

1964

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### Recommended Citation

Campbell, Richard D. and Ofstead, Ronald F. (1964) "The Photodimer from B-Nitrostyrene," *Proceedings of the Iowa Academy of Science*, 71(1), 197-205.

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## The Photodimer from $\beta$ -Nitrostyrene

RICHARD D. CAMPBELL<sup>1</sup> AND RONALD F. OFSTEAD

*Abstract.* Photodimerization of  $\beta$ -nitrostyrene by sunlight or a mercury arc lamp yields 1,3-diphenyl-2,4-dinitrocyclobutane (II). Only one stereoisomer was obtained. Reduction of the dimer gave a diamine which was identical with the diamine produced by the Curtius rearrangement of  $\alpha$ -truxillic acid. Thus the structure of II is unequivocally established as 1, *trans*-3-diphenyl-2-*cis*-4-*trans*-dinitrocyclobutane. An isomer III of the dimer is identified as having the geometric structure corresponding to  $\gamma$ -truxillic acid by a similar series of steps.

The conversion of  $\beta$ -nitrostyrene (I) to a colorless solid by the action of light was first reported by Priebis (1). The product melted with decomposition at 172-180° compared with 58° for  $\beta$ -nitrostyrene. Starting material and product had the same elemental composition. Meisenheimer and Heim showed that the product was dimeric by molecular weight determination (2). By analogy with the cinnamic acid-truxillic acid photodimerization, a cyclobutane structure II was proposed. No evidence for this structure was offered. A head-to-head dimer IV must be considered, by analogy with truxinic acid.

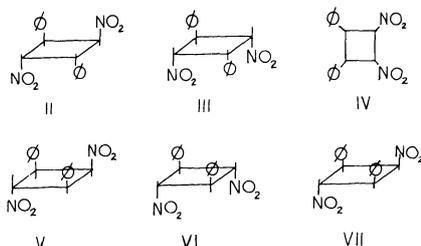


Figure 1. Possible Dimer Structures

Additional evidence for structure II is reported by Miller (3). The purified dimer II, m.p. 187°, gave only benzoic acid on oxidation. Structure IV would give benzil, which was not detected.

Evidence for the geometry of II was obtained (3) from the observation that treatment of II with alkali, and then acid, gave an isomer, m.p. 192-8°, assigned structure III. The isomerization appears to involve a kinetically controlled protonation of the common anion of II and III. Isomers II and III were interconverted in boiling ethanol. Reduction of III gave a diamine which reacted with phosgene to form a cyclic ureylene structure.

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Thus the evidence obtained by Miller requires the nitro groups in III to be *cis*, and the phenyl groups of II and III to hold the same geometric relationship. These requirements are also met by structures V and VI. However, since no trace of a substance corresponding to VII was found, the possibility that the structure of the photodimer is V must be considered more remote than the alternative proposed by Miller.

A series of reactions which provides further evidence for the geometry of II was reported (3). Bromination of II in alkaline solution followed by removal of excess bromine by air sweeping provided a mixture of monobromination products (XVI and XVII as racemic forms). Treatment with *l*-brucine resulted in a product mixture which had an observed negative optical rotation (3). Asymmetrically selective dehydrobromination of racemic XVI or XVII by *l*-brucine is expected to remove one racemate at a higher rate than its enantiomorph resulting in partial resolution. The mixture of products expected from this reaction is complex, and the elimination products are all optically active. Hence the sign of magnitude of optical rotation cannot be related to unreacted XVI or XVII.

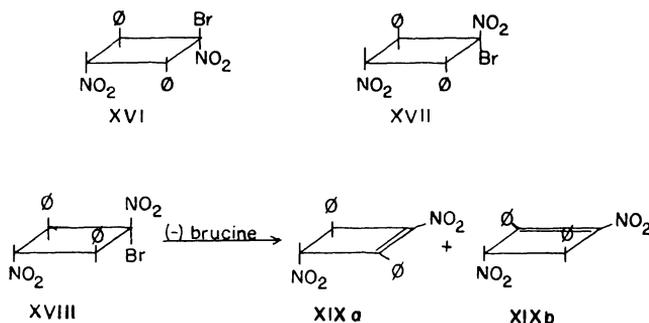


Figure 2. Partial Resolution

It was argued (3) that *cis* phenyl geometry in the photodimer would lead to symmetrical monobromo products (e.g., XVIII) incapable of being resolved, and thus the *cis* phenyl geometry was excluded by the *l*-brucine experiment. An alternative explanation of the observed optical rotation can be seen by considering the elimination of XVIII (symmetrical) with *l*-brucine (unsymmetrical) to give products XIXa and XIXb (unsymmetrical) which are enantiomorphs and would be formed in *unequal amounts*. Thus the optical activity of the material isolated from the *l*-brucine experiment could be due to products XIX. The melting points of the partially resolved products correspond closely with racemic XVI and XVII, however, and render the alternative explanation improbable.

An unequivocal establishment of the geometry of the photodimer is available in the diamine VIII. This compound was reported by White (4). It was obtained *via* the Curtius rearrangement from  $\alpha$ -truxillic acid (XII), whose configuration has been established (5). The Curtius rearrangement is stereospecific (4,6). White further substantiated (4) the geometry of VIIIa by the Bischler-Napieralski cyclization of the diacetyl derivative IXa<sup>2</sup>.

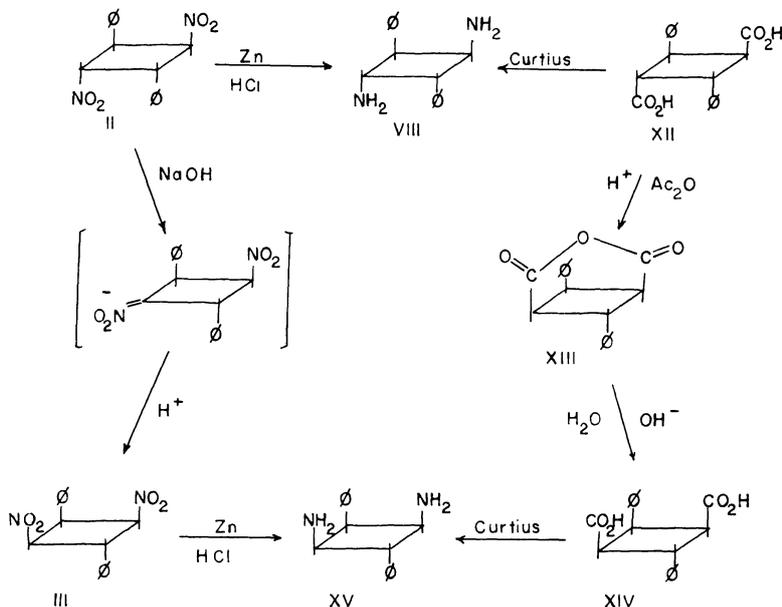


Figure 3. Structure Proof

Reduction of the photodimer II by zinc and hydrochloric acid in aqueous methanol produced diamine VIII. The diamine was isolated by low-temperature crystallization. Because VIII is a liquid at room temperature, and sensitive to air, the diacetyl derivative IX was prepared for identification. The diacetyl derivative IXa prepared by the independent route (4) was found to be identical with IX by no depression of the melting point of mixtures of the two samples, and by identical infrared spectra.

Isomerization of the photodimer II was effected by the method of Miller (3). The base-catalyzed reaction involves intermediate formation of a trigonal anion. Thus *trans-cis* isomerization of the nitro groups occurs, with retention of the *trans* configuration of the phenyl groups. The product of the isomerization structure III, melted at 195-197°. The infrared spectra of the

<sup>2</sup>Roman numerals followed by "a" designate derivatives obtained starting with truxillic acids. Thus VIII is obtained from II, and VIIIa is obtained from  $\alpha$ -truxillic acid (XII).

two isomers did not differ significantly in the  $4000\text{-}1300\text{ cm}^{-1}$  region, in which functional group stretching frequencies appear. In the "finger-print" region ( $1000\text{-}700\text{ cm}^{-1}$ ) the two isomers differ in respect to the presence of nine absorption bands, and in relative intensities and separation of two bands. (Fig. 4).

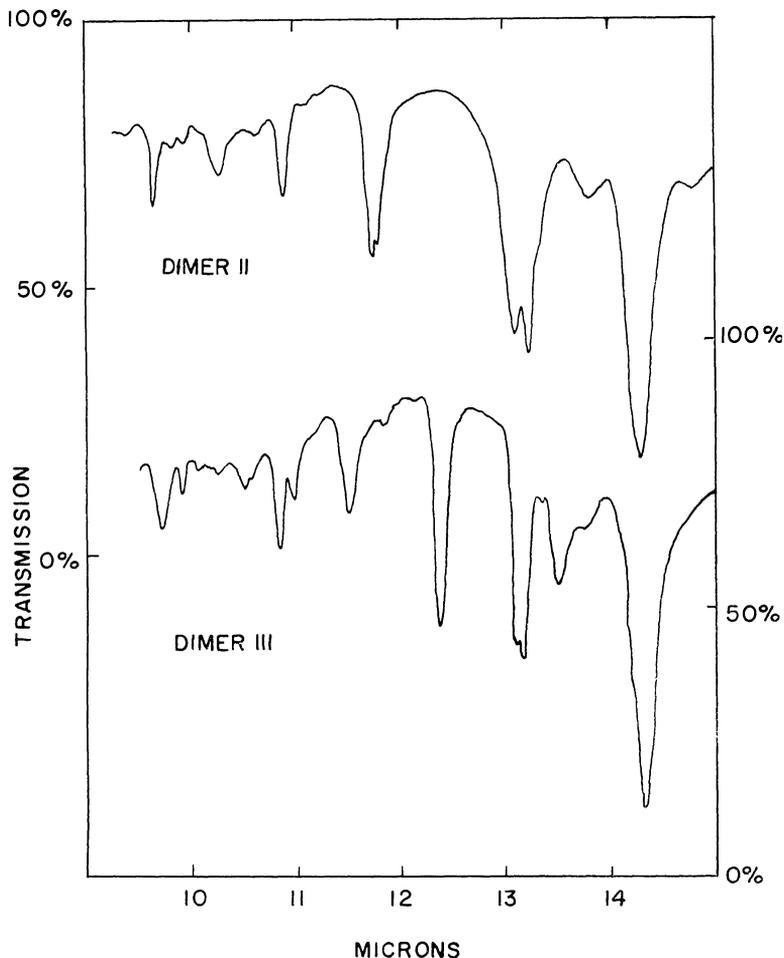


Figure 4. Infrared Spectra

The geometry of the isomer III was unequivocally established by reduction of diamine XV and conversion to the diacetyl derivative XVII. The same diamine was obtained from  $\gamma$ -truxillic acid XIV (5) by the Curtius rearrangement. The diacetyl derivatives XVII and XVIIa were shown to be identical by infrared spectra and the melting point of mixtures. This result demonstrates the geometry of III and substantiates the structure assignment of II.

The photodimerization of  $\beta$ -nitrostyrene does not occur in solution. Several attempts (1-3) to detect the dimer in irradiated solutions of  $\beta$ -nitrostyrene in various solvents and at widely varied concentrations have proved fruitless. Apparently the intermediate bimolecular complex of I is not sufficiently stable for solution dimerization to occur. Miller (3) presents convincing evidence for *trans* (7) to *cis* isomerization of I in solution.

The orientation of neighboring molecules of I in the solid must be the controlling factor in the ease and stereospecificity of the photodimerization. Fig. 5 shows three possible orientations of adjacent  $\beta$ -nitrostyrene molecules which could give rise to the cyclobutane ring in the dimer. Only orientation A could produce dimer II. Orientation B would give isomer IV, C would give V. In view of the fact that truxillic and truxinic acids are formed from different crystalline forms of cinnamic acid, we are now studying the application of these techniques to  $\beta$ -nitrostyrene.

The X-ray study of single crystals of I is being conducted. Preliminary data show a unit cell containing four molecules of  $\beta$ -nitrostyrene. The refined data are expected to confirm configuration A, and will be published at a future date.

### EXPERIMENTAL<sup>3</sup>

*Preparation of  $\beta$ -Nitrostyrene Dimer II.* — Dimerizations of solid *trans*- $\beta$ -nitrostyrene (I) were conducted by placing a thin layer of  $\beta$ -nitrostyrene (8) on the bottoms of large crystallizing dishes covered with polyethylene film or in Vycor glassware. Irradiations in direct sunlight were conducted using nine-weeks exposure and irradiations employing an unshielded Mazda EH4 100 watt ultraviolet lamp were conducted for three weeks. Heat from direct summer sunlight or from the ultraviolet lamp appeared to cause some decomposition since cleaner reactions occurred using winter sunlight exposures or ultraviolet lamp exposures at zero degrees. Dimeric product was obtained by washing the reaction mixture with cold benzene to remove unreacted  $\beta$ -nitrostyrene and recrystallizing the residue from benzene. While this procedure for product isolation results in a reduction in yield of the dimeric product, the conditions were employed in order to avoid isomerization during product isolation. Yields of 25 to 40% of pure  $\beta$ -nitrostyrene dimer II, melting point 183-185°, were obtained in this manner. Priebis (1) reports 172-180° (2,3).

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_4$ : C, 64.42; H, 4.70; N, 9.40. Found: C, 64.69; H, 4.89; N, 9.24.

<sup>3</sup>Analyses by R. T. Foster, State University of Iowa, Iowa City, Iowa. All melting points uncorrected.

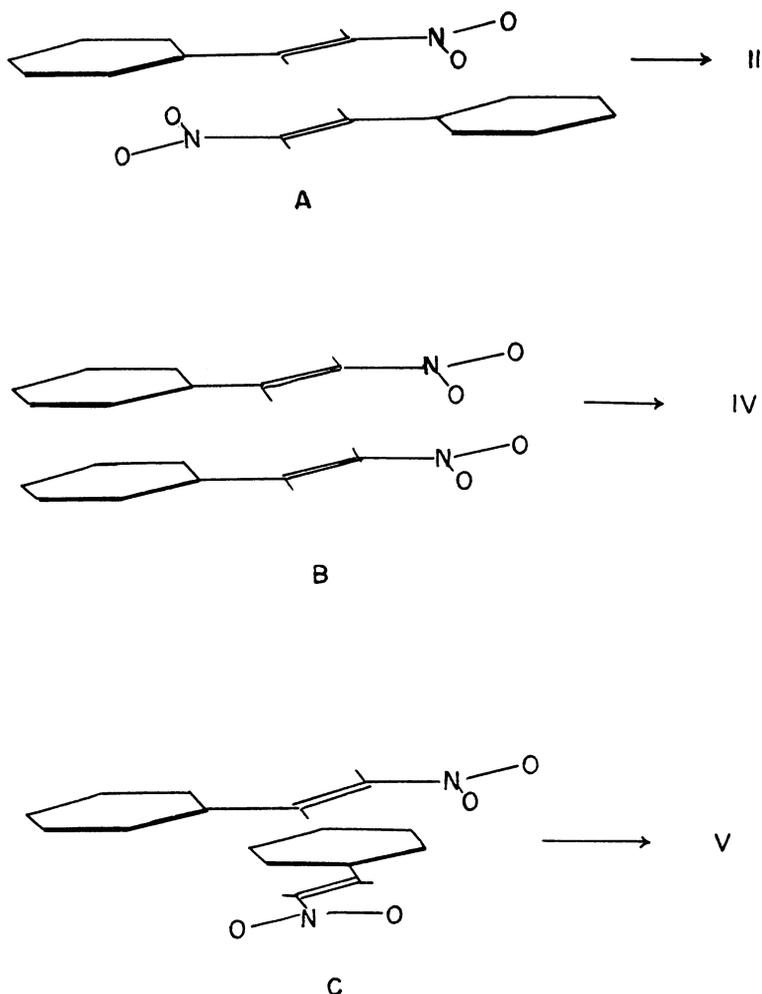


Figure 5. Crystal Molecular Orientations

*Reduction of the Photodimer II. 1,3-Diamino-4,2-diphenylcyclobutane (VIII).* -  $\beta$ -Nitrostyrene dimer II (3.0 g., 10 mmoles), granular zinc (10 g.), and methanol (200 ml.) were placed in a flask equipped with condenser and magnetic stirrer and a slow stream of nitrogen was passed through the system. Silute hydrochloric acid (150 ml., 6 N) was added over a period of two and one-half hours, with cooling of the reaction mixture to maintain a temperature of about 25°. Unreacted zinc was removed by filtration, the solution was extracted with chloroform to remove methanol, the aqueous layer made strongly alkaline with sodium hydroxide, and extracted four times with ether. The combined ether extracts were filtered through anhy-

drous sodium sulfate, dried over barium oxide, and the dry ether solution stored over barium oxide. Portions of the ether solution were used to prepare a picrate X (m.p. 210°),<sup>4</sup> a benzoate salt XI (m.p. 197-8°),<sup>4</sup> and the diacetyl derivative IX (m.p. 241-242.5°).<sup>4</sup> The latter sample was used for identification.

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_2$ : C, 74.5; H, 6.87.  
Found: C, 74.0; H, 6.64.

The pure amine could not be isolated by distillation due to decomposition. Isolation was accomplished by cooling a hexane solution of the amine at -78° for several hours, causing formation of a white solid. The solid material was then isolated by filtration at -78° in a special low-temperature filtration apparatus. The solid was quickly transferred to a vial and melted immediately to give a colorless liquid. The amine appears to be very sensitive to air oxidation as strong red colors appeared after a short time.

*$\alpha$ -Truxillic Acid (XII).* Solar irradiation of the  $\alpha$  form of *trans*-cinnamic acid gave  $\alpha$ -truxillic acid by the procedure of Bernstein and Quimbey. The product was obtained in 61% yield and melted at 276-278° (9).

In an alternative method, the photodimer of cinnamylidene malonic acid (10) was prepared by solar irradiation in aqueous suspension (11). The dimer (88 g., 0.20 mole) was stirred in a solution of 165 g (0.57 mole) of potassium dichromate in 2 l. of dilute sulfuric acid at 65° for two hours. On cooling, the solid  $\alpha$ -truxillic acid separated. It was collected by filtration, washed, and dried. Recrystallization from aqueous ethanol gave 28 g. (50%) of  $\alpha$ -truxillic acid (m.p. 273°).

*Preparation of Diphenyldiaminocyclobutane VIIIa from  $\alpha$ -Truxillic Acid.* -  $\alpha$ -Truxillyl chloride (4.9 g., 1.5 mmole, m.p. 124-5°) and sodium azide (6.5 g., 0.10 mole) were used in the preparation of diphenyldiaminocyclobutane VIIIa employing the procedure of White and Dunathan (4). The pure amine was not isolated. Derivatives prepared included the picrate (m.p. 210-211°), the benzoate salt (m.p. 199-200°), and the diacetyl derivative (m.p. 242-3°).

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_2$ : C, 74.5; H, 6.87; N, 8.69.  
Found: C, 73.9; H, 7.02; N, 9.2.

*Preparation of  $\beta$ -Nitrostyrene Dimer III.* -  $\beta$ -Nitrostyrene dimer II (2.0 g., 6.7 mmole) was dissolved in tetrahydrofuran (40 ml.) and ethanol (20 ml.). To this solution was added 0.25 M aqueous sodium hydroxide (30 ml., 7.5 mmole) and the resulting orange solution was diluted with water (50 ml.). This

<sup>4</sup> E. H. White reports melting points of 210-11°, 200° and 251° for the picrate, benzoate and diacetyl derivatives, respectively, via  $\alpha$ -truxillic acid (4).

solution was added to an aqueous solution of urea (5 g.) and acetic acid (10 ml.). The white precipitate which formed was removed by filtration, washed with water, and air dried to give 1.8 g. (90%) of crude product. Recrystallizations from benzene gave 1.2 g. (60%) of  $\beta$ -nitrostyrene dimer III melting at 195-197°.

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_4$ : C, 64.4; H, 4.70; N, 9.40.

Found: C, 64.4; H, 4.82; N, 9.62.

*Reduction of Dimer III. 1,3-Diamino-2,4-diphenylcyclobutane (XV).* — The reduction procedure applied to III was identical to that employed in the reduction of photodimer II to diamine VIII. In this manner were prepared the picrate XVI (m.p. 215-220°) and the diacetyl derivative XVII (m.p. 304-306°). The latter sample was analyzed.

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_2$ : C, 74.5; H, 6.8; N, 8.7.

Found: C, 73.9; H, 7.12; N, 9.1.

*Preparation of  $\gamma$ -Truxillic Anhydride (XIII).* —  $\alpha$ -Truxillic acid (17.0 g., 0.057 mole), freshly distilled acetic anhydride (100 ml.), and 85% phosphoric acid (2 dr.) were placed in a distilling apparatus consisting of a 22 in. wrapped Vigreux column fitted with a distilling head. Slow distillation yielded an initial fraction at 123°. When the temperature of the distillate reached 136°, fresh acetic anhydride (30 ml.) was added and distillation resumed until a total of 100 ml. of distillate had been removed. Removal of further acetic anhydride under vacuum, cooling of the reaction mixture, and recrystallization of the resulting precipitate from acetic anhydride yielded a total of 9.2 g. (58%) of the solid anhydride, melting point 189.5-190.0°. Rodd (5) reports 191°.

*Preparation of  $\gamma$ -Truxillic Acid (XIV).* — saturated solution of  $\gamma$ -truxillic anhydride (8.0 g., 0.029 mole) in dioxane was added to warm aqueous sodium hydroxide with rapid stirring. The solution was acidified and cooled to yield 8.2 g. (96%) of  $\gamma$ -truxillic acid, melting at 227.5-228.5°. Rodd (5) reports 228°.

*Preparation of Diphenyldiaminocyclobutane XV a from  $\gamma$ -Truxillic Acid.* —  $\gamma$ -Truxillyl chloride (3.0 grams, 9.0 mmoles, m.p. 139 0-139.7°), sodium azide (4.0 grams, 0.062 mole) and ethanol-free chloroform were stirred under dry nitrogen at 0° for 15 hours. The reaction mixture was tird under nitrogen at room temperature for six hours, and then refluxed for one hour. The reaction mixture was filtered to remove inorganic salts and the chloroform was removed by distillation. Purified dioxane (300 ml.) and 6 N hydrochloric acid (150 ml.) were added and the mixture was stirred overnight at room temperature under nitrogen. Dioxane was removed by extraction with chloroform

and the aqueous layer made alkaline with aqueous sodium hydroxide. The amine was separated by ether extraction and the combined ether extracts were dried and stored over barium oxide. Derivatives prepared included the picrate (m.p. 215-225°) and the diacetyl derivative XVIIa (m.p. 301-305°).

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_2$ : C, 74.5; H, 6.87; N, 8.69.  
Found: C, 74.3; H, 6.99; N, 8.6.

The pure amine was isolated by the same technique employed for isolation of the diphenyldiaminocyclobutane VIIIa.

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## Reaction of Cinnamoyl Chloride with a Dialkylcadmium Reagent<sup>1</sup>

KENNETH W. KRAUS<sup>2</sup>, RICHARD T. BOGAN AND RICHARD M. WEIER

*Abstract.* It was demonstrated that a dialkylcadmium reagent would successfully react with the unsaturated acid chloride, cinnamoyl chloride, under both ordinary conditions and at 0° in the presence of ferric chloride to give the alkyl styryl ketone in yields of 54% and 46% respectively. The n-butyl styryl ketone obtained in the reaction displayed infrared absorption at 5.92  $\mu$  (C=O) and at 6.04  $\mu$  (C=C). The dipole moment was found to be 3.16 D in benzene solution at 25°.

It has been reported (1) that alkyl styryl ketones were not isolated from the reaction of cinnamoyl chloride with dialkylcadmium reagents, although benzalacetophenone was obtained when the same acid chloride was treated with diphenylcadmium. It is significant however, that these attempts were made prior to important modifications in the reaction of organocadmium

<sup>1</sup> (a) Richard T. Bogan was an N.S.F. Undergraduate Research Participant during the summer of 1962 and the 1962-63 academic year; (b) Richard M. Weier was an N.S.F. Undergraduate Research Participant during the 1961-62 academic year.

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