[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

AN INTERMEDIATE IN THE NITROLYSIS OF 1,3-DICYCLOHEXYLIMIDAZOLIDINE

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The nitrolysis of 1,3-dicyclohexylimidazolidine dinitrate (I, R = C_6H_{11}) is of interest because it shows that the reaction is not limited to tertiary amines such as hexamethylenetetramine which contain only methyleneimine groups. A further interest accrues because the nitrolysis of I is relatively slow and thus more amenable to study than that of hexamethylenetetramine. The initial product of nitrolysis was shown to be N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (VI) (1). Formaldehyde seemed to be released simultaneously with nitrolysis, and nitrate-esterification of intermediate methylolamine did not seem to occur.

It was shown later (4) that when chloroform was included in the nitrolysis system the products were N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane and N-formyl-N′-nitro-N,N′-dicyclohexyl-1,2-diaminoethane. It has now been found that when the nitrolysis is effected initially at −10° an intermediate may be isolated.

The empirical formula for this compound, $C_{15}H_{30}N_6O_{11}$, shows that it comprises the elements of two molecules of nitric acid and one of nitrogen pentoxide per mole of dicyclohexylimidazolidine. This is expressed by structure II. There is presently no evidence for a more detailed structure such as N-nitro-N-nitroxymethyl-N,N′-dicyclohexyl-1,2-diaminoethane dinitrate since the reagents which are known to characterize a nitroxymethylene group (sodium acetate in acetic acid or anhydride and hot methanol) served only to regenerate I or its hydrolysis product, N,N′-dicyclohexyl-1,2-diaminoethane dinitrate (V).

Indeed the intermediate behaves as if it were the diammonium salt, dicyclohexylimidazoline dinitrate (I) to which is coördinated a molecule of nitrogen pentoxide. In some respects the latter moiety seems to act like nitronium nitrate. Thus the intermediate represented by structure II is effective in the conversion of phenol to *p*-nitrophenol, N,N-dimethylaniline to *p*-nitrodimethylaniline and, most significantly, imino-*bis*-acetonitrile to its nitrimino analog (VII). In each case the dinitrate, V, is also formed [as might be expected under these reaction conditions since it is a known decomposition product of I (1)]. However the intermediate, II, which is capable of nitrating other substances, will not undergo self-nitrolysis. Thermal decomposition yields only nitric acid, formaldehyde, and N,N′-dicyclohexyl-1,2-diaminoethane dinitrate (V). This resistance toward nitrolysis may be explained by the assumption that II is a diammonium salt, a proton of which is not displaced by the nitronium nitrate with which it is coördinated.

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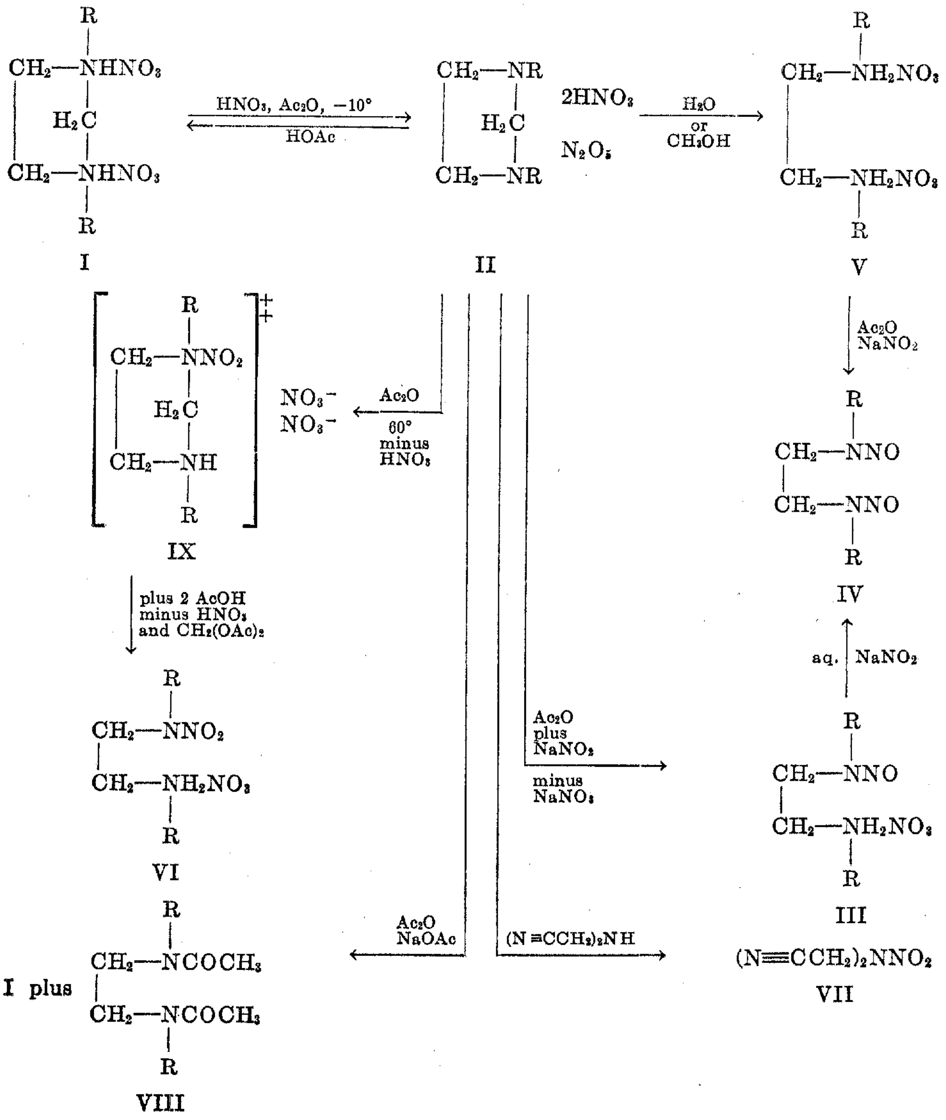
The situation is different in acetic anhydride. At 60° in this medium an efficient conversion of the intermediate, II, to N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (VI) occurs. Because of the various equilibria prevailing in the system: nitric acid-acetic anhydride, this conversion may be expressed in several ways. We have described it as an initial interchange of a cation in the diammonium salt, II, to form a monoammonium-mononitronium salt, IX, with release of a molecule of nitric acid. This nitric acid will react with acetic anhydride with formation of acetic acid.



$$Ac_2O + HNO_3 \rightleftarrows AcOH + AcNO_3$$
$$Ac_2O + 2\ HNO_3 \leftrightarrows 2\ AcOH + N_2O_5$$

The acetic acid in turn may be expected to solvolyze the imidazolidonium ion to release nitric acid and formaldehyde, wholly or partly as its diacetate.

The alternative possibility that II is converted by acetic anhydride to the free amine corresponding to I, namely dicyclohexylimidazolidine, which then is attacked by nitronium nitrate or acetate, is less likely. In this event one might expect acetylation to occur with formation of N-nitro-N′-aceto-1,2-diaminoethane or *sym*-N,N′-diacetaminoethane. These compounds are formed when dicyclohexylimidazolidine dinitrate alone is treated at 60° with acetic anhydride (1). However these aceto derivatives are not detectable products of the reaction of II with acetic anhydride unless sodium acetate is included as a means of eliminating the elements of nitric acid from the system.

The possibility that the formation of N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (VI) from II in acetic anhydride might initially involve solvolysis to N,N′-dicyclohexyl-1,2-diaminoethane dinitrate (V) is also unlikely. Nitration of V to VI ordinarily requires a catalytic amount of chloride catalyst, which must be increased to a molar equivalent if V is to be converted to N,N′-dicyclohexyl-1,2-dinitraminoethane (2). Nevertheless one cannot exclude the possibility that the mononitro derivative, VI, might be formed from activated V at the instant of its formation by hydrolysis of II. This postulation would not be vitiated by the absence of N,N′-dicyclohexyl-1,2-dinitraminoethane among the products from II in acetic anhydride, because of the proven difficulty of formation of the dinitro derivative.

If such a prior solvolysis of II occurred, the postulation of the ionic structure IX would have no significance. However, support for the concept of structure IX is afforded by analogy with the nitrosation of II. When the intermediate, II, was treated with more than two equivalents of sodium nitrite in acetic anhydride only the mono-nitroso derivative, N-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (III) was isolable. None of the N,N′-dicyclohexyl-1,2-dinitrosaminoethane (IV) was found. On the other hand, IV was isolated in good yield when N,N′-dicyclohexyl-1,2-diaminoethane dinitrate was treated with sodium nitrite in acetic anhydride. Of course this behavior reflects the greater stability of the typical nitrosonium ion over that of the nitronium ion type. Furthermore such behavior indicates maintenance of the imidazolidine ring until the time that substitution of nitro or nitroso actually occurs, and thus seems to justify the postulation of structure IX.

EXPERIMENTAL[2]

1,3-Dicyclohexylimidazolidine dinitrate-nitrogen pentoxide complex (II). To 21 ml. (0.5 mole) of absolute nitric acid at −10° to −5° was added dropwise with stirring (at a rate which maintained the initial temperature with efficient cooling) a solution of 5.9 g. (0.025

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[2] Melting points have been corrected against reliable standards. All x-ray diffraction was carried out with Cu K_α (Ni filtered) radiation and is recorded in relative intensities $[I/I_0]$ for d spacings in Å.

mole) of N,N′-dicyclohexylimidazolidine in 25 ml. of chloroform (ethanol-free and dry). When solution was complete 100 ml. (1.03 mole) of distilled acetic anhydride was added as rapidly as was possible in order to maintain the initial temperature. After addition was complete the suspension was stirred ten minutes at −10°, then filtered and the unwashed solid immediately transferred to a desiccator and dried for 150 minutes at 25° (0.1 mm.). The yield was 9.5 g. (81%) of white crystals melting at 121–122° (decomp.). Further drying at 55° raised this melting point to 121–123° (decomp.). The compound could be crystallized by rapid solution in ethyl nitrate but this did not enhance its purity. A comparable yield of product was obtained when chloroform was not included in the reaction mixture, but the melting point was 116–121°.

Anal. Calc'd for $C_{15}H_{30}N_6O_{11}$: C, 38.3; H, 6.43; N, 17.9.
Found: C, 38.1; H, 6.83; N, 17.7.

The principal x-ray diffraction spacings are: [10] 4.19; [9] 12.53; [8] 8.48; [7] 6.17; [6] 9.11, 2.97, 2.84; [5] 10.64, 4.52, 3.74; [4] 3.12; [3] 3.30; [2] 3.95, 3.68, 3.42; [1] 6.70, 5.40, 5.08.

If, instead of isolating II, the nitrolysis mixture was warmed to 15–45° over seven hours when chloroform was present the main products were N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane and the N-nitro-N′-formyl analog (4).

N-Nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (VI). To 10 ml. (1.02 mole) of acetic anhydride at −5° was added 2.0 g. (0.00425 mole) of II. This stirred suspension was quickly warmed to 60° to dissolve the solid within one minute, then cooled at once to 0° and drowned with 8 vols. of ethyl ether. A crude yield, m.p. 172–174° of 1.39 g. (99%) was filtered off. Crystallization from 10% nitric acid raised the m.p. to 176–177° with 4% loss. The product was identified by mixture melting point.

N-Nitroso-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (III). *A. In acetic anhydride.* To 15 ml. (0.154 mole) of acetic anhydride at 0° was added with stirring 0.38 g. (0.0055 mole) of sodium nitrite and then 1 g. (0.0021 mole) of II. After ten minutes at 35° the mixture was filtered to remove sodium nitrate. When three volumes of ethyl ether were added to the filtrate 0.35 g. (52%) of III was precipitated, m.p. 150–151°. Repeated crystallization from ethanol and from acetone-ether raised the m.p. to 151–152° (decomp.). When three equivalents of sodium nitrite were employed the crude yield (m.p. 147–149°) was raised to 84%. Crystallization from 5% nitric acid raised this melting point to 151–152°.

B. In water. A solution of 0.21 g. (0.003 mole) of sodium nitrite in 5 ml. of water was stirred at 25° while 0.79 g. (0.0017 mole) of II was added during seven minutes. There was no apparent solution, but the solid which was filtered off after two hours melted at 143–147° (decomp.). The mixture melting point and x-ray diffraction pattern showed this product to be identical with that prepared in acetic anhydride. The yield was 0.26 g. (48%).

X-ray diffraction: [10] 3.98; [8] 4.74, 4.33; [7] 5.90; [5] 3.72; [4] 5.15; [3] 2.05; [2] 3.11, 2.89; [1] 2.67, 2.49.

Anal. Calc'd for $C_{14}H_{28}N_4O_4$: C, 53.1; H, 8.94; N, 17.7.
Found: C, 53.1; H, 8.91; N, 17.7.

N,N′-Dinitroso-N,N′-dicyclohexyl-1,2-diaminoethane (IV). *A. From N,N′-dicyclohexyl-1,2-diaminoethane dinitrate* (V). To 15 ml. (0.154 mole) of acetic anhydride at −10° was added 1.2 g. (0.0171 mole) of sodium nitrite and 2.0 g. (0.0057 mole) of V. This stirred suspension was warmed slowly to 25° and maintained at that temperature for one hour. After removing the solvent at 8 mm. the dry residue was extracted with hot absolute ethanol. The filtered extract when cooled precipitated 1.28 g. (80%) of dinitroso derivative, m.p. 144–145°, identical with that prepared in aqueous solution.

B. From N-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (III). Compound III was nitrosated in 92.5% yield by the method (1) previously used for nitrosation of VI.

Thermal decomposition of II. Compound II (2 g.) was spread in a 125-ml. Erlenmeyer flask connected to a Dry Ice trap. After two hours at 50° (0.2 mm.) the substance was unchanged in appearance and melting point. After four hours at 85–90° (0.2 mm.) the sample had decomposed to a distillate of nitric acid and formaldehyde and a residue from which N,N′-dicyclohexyl-1,2-diaminoethane dinitrate (V) could be isolated in 30% yield after crystallization from 10% nitric acid.

Solvolysis of II. A. In water. Compound II (1 g.) in 10 ml. of water was steam-distilled until formaldehyde evolution was negligible. The 15 ml. of distillate was treated with 200 ml. of saturated dimedone solution (5) to yield 0.484 g. (78%) of the formaldehyde derivative, m.p. 189–190°. The available nitric acid from the hydrolysis of II was determined by boiling a solution of 0.2 g. in 75 ml. of 0.25% aqueous sulfuric acid for five minutes and then precipitating nitrate ion with excess of nitron reagent. The yield of nitron nitrate was 92.2% (92.4, 92.4, 91.4), or 3.69 mole-equivalents.

B. In acetic acid. When II was added to hot acetic acid it dissolved with a slight yellow color. The solution was cooled quickly. The crystals which separated were filtered off and washed with acetic acid and ethyl ether, m.p. 144–145° (decomp.). This melting point was raised to 146–148° (decomp.) by quick crystallization from acetic acid. The compound was identified by mixture melting point and by comparison of its x-ray diffraction pattern with that of N,N-dicyclohexylimidazolidine dinitrate (I): [10] 3.93, 4.52; [9] 4.82; [8] 3.07; [7] 5.36, 10.6; [6] 6.46; [5] 5.81; [4] 3.60; [3] 2.97, 3.40; [2] 2.40; [1] 1.77. In this connection it should be pointed out that compound I was incorrectly designated as the mononitrate in the original communication (1).

C. In acetic acid with sodium acetate. A mixture of 4.70 g. (0.01 mole) of II and 1.64 g. (0.02 mole) of sodium acetate in 10 ml. of glacial acetic acid was shaken for ten hours, then filtered to remove 4.25 g., m.p. 150° (decomp.). The x-ray diffraction pattern showed that this was a mixture of sodium nitrate and N,N-dicyclohexylimidazolidine dinitrate (I). Dilution of the filtrate with an equal volume of ether precipitated 0.38 g. of N,N-dicyclohexyl-1,2-diaminoethane dinitrate (V), m.p. 190°.

D. In acetic anhydride with sodium acetate. To a solution of 3.28 g. (0.04 mole) of sodium acetate in 40 ml. of acetic anhydride at 70° was added 4.70 g. (0.01 mole) of II. After five minutes the mixture was allowed to cool spontaneously and was filtered two hours later. After having been washed with acetic anhydride, acetic acid, and absolute ether the remaining sodium nitrate weighed 3.19 g. (94% of total nitrate).

The filtrate was evaporated *in vacuo* and the residual oil was taken up in absolute ether in order to separate it from 0.125 g. of sodium acetate. Evaporation of the ether left 3.82 g. of red oil which was dissolved in 70 ml. of absolute ethanol. After chilling to −60° this solution was treated with 1.4 ml. of absolute nitric acid. The precipitate, wt. 1.5 g., was found by mixture melting point (149°) and by comparison of the x-ray diffraction powder pattern to be N,N-dicyclohexylimidazolidine dinitrate (I). Thus at least 40% of the II used in this experiment had simply lost the elements of nitric anhydride.

The ethanolic filtrate was evaporated to a small volume. The crystals which precipitated weighed 0.5 g., m.p. 144–152°. After crystallization from ethanol (m.p. 149–152°) this product (16% yield) was shown by mixture melting point with an authentic sample (m.p. 154–154.5°) (1) to be N,N-diaceto-N,N-dicyclohexyl-1,2-diaminoethane (VIII).

E. In methanol. A suspension of 15.2 g. (0.032 mole) of II in 300 ml. of methanol was dissolved, boiled for ten minutes, and then chilled. The precipitate (7.61 g.) was found by mixture melting point (186°) and by x-ray diffraction pattern to be N,N-dicyclohexyl-1,2-diaminoethane dinitrate (V): [10] 4.53, 3.91; [9] 4.98; [8] 2.06; [7] 5.43; [5] 2.98; [4] 4.19, 3.35, 2.69; [3] 1.79; [2] 2.25; [1] 2.49.

In addition to this 68% yield, the filtrate, evaporated *in vacuo* to a volume of 45 ml., yielded 2.81 g. of N,N'-dicyclohexylimidazolidine dinitrate, m.p. 152° (decomp.). This 24% yield was identified by crystallization from water or methanol which converted it to N,N'-dicyclohexyl-1,2-diaminoethane dinitrate (m.p. 192°) with evolution of formaldehyde.

The methanolic filtrate was further reduced by vacuum evaporation from 45 ml. to a volume of 5 ml. in a search for esters of formaldehyde hydrate. The final liquid boiled at 35–45° (17 mm.), n_D^{20} 1.3881, d_4^{20} 1.25. It contained 48% of nitroxy group according to analysis with nitron, but no formaldehyde could be detected with dinitrophenylhydrazine or dimedone.

F. In methanol plus sodium acetate. To a solution of 4.1 g. (0.05 mole) of sodium acetate in 150 ml. of methanol was added 7.9 g. (0.017 mole) of II. The whole was shaken until solution was complete. After three hours the mixture was evaporated *in vacuo* to a volume of 50 ml., and 50 ml. of ethyl ether was added. The sodium nitrate thus precipitated weighed 4.1 g. or 95% of the expected amount. The filtrate was evaporated to 10 ml. and then diluted with 100 ml. of ethyl ether. The crystal crop, m.p. 170–192°, wt. 2.0 g., was crystallized from 25 ml. of hot methanol. It then melted at 218° (decomp.).

Anal. Calc'd for $C_{14}H_{30}N_4O_6$: C, 48.0; H, 8.63; N, 16.0.
Found: C, 47.8; H, 8.85; N, 15.8.

When this product which gave a positive brucine test was dissolved in hot water and treated with alkali, it precipitated N,N-dicyclohexyl-1,2-diaminoethane monohydrate (2), m.p. 92°. This product, which represents 50% of nitrate not found as the sodium salt, is evidently a modification of the dinitrate V melting at 192°, as shown by its x-ray diffraction pattern: [10] 13.59; [9] 4.49; [8] 3.93; [7] 4.69; [4] 5.84; [3] 4.12, 2.96, 2.82; [2] 3.37; [1] 6.86, 3.79, 3.60.

The etherous diluate from which the 2 g. was obtained was evaporated *in vacuo* to 5 ml. and then dissolved in 25 ml. of water. To this solution was added 1.53 g. (0.014 mole) of oxalic acid in 15 ml. of water. The infusible precipitate weighed 3.0 g. It was crystallized from water (27 ml. per g.) and characterized by its x-ray diffraction pattern: [10] 5.29, 4.48, 4.07; [8] 3.77; [7] 2.69; [6] 2.26; [5] 3.15; [4] 4.79, 2.57; [2] 2.07, 1.83; [1] 2.88.

Anal. Calc'd for $C_{17}H_{31}N_2O_6$: C, 56.8; H, 8.73; N, 7.79.
Found: C, 56.7; H, 8.85; N, 7.90.

Since an alkaline solution of this salt will yield N,N-dicyclohexyl-1,2-diaminoethane monohydrate when treated with alkali it is evidently a salt comprising two molecules of amine per three molecules of oxalic acid. The yield therefore represents 48% of the theoretical amount.

Nitration of phenol by II. To 0.2 g. of molten, distilled phenol (50°) was added 1.0 g. of II portionwise as rapidly as it dissolved. When addition was complete the temperature was raised to 90° for five minutes, then lowered to 25° and 10 ml. of water was added, followed by alkali until the reaction mixture was basic. After ether extraction the aqueous phase was acidified with hydrochloric acid and ether-extracted. This extract was dried, evaporated, dissolved in benzene, and subjected to a chromatographic separation on a calcium carbonate column (3). No phenol, but some tars and 0.094 g. (32%) of *p*-nitrophenol were obtained.

Nitration of dimethylaniline by II. To a stirred suspension of 2.28 g. (0.0049 mole) of II in 10 ml. of ethyl nitrate was added 0.59 g. (0.62 ml., 0.0049 mole) of dimethylaniline at 25°. After one hour the solution was stirred for the same time at 50–55°. The yellow solution was filtered, evaporated under reduced pressure, and the remaining yellow crystals were twice-crystallized from ethanol. The *p*-nitrodimethylaniline weighed 0.16 g. (20%) and melted at 163–164°, with no depression on mixture melting point.

Nitration of imino-bis-acetonitrile by II. A suspension of 4.70 g. (0.01 mole) of II with 0.95 g. (0.01 mole) of imino-*bis*-acetonitrile in 20 ml. of ethyl nitrate gave no evidence of reaction during six hours at 25°. On the other hand reaction occurred during one hour of reflux on the steam-bath. The mixture was then filtered to remove a quantitative yield of N,N-dicyclohexyl-1,2-diaminoethane dinitrate (V). The filtrate was evaporated *in vacuo.* The residue, weighing 0.95 g., was dissolved in 3 ml. of acetone and diluted to 25 ml. with water. The identity of the nitrimino-*bis*-acetonitrile (VII) which crystallized (wt. 0.32 g., 23% of theoretical) was confirmed by melting point (92–93°) and by mixture melting point with an authentic sample.

When imino-*bis*-acetonitrile was treated comparably with ethyl nitrate, but without II, it was recovered unchanged.

SUMMARY

1. An intermediate comprising the cyclic amine together with the elements of two equivalents of nitric acid and one of nitrogen pentoxide has been isolated by reducing the temperature at which dicyclohexylimidazolidine is nitrolyzed.

2. This intermediate cannot be converted to N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane *per se* although it alone is effective in nitration of phenol, dimethylaniline, and imino-*bis*-acetonitrile.
3. When the intermediate is heated with acetic anhydride it is nitrolyzed; if sodium nitrite is included it is nitrosolyzed.
4. This behavior has led to the postulate that nitrolysis proceeds *via* an ammononitronium type of salt and is effective only when acetic anhydride decreases the prevalence of ammonium type of salt in the system.

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