other specimens of nitrocyclohexene. 1-Nitro*cyclo*hexene, b. p. 45—50°/0·1 mm. (Found : C, 56·0; H, 7·53; N, 10·8%; *I.V.*, 29), prepared according to Wieland (*loc. cit.*), was insoluble in N-sodium hydroxide; 1·9 g. gave 1·1 g. of adipic acid on oxidation, and the hydrogen uptake (Adams's catalyst) was 7 atoms per mol. 3(?)-Nitro*cyclo*hexene, b. p. 34°/0·01 mm. (Found: C, 56·25; H, 7·1; N, 10·9%; *I.V.*, 155), prepared by the action of alkali on *cyclo*hexene *ψ*-nitrosite (Wieland) was soluble (with partial hydrolysis *) in N-sodium hydroxide; 0·8 g. gave 0·15 g. of adipic acid, corresponding to the presence of 16% 1-nitro*cyclo*hexene, and the hydrogen uptake (Adams's catalyst) was 7·5 atoms per mol.

Residue. This slowly decomposed at room temperature and could not be distilled without severe decomposition. An effective separation from *cyclo*hexene *ψ*-nitrosite was achieved by dissolution in methanol at 0°, in which the nitrosite was insoluble; removal of the alcohol gave a brown viscous oil. The products of four separate reactions were remarkably constant in composition [Found : C, 44·6±0·5; H, 6·1±0·1; N, 13·9±0·1%; *I.V.*, 4; *M* (f. p. depression in benzene), 164], which corresponded to the formula $C_6H_{10}O_{3\cdot6}N_{1\cdot6}$. Oxidation of 4·6 g. with alkaline permanganate (3%, 270 c.c.) proceeded only slowly and yielded an unidentified neutral oil (0·55 g.) and adipic acid (1·7 g.). Oil (5·4 g.) in alcoholic potassium hydroxide (100 c.c., 0·82N) at the b. p. for 15 mins. yielded a large and a small portion respectively soluble and insoluble in alkali. Distillation of the former yielded a little impure nitro*cyclo*hexene, b. p. 40—47°/0·1 mm. (Found: C, 57·1; H, 7·4; N, 10·6. Calc. for mixture of 96·75% $C_6H_9{\cdot}NO_2$ and 3·25% $C_6H_9{\cdot}OH$: C, 57·15; H, 7·25; N, 10·5%), and a considerable residue from which an unidentified crystalline *solid* separated, m. p. 107—108° from benzene (Found: C, 46·0; H, 5·15; N, 17·7. $C_6H_8O_3N_2$ requires C, 46·1; H, 5·15; N, 17·95%).

The reaction of nitric oxide with *cyclo*hexene did not proceed in alcoholic solution, or in a medium containing acetic acid. Nitric oxide did not react with nitro*cyclo*hexene in carbon tetrachloride.

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