Mechanism of Isomerization of a β-Keto Sulfide

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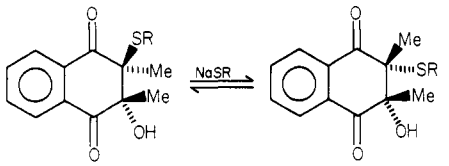
During model studies on the mechanism of the enzyme vitamin K epoxide reductase,[1] I observed an interesting reversible isomerization of (±)-*r*-2-(ethylthio)-2,*cis*-3-dimethyl-*trans*-3-hydroxy-2,3-dihydro-1,4-naphthoquinone (**1a**) and its isomer (**2a**) in the presence of sodium ethylthiolate. Oki et al.[2] have found that β-keto sulfides are reduced by thiolates, via their enolates, to give ketones and disulfides. Conversely, it is known[3] that enolates are oxidized by disulfides to give β-keto sulfides and thiolates. Consequently, a reasonable mechanism for the isomerization of **1** to **2** in the presence of sodium ethylthiolate would be reduction of **1** by NaSEt to the enolate **3** followed by oxidation of the enolate by the resulting disulfide to give **2** (Scheme I). Here I describe experiments which suggest that this redox mechanism is *not* the major pathway of isomerization, but rather a retro-aldol–aldol condensation mechanism (Scheme II) is favored.



1a, R = Et **2a**, R = Et
b, R = Ph **b**, R = Ph

Results and Discussion

When **1a**[4] was treated with sodium ethylthiolate in acetonitrile for 2 h, a mixture of **2a** (80%) and **1a** (20%)[6] was obtained. Furthermore, treatment of either **1a** or **2a** with NaSEt in ethanol for 15 min produced essentially the same mixture of three compounds: 2,3-dimethyl-1,4-naphthoquinone (43% from **1a**; 45% from **2a**),[6] **2a** (30% from **1a**; 29% from **2a**), and **1a** (28% from **1a**; 27% from **2a**). The equilibrium mixture for **1a** and **2a** in ethanol apparently is different than in acetonitrile, but nonetheless these two isomers are interconvertible.

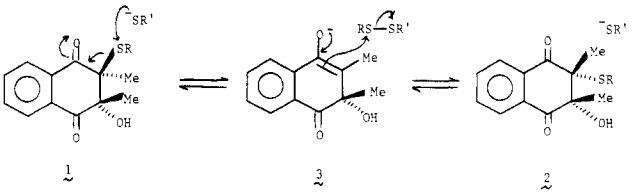
Experiments were carried out to determine the mechanism of this interconversion. By any reasonable mechanism, it is expected that only a catalytic amount of thiolate should be necessary for the isomerization to proceed to equilibrium. In fact, treatment of **1a** in acetonitrile with only 10 mol % of NaSEt led to the formation of **2a** (77%) and **1a** (23%), the same equilibrium mixture that was obtained (vide supra) in the presence of 1 equiv of NaSEt. The unlikely possibility of an S_N2 reaction was tested by treating **1a** with sodium thiophenolate in acetonitrile. Three compounds were isolated: **2a** (58%), **1a** (12%), and 2,3-dimethyl-1,4-naphthoquinone (30%). No phenylthio derivatives (i.e., **2b** or **1b**) were found which would have resulted from an S_N2 reaction.

One possible explanation for this result could be that the redox mechanism described above was operative; however, because thiophenolate is a better leaving group than ethylthiolate,[7] nucleophilic attack on the newly formed mixed disulfide only occurred at the sulfur bearing the ethyl group. If this is the case, then the converse experiment, namely, the reaction of **1b** with NaSEt, also should give only the ethylthio derivative **2a**. Treatment of **1b** with NaSEt, however, resulted in the formation of **2b** (90%), **1b** (7%), and 2,3-dimethyl-1,4-naphthoquinone (3%). No ethylthio derivatives (**2a** or **1a**) were isolated. The equilibrium mixture for the phenylthio isomers favors isomer **2** under these conditions more so than in the case of ethylthio isomers. This is most likely a result of a steric effect, but there also may be some hydrogen bonding between the aromatic electrons and the *cis*-hydroxyl group. These last two experiments are contradictory, then, if a redox mechanism is considered with the stipulation that preferential attack of a nucleophile occurs at the sulfur bearing the Et group.

Further confirmation that the redox mechanism is unlikely was obtained by carrying out the reaction of **1a** with NaSPh in the presence of 1 equiv of diphenyl disulfide and the reaction of **1b** with NaSEt in the presence of 1 equiv of dimethyl disulfide. If a disulfide is generated in the reaction, it should mix with the large amount of added disulfide already present in solution, and products should be derived mostly from reaction of the purported enolate (**3**) and the added disulfide. However, when these experiments were carried out, the results were the same whether or not added disulfide was present. If a disulfide (redox) mechanism were favored, the results of these experiments would require that the intermediate mixed disulfide never diffuse away from the enolate (**3**) and never tumble in solution before enolate attack. This seems highly improbable.

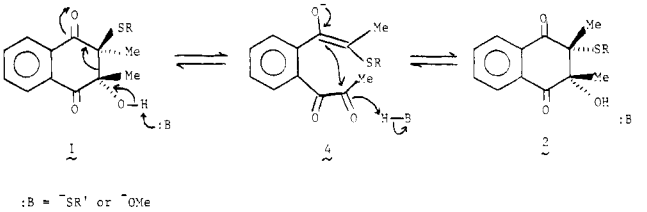
An alternative mechanism is that the thiolate is not acting as a nucleophile but rather as a base, as depicted in Scheme II. According to this mechanism the sulfide bond never breaks, and no disulfide is formed. Instead, deprotonation of the hydroxyl group leads to a retro-aldol reaction to give enolate **4** which undergoes an intramolecular aldol condensation to form the thermodynamic mixture of isomers. This mechanism does not require a

Scheme I. Redox Mechanism for the Interconversion of 1 and 2



1 **3** **2**

Scheme II. Retro-Aldol-Aldol Condensation Mechanism for the Interconversion of 1 and 2



1 **4** **2**

:B = $^-$SR' or $^-$OMe

‡ Alfred P. Sloan Research Fellow, 1981–1983.

(1) Silverman, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 5939.
(2) Oki, M.; Funakoshi, W.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 828.
(3) Trost, B. M.; Salzmann, T. N. *J. Am. Chem. Soc.* **1973**, *95*, 6840.
(4) The stereochemical assignment made for compounds **1** was derived from the known reaction of thiols with epoxides to yield exclusive *anti*-β-hydroxy sulfides.[5] The spectra and elemental analyses of compounds **2** suggest that they are isomers of **1**.
(5) Wohl, R. A. *Chimia* **1974**, *28*, 1.
(6) The total amount of compounds isolated in the experiments described here generally added up to 100 ± 5% of the total mass expected. The percentages given are normalized to 100%.
(7) Parker, A. J.; Kharasch, N. *J. Am. Chem. Soc.* **1960**, *82*, 3071.

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thiolate at all, only a base. Treatment of **1a** with sodium methoxide in acetonitrile produced **2a** (85%) and **1a** (15%). No 2,3-dimethyl-1,4-naphthoquinone was formed either in acetonitrile or in ethanol since that product *is* derived from a redox reaction which requires thiolate as a nucleophile and which produces disulfide.[1] It could be formed from either **3** or **4**. These experiments suggest that the retro-aldol–aldol condensation mechanism is a lower energy pathway than the redox mechanism and is the major pathway for isomerization of **1** and **2**.

Experimental Section

General Methods. NMR spectra were recorded on a Varian EM360 (^{1}H) or a Varian CFT 20 (^{13}C) spectrometer with internal Me_4Si as a standard. IR spectra were obtained on a Perkin-Elmer 283 spectrophotometer. Melting points were determined with a Thomas-Hoover Unimelt melting point apparatus and are uncorrected. Elemental analyses were performed by Microtech Laboratories.

Acetonitrile was distilled from CaH_2 and stored under Ar. Triethylamine was stirred with acetic anhydride, distilled from BaO, and stored under Ar. All other solvents and chemicals were reagent grade and used without further purification.

The sodium salts of ethanethiol and thiophenol were prepared by adding the thiols to an equimolar solution of NaOEt in EtOH under Ar. The solvents were evaporated, and the salts were triturated with ether, filtered, dried under vacuum, and stored under Ar.

Preparative layer (2 mm) silica gel 60F chromatography plates (20 × 20 cm) made by E. Merck were used for all separations. The compounds, after development, were visualized by UV light, the UV-active bands were scraped off and the compounds eluted by trituration with $CHCl_3$ (3 × 75 mL). After evaporation of the solvent, the residue was taken up in CH_2Cl_2 and filtered, and the solvent was removed in vacuo.

The isomerization reactions were carried out by three general methods.

Method A. NaSR (x mmol) was added to a solution of one of the isomers (x mmol) in acetonitrile in an ice bath under Ar. After being stirred for a certain period of time, the reaction mixture was filtered, and the solvent was evaporated. The resulting oil was taken up in CH_2Cl_2, streaked on a silica gel preparative-layer chromatography plate, and developed two times with CH_2Cl_2. The components were isolated as described above and identified by comparison of their IR spectra with those of authentic samples.

Method B. This was the same as method A except when the reaction was completed, 10 mL each of CH_2Cl_2 and H_2O were added. The CH_2Cl_2 layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), the combined CH_2Cl_2 extracts were dried ($MgSO_4$), and the solvent was evaporated. Chromatography was carried out, and the products were identified as described above.

Method C. This was the same as method B except the reaction was carried out in 95% EtOH, and the NaSEt was prepared as follows: ethanethiol (0.5 mL, 6.7 mmol) was added to a solution of sodium ethoxide which was prepared from the reaction of sodium metal (155 mg, 6.7 mmol) and 95% ethanol (5.6 mL).

(±)-*r*-2-(Ethylthio)-2,*cis*-3-dimethyl-*trans*-3-hydroxy-2,3-dihydro-1,4-naphthoquinone (1a). Into a stirred solution of 2,3-dimethyl-1,4-naphthoquinone 2,3-epoxide[8] (404 mg, 2.0 mmol) in dry acetonitrile (4.0 mL) under Ar were syringed ethanethiol (0.45 mL, 6.0 mmol) and triethylamine (280 μL, 2.0 mmol). The reaction solution was allowed to stand at room temperature under an Ar balloon for 3.5 h. The solvent was evaporated in vacuo, and the resulting yellow oil was dissolved in CH_2Cl_2, streaked on a preparative-layer silica gel plate, and developed two times with CH_2Cl_2. The product, isolated as described in the General Methods, was obtained as an off-white solid, 527 mg (quantitative). Recrystallization from *n*-hexane gave **1a** as white needles: 437 mg; mp 93–93.5 °C; TLC (silica gel, $CHCl_3$) R_f 0.12. It was found that the chromatography could be omitted and, after one recrystallization, the product was of the same purity as when chromatography was employed: ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3 H), 1.63 (s, 3 H), 1.72 (s, 3 H), 2.40 (m, 2 H), 3.11 (s, 1 H), 7.45–8.15 (m, 4 H); ^{13}C NMR (decoupled) ($CDCl_3$) δ 13.84, 16.55, 18.87, 23.81, 61.04, 80.32, 126.89, 127.21, 132.20, 132.73, 133.85, 134.16, 192.82, 195.28; IR (KBr) 3460 (s), 1700 (s), 1690 (s), 1593 (m), 1450 (m), 1265 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.69; H, 6.02; S, 12.13.

(±)-*r*-2-(Phenylthio)-2,*cis*-3-dimethyl-*trans*-3-hydroxy-2,3-dihydro-1,4-naphthoquinone (1b). To a stirred solution of 2,3-dimethyl-1,4-naphthoquinone 2,3-epoxide[8] (404 mg, 2.0 mmol) in dry acetonitrile (3.0 mL) under Ar was syringed thiophenol (0.41 mL, 4.0 mmol) and triethylamine (0.28 mL, 2.0 mmol). An exothermic reaction occurred which was cooled in an ice bath. After a few minutes, CH_2Cl_2 (20 mL) and 5% Na_2CO_3 (20 mL) were added. The organic layer was separated, the aqueous layer was extracted once with CH_2Cl_2, and the combined CH_2Cl_2 extracts were dried ($MgSO_4$). The CH_2Cl_2 was evaporated, and the resulting beige solid was triturated with hexane. Recrystallization of the residue from CH_2Cl_2–hexane gave the product as shiny white crystals: 497 mg (80%); mp 115.5–116.5 °C; TLC (silica gel, $CHCl_3$) R_f 0.15; NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.73 (s, 3 H), 2.98 (br s, 1 H), 7.23 (s, 5 H), 7.45–8.2 (m, 4 H); IR (KBr) 3460 (s), 1697 (s), 1683 (s), 1590 (m), 1263 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.26. Found: C, 68.94; H, 5.21; S, 10.17.

(±)-*r*-2-(Ethylthio)-2,*trans*-3-dimethyl-*cis*-3-hydroxy-2,3-dihydro-1,4-naphthoquinone (2a). To a stirred solution of 2,3-dimethyl-1,4-naphthoquinone 2,3-epoxide[8] (404 mg, 2.0 mmol) in dry acetonitrile (8.0 mL) under Ar in an ice bath was added sodium ethylthiolate (336 mg, 4.0 mmol). After 4 h the reaction mixture was filtered, and the solvent was evaporated to give a dark yellow foam (440 mg) which was taken up in CH_2Cl_2, streaked on a silica gel preparative layer plate, and developed with CH_2Cl_2 three times. The major component (middle of three) was isolated as described in the General Methods. Kugelrohr distillation [oven temperature 110–115 °C (0.05 mm)] gave the product as a pale yellow oil: 253 mg (63%); TLC (silica gel, $CHCl_3$) R_f 0.27; ^{1}H NMR ($CDCl_3$) δ 1.04 (t, 3 H), 1.37 (s, 3 H), 1.75 (s, 3 H), 2.32 (m, 2 H), 4.22 (br s, 1 H), 7.6–8.25 (m, 4 H); ^{13}C NMR (decoupled) ($CDCl_3$) δ 13.73, 15.27, 23.81, 24.79, 62.52, 80.08, 126.77, 127.53, 131.10, 133.17, 134.15, 134.89, 191.53, 198.92; IR (film) 3480 (s), 1698 (s), 1683 (s), 1592 (m), 1443 (m), 1265 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.40; H, 6.07; S, 11.87.

(±)-*r*-2-(Phenylthio)-2,*trans*-3-dimethyl-*cis*-3-hydroxy-2,3-dihydro-1,4-naphthoquinone (2b). The same procedure was used for **1b** with substitution of sodium thiophenolate for sodium ethylthiolate. Kugelrohr distillation [oven temperature 165–170 °C (0.05 mm)] gave the product as a viscous yellow oil which upon scratching solidified: mp 85.5–89 °C; TLC (silica gel, $CHCl_3$) R_f 0.31; NMR ($CDCl_3$) δ 1.37 (s, 3 H), 1.68 (s, 3 H), 4.29 (br s, 1 H), 6.85–7.4 (m, 5 H), 7.5–8.25 (m, 4 H); IR (KBr) 3460 (m), 1700 (s), 1680 (s), 1592 (m), 1270 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.26. Found: C, 69.27; H, 5.21; S, 10.46.

Isomerization of 1a to 2a in CH_3CN. Method A was used with NaSEt (51 mg, 0.61 mmol) and **1a** (162 mg, 0.61 mmol) in 3.0 mL of CH_3CN for 2.5 h. The products were identified as **2a** (125 mg, 77%) and **1a** (31 mg, 19%).

Isomerization of 1a to 2a in EtOH. Method C was used with a solution of NaSEt (0.58 mL, 0.64 mmol) and **1a** (170 mg, 0.64 mmol) in 2.0 mL of 95% EtOH for 15 min. The products were identified as 2,3-dimethyl-1,4-naphthoquinone[9] (54 mg, 44%), **2a** (50 mg, 29%), and **1a** (48 mg, 27%).

Isomerization of 2a to 1a in EtOH. Method C was used with a solution of NaSEt (0.73 mL, 0.81 mmol) and **2a** (213 mg, 0.81 mmol) in 2.0 mL of 95% EtOH for 15 min. The products were identified as 2,3-dimethyl-1,4-naphthoquinone[9] (68 mg, 45%), **2a** (62 mg, 29%), and **1a** (58 mg, 27%).

Isomerization of 1a to 2a with Catalytic NaSEt. Method B was used with NaSEt (5.7 mg, 0.067 mmol) and **1a** (177 mg, 0.67 mmol) in 2.0 mL of CH_3CN for 6.5 h. The products were identified as **2a** (132 mg, 75%) and **1a** (39 mg, 22%).

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Isomerization of 1a with NaSPh. Method B was used with NaSPh (132 mg, 1.0 mmol) and **1a** (264 mg, 1.0 mmol) in 3.0 mL of CH_3CN for 2 h. The products were identified as 2,3-dimethyl-1,4-naphthoquinone (58 mg, 31%), **2a** (161 mg, 61%), and **1a** (34 mg, 13%).

Isomerization of 1b with NaSEt. Method B was used with NaSEt (67 mg, 0.8 mmol) and **1b** (261 mg, 0.8 mmol) in 3.0 mL of CH_3CN for 45 min. The products were identified as 2,3-dimethyl-1,4-naphthoquinone (6 mg, 4%), **2b** (245 mg, 94%), and **1b** (18 mg, 7%).

Isomerization of 1a with Sodium Methoxide. Sodium methoxide (11 mg, 0.2 mmol) was added to a solution of **1a** (106 mg, 0.4 mmol) in acetonitrile (1.0 mL) in an ice bath under Ar for 1.5 h. The reaction solution was worked up as described in method B. The products were identified as **2a** (92 mg, 87%) and **1a** (16 mg, 15%). When ethanol was used as the solvent at room temperature only **2a** and **1a** were obtained.

Acknowledgment. I am grateful to Frederick G. Bordwell and Mark W. Holladay for helpful discussions.

Registry No. **1a**, 78870-54-9; **1b**, 78870-55-0; **2a**, 78870-56-1; **2b**, 78870-57-2; 2,3-dimethyl-1,4-naphthoquinone 2,3-epoxide, 53948-58-6; 2,3-dimethyl-1,4-naphthoquinone, 2197-57-1.

A Facile Synthesis of *N*-Acyl-2-pyrrolines

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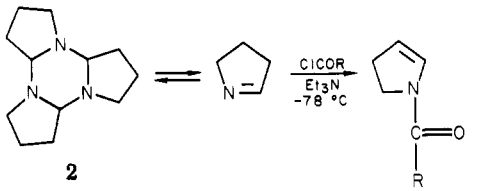
In conjunction with our studies of the amidoalkylation reaction,[1] multigram quantities of *N*-acyl-2-pyrrolines (**1**) were needed. Interestingly, only a few methods for the synthesis of this class of compounds had been reported. Stille and co-workers prepared **1** by a novel transition metal mediated isomerization of *N*-acyl-3-pyrrolines[2] and also cyclized (acylamino)butyraldehydes to produce **1**.[3] Although these methods are excellent for small-scale preparation, large-scale reactions would entail considerable expense. Acylation of 1-pyrroline with an acid chloride or alkyl chloro carbonate would be an attractive route to **1**. This reaction is well-known for acyclic imines.[4] Cushman has recently reported an elegant synthetic use of this reaction.[5] However, 1-pyrroline is unstable and has been little studied.[6] The trimer of 1-pyrroline, **2**, is readily available by oxidation of pyrrolidine with sodium peroxodisulfate and 0.5% silver nitrate[7] and has been used as a synthetic equivalent of 1-pyrroline.[8]

After several unsuccessful attempts to obtain **1** by the reaction of alkyl chloroformates with **2**, we decided to explore the possibility that **2** could dissociate into 1-pyrroline upon heating. Flow pyrolysis at 320 °C followed by reaction with methyl chloroformate afforded modest yields of **1** (R = OCH_3) but was accompanied by much decomposition. Interestingly, Nomura had noted that **2** "decomposed" at 50 °C.[7] This observation prompted us to distill a 0.1 M tetrahydrofuran (THF) solution of freshly prepared **2** into a flask *precooled to −78 °C*. The addition of triethylamine and methyl chloroformate afforded a 77% yield of **1** (R = OCH_3), based on the trimer consumed. Presumably the trimer dissociates in the refluxing tetrahydrofuran solution and 1-pyrroline codistills with the tetrahydrofuran. Trimerization must be slow at −78 °C. The products can be purified by distillation or column chromatography on silica gel. The results of our acylation experiments are given in Table I.

Table I. Preparation of 1

acylating agent	% yield[a] of product	1, R
CH_3OCOCl	78	OCH_3
$EtOCOCl$	79	OEt
CH_3COCl	71	CH_3
$PhCH_2OCOCl$	74	$PhCH_2O$
$ClCH_2COCl$	57	$ClCH_2$
Cl_3CCH_2OCOCl	39	Cl_3CCH_2O

[a] Yield is based on consumed trimer and weight of purified product. Typically 55-60% of the trimer is consumer on a 50-mmol scale.



2 **1**

This method permits the preparation of multigram quantities of **1**. The availability of solutions of 1-pyrroline should assist further investigations into the chemistry of 1-pyrrolines.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. THF was distilled from $LiAlH_4$ prior to usage. Infrared spectra were determined on a Acculab 6 spectrometer. NMR spectra were determined by using either a Hitachi Perkin-Elmer R-20B 60-MHz or a Varian HA-100 100-MHz instrument. ^{13}C NMR spectra were determined on a JEOL FX-90Q Fourier transform spectrometer. Both proton and carbon chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. High-resolution mass spectra were recorded on an AEI MS-902 high-resolution mass spectrometer.

General Procedure. The trimer (10.35 g, 50 mmol, 0.1 M in THF) was distilled through a short-path distillation appartus into a flask cooled to −78 °C. Triethylamine (10.1 g, 100 mmol) was added. The acylating agent (100 mmol) was then added dropwise and the suspension was allowed to warm to ambient temperature overnight. The product that was obtained after filtration and removal of the solvent in vacuo was purified by distillation or column chromatography.

***N*-(Methoxycarbonyl)-2-pyrroline**: bp 77–80 °C (12 mmHg); NMR ($CDCl_3$) δ 2.66 (br t, J = 9 Hz, 2 H), 3.72 (s, 3 H), 3.74 (t, J = 9 Hz, 2 H), 5.14 (m, J = 2, 4 Hz, 1 H), 6.55 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.1, 44.5, 51.6, 107.6, 128.6, 152.2; IR (film) 1700, 1620 cm^{-1}. High-resolution mass spectrum requires m/e 127.06333, found 127.06346.

***N*-(Ethoxycarbonyl)-2-pyrroline**: NMR ($CDCl_3$) δ 1.28 (t, J = 7 Hz, 3 H), 2.62 (br t, J = 9 Hz, 2 H), 3.77 (br t, J = 9 Hz, 2 H), 4.17 (q, J = 7 Hz, 2 H), 5.00 (m, 1 H), 6.52 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 28.6, 44.8, 66.9, 107.8, 129.2; IR (film) 1700, 1620 cm^{-1}.

***N*-Acetyl-2-pyrroline.** The boiling point is 70 °C at 1 mmHg (Kugelrohr). The spectrum is complicated since **3** exists as a

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