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Synthesis of the Mixed Alkyl Esters of Phenylphosphonic Acid by Two Variations of the Atherton–Todd Protocol

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ABSTRACT: *Phenylphosphonates with mixed alkyl groups were synthesized from ethyl phenyl-H-phosphinate by two modified Atherton–Todd methods. Using aqueous sodium hydroxide under phase transfer catalytic conditions, the alkyl ethyl phosphonates were obtained in only moderate yields. However, applying 1-methylimidazole as the base, the diesters could be prepared in yields of 76–85%. The imidazole hydrochloride formed as a by-product acts as an ionic liquid phase in the reaction, from which the base can be regenerated.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 26:29–34, 2015; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21204

INTRODUCTION

Phosphonates have an ever-increasing importance as reagents and intermediates in organic synthesis [1]. Alkyl/aryl phosphonates are frequent intermediates in the synthesis of various bioactive compounds. The P—C bond present in these compounds makes them resistant to enzymatic hydrolysis [2]. Phosphonates are widely applied as synthetic intermediates [3–7]. Phosphonates were also recognized as "markers" of chemical warfare agents and are indexed in the CWC text under 2 B4 category [8, 9].

A number of different methods are available for the synthesis of alkyl/aryl phosphonates. A common method for the synthesis of phosphonic acid diesters is the reaction of phosphonic dichlorides with aliphatic alcohols or phenols [10].

Esterification of alkyl/aryl phosphonic acids to the corresponding alkyl/aryl phosphonates/phosphates was performed under mild conditions with quantitative yields using silica chloride as an effective heterogeneous catalyst [11].

Phenyl-*H*-phosphinic acid was converted to the diesters by microwave (MW)-assisted esterification, followed by oxidation and then by a second esterification [12].

The Michaelis–Arbuzov reaction, or simply the Arbuzov reaction, is one of the most versatile techniques for the formation of carbon–phosphorus bonds, which implies the reaction of a trialkyl phosphite with an alkyl halide, involving the change of valency of phosphorus from the trivalent to

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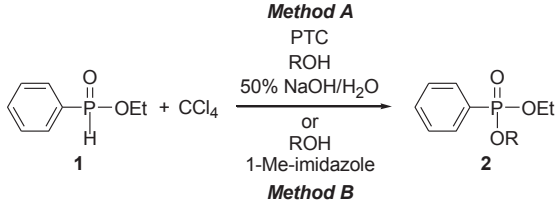
the pentavalent state. Using other P-reagents, the method may also be employed for the synthesis of phosphinates and phosphine oxides [13]. Since its discovery a lot of phosphonate esters were prepared including haloalkyl phosphonates and substituted diethyl arylphosphonates. The Michaelis–Arbuzov reaction shows remarkable rate acceleration under MW irradiation [14–16]. The interaction of arylmethyl halides with triethyl phosphite in the presence of a Lewis acid at room temperature afforded the corresponding phosphonate esters in good yields [17].

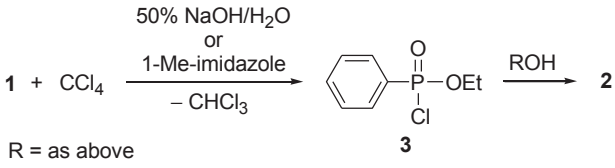
Another widely used method for the synthesis of phosphonates is the Michaelis–Becker reaction, in which dialkylphosphites react, in the presence of a base, with different halogeno compounds [18]. Since than, a lot of examples have been described, but one of the most convenient methods involves the use of phase transfer catalysis that can be carried out in different ways [19]. The MW-assisted Michaelis–Becker synthesis is another approach to obtain dialkyl phosphonates and tetraalkylbisphosphonates [20]. The next method for the synthesis of aryl phosphonates is the coupling of dialkyl phosphites and aryl halides using tetrakis(triphenylphosphine)palladium as the catalyst in the presence of triethylamine. Polyethylene glycol 600 was applied as an efficient additive [21]. These kind of transformations belong to the group of the Hirao reaction [22, 23].

Phosphonic diesters with two different substituents can be obtained by the reaction of phosphonic ester chlorides with alcohols or phenols. If no base is used, the reaction should be carried out at low temperature and the hydrogen halide is removed by reduced pressure or by a stream of an inert gas, but normally the preparation of these esters requires an acid scavenger [10]. Mixed phosphonate diesters could also be synthesized under mild conditions and in high yields using 1*H*-tetrazole, which catalyzes the selective monoesterification of phosphonic dichlorides. The subsequent reaction of this phosphonic ester chloride with a different alcohol led to mixed esters. Tetrazole enhances the selective reactivity of the phosphonic dichloride, probably via nucleophilic catalysis [24].

In this paper, we describe the synthesis of mixed alkyl esters of phenylphosphonic acid from ethyl phenyl-*H*-phosphinate using two versions of the Atherton–Todd reaction [25]. A literature survey showed that the Atherton–Todd protocol has never been applied to the synthesis of phosphonates with two different alkyl groups. Only the preparation of alkyl aryl phosphonates was reported [26–28].



SCHEME 1 Two approaches used for the synthesis of mixed alkyl phosphonates.



SCHEME 2 Mechanism for the phosphorylation of ethyl phenyl-*H*-phosphinate.

RESULTS AND DISCUSSION

The phase transfer catalyzed version of the Atherton–Todd reactions is a powerful method for the synthesis of phosphorus derivatives (phosphonates, phosphates, and related phosphorus compounds) [19, 29, 30]. Zwierzak [29] showed that dialkyl phosphites can be applied for phosphorylation in a liquid–liquid system, using a phase transfer catalyst. In this paper, this method was applied for the synthesis of mixed alkyl phenylphosphonates **2** by reacting ethyl phenyl-*H*-phosphinate (**1**) with different alcohols in the presence of tetrachloromethane, aqueous sodium hydroxide, and tetrabutylammonium halide (TBAX) (Scheme 1, Method A). The other method used involved the use of 1-methylimidazole as the base (Scheme 1, Method B).

Both methods involve the transformation of ethyl phenyl-*H*-phosphinate (**1**) into the corresponding ester-chloride **3** [31] in the presence of tetrachloromethane and a base (aqueous sodium hydroxide or 1-methylimidazole). Then, intermediate **3** reacts further with the alcohol to give the mixed phosphonate (**2**) (Scheme 2).

We used the above-mentioned methods for the synthesis of mixed alkyl esters of phenyl phosphonic acid starting from ethyl phenyl-*H*-phosphinate (**1**).

All reactions were performed with a 25% excess of phenyl-*H*-phosphinate (**1**) to compensate the inevitable hydrolysis of starting material **1**. The reaction is exothermic and, in most of the cases, needs external cooling. When methanol was phosphorylated by the tetrachloromethane and 50% aqueous sodium hydroxide system using a catalytic amount (5 mol%) of TBAX (where X = Cl or Br), mixed ethyl methyl ester **2a** was obtained in a low (20%) yield. The crude mixture was complex and the purification process was difficult. The predominant byproduct was phenylphosphonic acid formed by hydrolysis. When ethanol was used, the yield of the corresponding ester **2b** was increased to 35%. Further increasing the length of the alkyl chain, the yield amounted to 46–50%. At the end of the reaction, the mixtures were filtered or diluted with water or dichloromethane in order to be able to work up the reaction. When secondary or even tertiary alcohols were used, only traces of the phosphonates (**2**) were obtained that is probably the consequence of steric hindrance. The nature of the anion (chloride or bromide) of the catalysts had not much impact. The process was not fully optimized; however, certain changes such as the use of lower concentration of sodium hydroxide, the order of the addition of reagents, and change in the reaction time led to side reactions and the formation of undesirable compounds. It can be concluded that the yields of mixed diesters **2a–h** synthesized by this method were low (20–50%). Hence, the above process has a limited usefulness, especially, when secondary and tertiary alcohols were employed.

Then, another variation of the Atherton–Todd reaction was tried out for the synthesis of our target compounds **2**. The classical Atherton–Todd method [25] uses triethylamine as the base, which has some of the following drawbacks: the product is difficult to separate from the mixture and is contaminated with the ammonium salt, a higher reaction temperature (reflux) is necessary, and the yields are moderate. This method was modified by us by using 1-methylimidazole as the acid scavenger. When triethylamine was replaced by 1-methylimidazole, the 1-methylimidazolium chloride resulted formed an ionic liquid that separated as a distinct phase. In a few cases, the mixture has to be heated, as 1-methylimidazolium chloride is viscous at room temperature. After the reaction, the 1-methylimidazolium chloride separated was treated with a base and 1–methylimidazole was regenerated. This is the advantage of this method. To increase the yields (76–85%), the molar ratio of phosphinate (**1**) alcohol was decreased from 1.25 to 1, taking into account that the hydrolysis of the starting phosphinate **1** could be eliminated. All compounds (**2a–-h**) synthesized were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as HR-MS spectral data. Only phosphonic ester **2b** was known from the literature.

TABLE 1 Synthesis of the Mixed Esters of Phenylphosphonic Acid (**2a–h**)

Entry	*Compound*	*Yield Using Method A (%)*	*Yield Using Method B (%)*
1	**2a**	20	85
2	**2b**	35	83
3	**2c**	46	85
4	**2d**	49	82
5	**2e**	47	80
6	**2f**	50	79
7	**2g**	49	78
8	**2h**	48	76

Experimental data are listed in Table 1.

Analyzing the experimental data, it is obvious that in respect of the synthesis of dialkyl phenylphosphonates with mixed alkyl groups, the Atherton–Todd method applying 1-methylimidazole gives better results than the phase transfer catalyzed version.

It can also be seen that the Atherton–Todd synthesis is suitable for the preparation of alkyl alkyl' (mixed) phosphonates. Moreover, the use of 1-methylimidazole as the base is a novelty, as it means an advantage during the work-up procedure and the regeneration of the amine, decreasing the costs, and making possible a greener synthesis.

CONCLUSIONS

The Atherton–Todd synthesis was applied to the preparation of dialkyl phosphonates with two different alkyl groups. Alkyl ethyl phenylphosphonates were synthesized from ethyl phenyl-*H*-phosphinate by two modified versions of the original protocol. The liquid–liquid phase transfer catalytic accomplishment using aqueous sodium hydroxide as the base led to more modest results than the novel variation applying 1-methylimidazole as the base. In the latter case, the (with one exception) new products were obtained in yields of 76–85%. The novelty of our results, on the one hand, is that the Atherton–Todd protocol was extended to the synthesis of dialkyl phosphonates with mixed alkyl groups. On the other hand, it is a noteworthy invention that, if 1-methylimidazole is used as the base, the hydrochloride salt formed (as an ionic liquid) can be easily separated and the *N*-heterocycle can be regenerated.

EXPERIMENTAL

^{31}P, ^{13}C, and ^{1}H NMR spectra were obtained in $CDCl_3$ solution on a Bruker AV-300 spectrometer

operating at 121.5, 75.5, and 300 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and tetramethylsilane (TMS). Mass spectra were obtained using a Shimadzu LCMS-ITTOF mass spectrometer.

Ethyl phenyl-*H*-phosphinate was synthesized under MW conditions as described earlier [32], or supplied by Sigma-Aldrich (St Louis, MO, USA). Normal C1–C8 alcohols were purchased from Aldrich and distilled prior to use. Tetrachloromethane, dichloromethane, sodium hydroxide, hydrochloric acid, sodium sulfate, tetrabuthylammonium chloride, and 1-methylimidazole were also supplied by Aldrich and used without purification.

*General Procedure for the Synthesis of Ethyl Phenyl-H-Phosphinate (**1**) under MW Conditions [32]*

A mixture of 0.10 g (0.70 mmol) of phenyl-*H*-phosphinic acid and 1 mL (17.4 mmol) of ethanol was irradiated in a closed vial in a CEM MW reactor equipped with a pressure controller at 160°C for 1 h. Then, the alcohol was removed under reduced pressure, and the residue obtained was purified by flash column chromatography using silica gel and 3% methanol in dichloromethane as the eluant. The ester (**1**) was obtained as colorless oil.

General Procedure for the Preparation of Dialkyl Phenyl Phosphonates

Method A. A solution of 2.1 g (0.0125 mol) of ethyl phenyl-*H*-phosphinate in 5 mL of tetrachloromethane was added dropwise under stirring and external cooling (5–10°C) to a mixture of a 0.01 mol alcohol (MeOH: 0.40 mL, EtOH: 0.59 mL, ^{n}PrOH: 0.75 mL, ^{n}BuOH: 0.91 mL, ^{n}PentOH: 1.10 mL, ^{n}HexOH: 1.25 mL, ^{n}HeptOH: 1.42 mL, ^{n}OctOH: 1. mL), 10 mL of tetrachloromethane, 3.8 g (0.090 mol) of NaOH in 5 mL of water, and 0.14 g (0.5 mmol) of tetrabuthylammonium chloride, keeping the temperature below 15°C. After the addition, the mixture was stirred for another 3–4 h at 26°C, and then the mixture was diluted with 5 mL dichloromethane and the layers were separated. The organic phase was washed with 2.5 × 2 mL of 2% hydrochloric acid, dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The products (**2**) were purified by column chromatography using ethylacetate/chloroform = 5/3 as the eluent.

Method B. A solution of 0.80 g (0.010 mol) of 1-methyl imidazole in 5 mL of tetrachloromethane was added dropwise under stirring and external cooling (if necessary) to a mixture of a 0.013 mol alcohol (MeOH: 0.50 mL, EtOH: 0.73 mL, ^{n}PrOH: 0.93 mL, ^{n}BuOH: 1.15 mL, ^{n}PentOH: 1.35 mL, ^{n}HexOH: 1.60 mL, ^{n}HeptOH: 1.75 mL, ^{n}OctOH: 1.95 mL) and 1.7 g (0.010 mol) of ethyl phenyl-*H*-phosphinate in 5 mL of tetrachloromethane. After the addition, the mixture was stirred for another 3–4 h at 26°C, and then kept overnight without stirring and the layers were separated. The organic phase was washed with 2.5 mL of hydrochloric acid (2%), and then with 2.5 mL of distilled water, dried (Na_2SO_4), and solvent was evaporated under reduced pressure. The products (**2**) were purified by column chromatography using ethylacetate/chloroform = 5/3 as the eluent.

*Ethyl Methyl Phenylphosphonate (**2a**)*

Yield: 20% (Method A) and 85% (Method B); ^{31}P NMR ($CDCl_3$) δ: 20.21; ^{13}C NMR ($CDCl_3$) δ: 16.2 (J = 6.3, CH_3CH_2O), 52.4 (J = 5.5, CH_3O), 62.2 (J = 5.5, (CH_3CH_2O), 127.5 (J = 188.4, C_1), 128.4 (J = 15.0, C_2)*, 131.7 (J = 9.9, C_3)*, 132.5 (J = 3.0, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.30 (t, J = 7.0, 3H, CH_3CH_2O), 3.71 (d, J = 11.1, 2H, CH_3O), 3.99–4.21 (m, 4H, CH_2O), 7.39–7.58 (m, 3H, ArH), 7.72–7.84 (m, 2H, ArH); $[M + H]^+_{found}$ = 201.0683, $C_9H_{14}O_3P$ requires 201.0680.

*Diethyl Phenylphosphonate (**2b**)*

Yield: 35% (Method A) and 83% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.9; δ [33]: ($CDCl_3$) 19.7; $[M + H]^+_{found}$ = 215.0839, $C_{10}H_{16}O_3P$ requires 215.0837.

*Ethyl Propyl Phenylphosphonate (**2c**)*

Yield: 46% (Method A) and 85% (Method B); ^{31}P NMR ($CDCl_3$) δ: 19.76; ^{13}C NMR ($CDCl_3$) δ: 10.0 ($CH_3(CH_2)_2$), 16.3 (J = 6.4, CH_3CH_2O), 23.7 (J = 6.6, $CH_3CH_2CH_2$), 62.0 (J = 5.4, ($CH_3CH_2CH_2O$) 67.5 (J = 5.7, CH_3CH_2O), 128.2 (J = 188.1, C_1), 128.4 (J = 15.0, C_2)*, 131.7 (J = 9.8, C_3)*, 132.3 (J = 3.0, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, J = 7.4, 3H, $CH_3(CH_2)_2$), 1.29 (t, J = 7.0, 3H, CH_3CH_2O), 1.59–1.74 (m, 2H, $CH_3CH_2CH_2$), 3.87–4.20 (m, 4H, CH_2O), 7.39–7.57 (m, 3H, ArH), 7.73–7.84 (m, 2H, ArH); $[M + H]^+_{found}$ = 229.0995, $C_{11}H_{18}O_3P$ requires 229.0988.

*Ethyl Butyl Phenylphosphonate (**2d**)*

Yield: 49% (Method A) and 82% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.90; ^{13}C NMR ($CDCl_3$) δ: 13.5 ($CH_3(CH_2)_3$), 16.2 (J = 6.4, CH_3CH_2O), 18.6

($CH_3CH_2CH_2$), 32.3 (J = 6.6, $CH_3CH_2CH_2$), 62.1 (J = 5.4, ($CH_3(CH_2)_2CH_2O$), 65.7 (J = 5.7, CH_3CH_2O), 128.2 (J = 188.1, C_1), 128.4 (J = 15.0, C_2)*, 131.7 (J = 9.8, C_3)*, 132.3 (J = 3.0, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, J = 7.3, 3H, $CH_3(CH_2)_3$), 1.29 (t, J = 7.2, 3H, CH_3CH_2O), 1.31–1.43 (m, 2H, $CH_3CH_2(CH_2)_2$), 1.56–1.68 (m, 2H, $CH_3CH_2CH_2$), 3.91–4.18 (m, 4H, CH_2O), 7.38–7.57 (m, 3H, ArH), 7.72–7.84 (m, 2H, ArH); $[M + H]^+_{found}$ = 243.1139, $C_{12}H_{20}O_3P$ requires 243.1145.

*Ethyl Pentyl Phenylphosphonate (***2e***)*

Yield: 27% (Method A) and 80% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.89; ^{13}C NMR ($CDCl_3$) δ: 13.8 ($CH_3(CH_2)_4$), 16.2 (J = 6.4, CH_3CH_2O), 22.1 ($CH_3CH_2CH_2$), 30.0 (J = 6.5, $CH_3CH_2CH_2$), 62.0 (J = 5.5, ($CH_3(CH_2)_3CH_2O$), 66.0 (J = 5.7, CH_3CH_2O), 128.2 (J = 188.0, C_1), 128.3 (J = 15.0, C_2)*, 131.7 (J = 9.8, C_3)*, 132.3 (J = 3.0, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.84 (t, J = 6.4, 3H, $CH_3(CH_2)_4$), 1.29 (t, J = 6.2, 7H, CH_3CH_2O and CH_2), 1.58–1.70 (m, 2H, CH_2), 3.90–4.17 (m, 4H, CH_2O), 7.38–7.56 (m, 3H, ArH), 7.72–7.84 (m, 2H, ArH); $[M + H]^+_{found}$ = 257.1303, $C_{13}H_{22}O_3P$ requires 257.1301.

*Ethyl Hexyl Phenylphosphonate (***2f***)*

Yield: 50% (Method A) and 79% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.86; ^{13}C NMR ($CDCl_3$) δ: 16.3 ($CH_3(CH_2)_5$), 18.7 (J = 6.4, CH_3CH_2O), 24.8 ($CH_3CH_2CH_2$), 27.5 ($CH_3CH_2CH_2$), 32.7 (J = 6.5, CH_2CH_2O), 33.6 ($CH_2CH_2CH_2O$), 64.5 (J = 5.4, ($CH_3(CH_2)_4CH_2O$), 68.5 (J = 5.7, CH_3CH_2O), 130.7 (J = 188.1, C_1), 130.8 (J = 15.0, C_2)*, 134.1 (J = 9.8, C_3)*, 134.7 (J = 3.0, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.79 (t, J = 6.5, 3H, $CH_3(CH_2)_5$), 1.13–1.24 (m, 6H, CH_2), 1.25 (t, J = 7.0, 3H, CH_3CH_2O), 1.53–1.66 (m, 2H, CH_2), 3.88–4.13 (m, 4H, CH_2O), 7.34–7.51 (m, 3H, ArH), 7.68–7.80 (m, 2H, ArH); $[M + H]^+_{found}$ = 271.1460, $C_{14}H_{24}O_3P$ requires 271.1458.

*Ethyl Heptyl Phenylphosphonate (***2g***)*

Yield: 49% (Method A) and 78% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.76; ^{13}C NMR ($CDCl_3$) δ: 13.8 ($CH_3(CH_2)_6$), 16.1 (J = 6.4, CH_3CH_2O), 22.3 ($CH_3CH_2CH_2$), 25.2 ($CH_3CH_2CH_2$), 28.5 ($CH_3CH_2CH_2CH_2$), 30.2 (J = 6.5, CH_2CH_2O), 31.5 ($CH_2CH_2CH_2O$), 61.9 (J = 5.4, ($CH_3(CH_2)_5CH_2O$), 65.9 (J = 5.7, CH_3CH_2O), 128.0 (J = 188.2, C_1), 128.2 (J = 15.0, C_2)*, 131.5 (J = 9.8, C_3)*, 132.1 (J = 2.7, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.86 (t, J = 6.8, 3H, $CH_3(CH_2)_6$), 1.18–1.29 (m, 8H, CH_2), 1.30 (t, J = 7.0, 3H, CH_3CH_2O), 1.58–1.70 (m, 2H, CH_2CH_2O), 3.91–4.19 (m, 4H, CH_2O), 7.40–7.57 (m, 3H, ArH), 7.74–7.84 (m, 2H, ArH); $[M + H]^+_{found}$ = 285.1617, $C_{15}H_{26}O_3P$ requires 285.1614.

*Ethyl Octyl Phenylphosphonate (***2h***)*

Yield: 48% (Method A) and 76% (Method B); ^{31}P NMR ($CDCl_3$) δ: 18.66; ^{13}C NMR ($CDCl_3$) δ: 14.0 ($CH_3(CH_2)_7$), 16.3 (J = 6.5, CH_3CH_2O), 22.6 ($CH_3CH_2CH_2$), 25.5 ($CH_3CH_2CH_2$), 29.0 ($CH_3CH_2CH_2CH_2$), 29.1 ($CH_3CH_2CH_2CH_2CH_2$), 30.4 (J = 6.6, CH_2CH_2O), 31.7 ($CH_2CH_2CH_2O$), 62.1 (J = 5.5, ($CH_3(CH_2)_6CH_2O$), 66.1 (J = 5.6, CH_3CH_2O), 128.3 (J = 188.2, C_1), 128.4 (J = 15.0, C_2)*, 131.7 (J = 9.8, C_3)*, 132.3 (J = 2.7, C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, J = 7.0, 3H, $CH_3(CH_2)_7$), 1.16–1.28 (m, 10H, CH_2), 1.30 (t, J = 7.0, 3H, CH_3CH_2O), 1.61–1.68 (m, 2H, CH_2CH_2O), 3.94–4.17 (m, 4H, CH_2O), 7.41–7.55 (m, 3H, ArH), 7.76–7.82 (m, 2H, ArH); $[M + H]^+_{found}$ = 299.1782, $C_{16}H_{28}O_3P$ requires 299.1771.

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