

**CHAPTER - II**  
**EXPERIMENTAL**

Melting points were determined on Mel-temp apparatus laboratory devices. Cambridge, Mass U.S.A., and are uncorrected.

#### **Infrared absorption measurements**

The infrared absorption spectra were measured by means of Perkin - Elmer Infrared spectrometer (Double beam ratio recording) Model 983 G as Nujal mull.

#### **Mass spectrometry**

Mass spectral recording were obtained from Indian Institute of Chemical Technology, Hyderabad, India.

#### **Sources and purification of thiols**

**n-Propylmercaptan** : It was prepared by following a procedure<sup>1</sup> similar to the preparation of n-hexanethiol. n-Propyl bromide (64.0 g) thiourea (38.0 g), 100 ml of water and 65 ml of rectified spirit were taken in a 500 ml three-necked round-bottomed flask, equipped with a glycerin sealed stirrer and a reflux condenser. The mixture was refluxed with stirring for 4 hours and the reaction mixture was allowed to cool. The upper layer of the mercaptan was separated (A). The aqueous layer was acidified with a cold solution of 7 ml of concentrated sulphuric acid in 50 ml of water. This layer was allowed to cool and saturated with salt. The upper layer of the n-propylmercaptan (B) was removed and combined with (A). The aqueous solution was extracted with ether and the etherial extract was dried over anhydrous calcium sulphate and ether removed on water bath. The residue was combined with (A) and distilled to obtain the n-propylmercaptan. The fraction distilling at 67 - 68°C was collected, yield 28 g.

**Isopropylmercaptan** : It was prepared by following a procedure<sup>1</sup> similar to the preparation of n-hexanethiol. Isopropyl bromide (64.0 g) thiourea (38.0 g), 100 ml of water and 65 ml of rectified spirit were taken in a 500 ml three-necked round-bottomed flask, equipped with a glycerin sealed stirrer and a reflux condenser. The mixture was refluxed with stirring for 4 hours and the reaction mixture was allowed to cool. The upper layer of the mercaptan was separated (A). The aqueous layer was acidified with a cold solution of 7 ml of concentrated sulphuric acid in 50 ml of water. This layer was allowed to cool and saturated with salt. The upper layer of the isopropylmercaptan (B) was removed and combined with (A). The aqueous solution was extracted with ether and the ethereal extract was dried over anhydrous calcium sulphate and ether removed on water bath. The residue was combined with (A) and distilled to obtain the isopropyl mercaptan. The fraction distilling at 57 - 60°C was collected. The yield was 27 g.

**Benzylmercaptan** : It was prepared by following a procedure<sup>1</sup> similar to the preparation of n-hexanethiol. Benzylbromide (64.0 g), thiourea (38.0 g), 100 ml of water and 65 ml of rectified spirit were taken in a 500 ml three-necked round bottomed flask, equipped with a glycerin sealed stirrer and a reflux condenser. The mixture was refluxed with stirring for 4 hours and the reaction mixture was allowed to cool. The upper layer of the mercaptan was separated (A). The aqueous layer was acidified with a cold solution of 7 ml of concentrated sulphuric acid in 50 ml of water. This layer was allowed to cool and saturated with salt. The upper layer of the benzylmercaptan (B) was removed and combined with (A). The aqueous solution was extracted with ether and the ethereal extract was dried over anhydrous calciumsulphate and ether removed on water bath. The residue was combined

with (A) and distilled to obtain the benzylmercaptan. The fraction distilling at 192 - 194°C (literature<sup>1</sup> b.p. 194 - 195°C) was collected, yield 26 g.

***p* - Thiocresol** : The procedure adopted was same as described by Vogel<sup>2</sup>. Crushed ice (720 g) and concentrated sulphuric acid (240 g) are placed in a 1500 ml round-bottomed flask equipped with a mechanical stirrer and a double surface reflux condenser. The flask was immersed in a freezing mixture of ice and salt and the temperature was maintained - 5° to 0°C throughout the preparation. 65 g of *p*-toluenesulphonyl chloride was added in small portions with stirring over a period of half an hour. Then 120 g of zinc powder was added rapidly without the temperature rising above 0°C. The mixture was stirred for a further period of one and half hour. The ice-salt bath was removed and allowed the reaction mixture to warm up spontaneously, whilst continuing the stirring. Within 5 minutes, a violent reaction with evolution of much hydrogen took place. When the energetic reaction has subsided, the mixture was warmed with vigorous stirring over a ring burner until the solution became clear (6 hours) and *p*-thiocresol was subjected to steam distillation until organic material ceases to pass over. The organic layer of *p*-thiocresol was separated from the distillate m.p. 42 - 43°. The yield of *p*-thiocresol is 35 g.

***p*- Chlorothiophenol** : A mixture of 240 g of concentrated sulphuric acid and 720 g of crushed ice was taken in a two-litre round-bottomed flask. Sixty seven grams (0.3 mole) of *p*-chlorobenzenesulphonylchloride was added to the flask. Zinc dust (120 g, 2 gram atoms) was then added in a few lots, while the contents of the flask were shaken gently. The contents were then steam distilled. The distillate was

extracted with ether and dried over calcium chloride. Removal of ether gave *p*-chlorothiophenol which melted at 54 - 55°C. The yield was 40 g.

**α - Thionaphthol** : A mixture of 240 g of concentrated sulphuric acid and 720 g of crushed ice was taken in a two-litre round-bottomed flask. Sixty seven grams (0.3 mole) of α-naphthylsulphonyl chloride was added to the flask. Zinc dust (120 g, 2 gram atoms) was then added in a few lots, while the contents of the flask were shaken gently. The contents were then steam distilled. The distillate was extracted with ether and dried over calcium chloride. Removal of ether gave α-thionaphthol which melted at 80 - 81°C. The yield was 42 g.

### **1. Preparation of (E) - 1, 2 - bis(n-propylsulphonyl)stilbene**

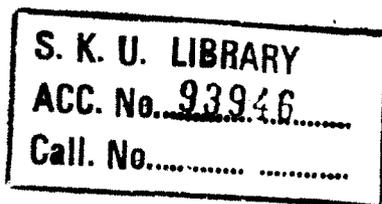
#### **(a) Preparation of (E) - 1,2 - bis(n-propylthio)stilbene**

A solution of 3 g of benzoin dissolved in 50 ml of AR glacial acetic acid was taken in a 100 ml two-necked round-bottomed flask, fitted with a gas inlet tube and a reflux condenser guarded with a calcium chloride drying tube. Then 5 g of n-propylmercaptan was added and the solution was saturated with dry hydrogen chloride gas for 2 hours. About 7.5 g of pulverized anhydrous zinc chloride was introduced into the reaction flask and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The colourless crystals separated were filtered off and washed with cold ethanol followed by light petroleum ether (b.p. 40 - 60°) to yield 3.5 g (75.43%) of

(E) - 1,2 - bis(n-propylthio)stilbene melting at 52 - 53°C. Recrystallization from benzene gave an analytical sample m.p. 56 - 57°C.

Anal. calcd. for  $C_{20}H_{24}S_2$  : C, 73.17; H, 7.32.

Found : C, 73.38; H, 7.11.



$\nu_{\text{max}}$  nujal 3362, 3195, 2901, 2854, 2762, 2673, 2541, 2463, 2359, 2335, 2231, 1686 w (C = C), 1598, 1460, 1376, 1335, 1275, 1217, 1199, 1148, 1074, 992, 752, 727, 691 (S - aryl), 593, 564 and 544  $\text{cm}^{-1}$ .

#### b. Oxidation of (E)-1,2-bis(n-propylthio)stilbene to (E)-1,2-bis(n-propylsulphonyl) stilbene

One gram of (E) - 1,2 - bis (n-propylthio)stilbene dissolved in 30 ml of glacial acetic acid was taken in a 100 ml round-bottomed flask fitted with a reflux condenser, and 20 ml of 30% hydrogen peroxide was added. The mixture was refluxed for one hour and cooled to room temperature. The crystals separated were filtered to yield 750 mg (62.75%) of (E) -1,2 - bis(n-propylsulphonyl)stilbene melting at 236 - 238°C. Recrystallization of the crude product from benzene gave a pure sample melting at m.p. 239 - 240°C

Anal. calcd. for  $C_{20}H_{24}S_2O_4$  : C, 61.22; H, 6.12.

Found : C, 61.41; H, 6.33.

$\nu_{\text{max}}$  nujal 3398, 3058, 3043, 2940, 2856, 2286, 1891, 1793, 1651 w (C = C), 1639, 1458, 1315 s ( $\text{SO}_2$ ), 1139 h ( $\text{SO}_2$ ), 723, 627 m (S - aryl), 561, 545  $\text{cm}^{-1}$ ;  
MS, m/z (% int): 286 (12), 212 (33), 180 (12), 178 (52), 121 (9.1), 106 (5), 105 (100), 75 (27.3), 43 (17) and 41 (12).

## 2. Preparation of (E) - 1,2 - bis(isopropylsulphonyl)stilbene

### a. Preparation of (E) - 1,2 - bis(isopropylthio)stilbene

A 100 ml two-necked round-bottomed flask was fitted with a gas inlet tube extending to the bottom of the flask and a reflux condenser, guarded with a

calciumchloride drying tube. Into the flask a solution of 3 g of benzoin in 30 ml of A.R. glacial acetic acid was introduced and treated with 5 g of isopropylmercaptan. The reaction mixture was saturated with dry hydrogen chloride for 2 hours. About 7.5 g of pulverized anhydrous zinc chloride was introduced into the reaction flask and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The colourless crystals separated were filtered off and washed with cold ethanol followed by petroleum ether (b.p. 40.60°) to yield 3 g (64.65%) of the product melting at 162 - 164°C. Recrystallization from benzene gave a pure sample, m.p. 165 - 166°C.

Anal. calcd. for  $C_{20}H_{24}S_2$ : C, 73.17; H, 7.32.

Found: C, 72.96; H, 7.1.

ν<sub>max</sub> 3771, 3049, 2911, 2850, 2680, 2604, 2387, 1753, 1648 w (C = C), 1573, 1460, 1376, 1240, 1154, 1048, 778, 735, 700, 628 (S - aryl), 608, 580, 541  $cm^{-1}$ ; MS, m/z (% int): 329 (5), 328 (80), 244 (6), 243 (36), 212 (5), 211 (18), 210 (100), 209 (5), 178 (27), 165 (11), 121 (17), 43 (20) and 41 (11).

**b. Oxidation of (E)-1,2-bis(isopropylthio)stilbene to (E)-1,2-bis(isopropylsulphonyl)stilbene**

Into a 100 ml round-bottomed flask fitted with a reflux condenser 1 g of (E)-1,2-bis(isopropylthio)stilbene and 30ml of glacial acetic acid were introduced. The solid was dissolved by heating the flask on a mantle and 25ml of 30% hydrogen peroxide was added. The mixture was refluxed for one hour and cooled to room temperature. The crystals separated were filtered to yield 800mg (66.94%) of

(E) - 1,2 - bis(isopropylsulphonyl)stilbene. Recrystallization of the crude product from benzene gave a pure sample, m.p. 281 - 282°C.

Anal. calcd. for  $C_{20}H_{24}S_2O_4$ ; C, 61.22; H, 6.12.

Found: C, 61.02; H, 5.89.

$\nu_{\text{max}}$  3879, 3836, 3383, 3119, 2981, 2879, 2830, 2275, 2169, 1891, 1656 m (C = C), 1444, 1375, 1319 s (SO<sub>2</sub>), 1127 s (SO<sub>2</sub>), 791, 702, 671 m (S - aryl), 581, 540 cm<sup>-1</sup>; MS, m/z (% int): 286 (24), 244 (15), 243 (100), 179 (45), 178 (79), 176 (8), 144 (8), 121 (38), 105 (38), 91 (12), 75 (20), 71 (6), 57 (11), 43 (83) and 41 (17).

### 3. Preparation of (E) - 1,2-bis(benzylsulphonyl) stilbene

#### (a) Preparation of (E) - 1,2 - bis(benzylthio)stilbene

A 100 ml two-necked round-bottomed flask was fitted with a gas inlet tube and a reflux condenser, guarded with a calcium chloride drying tube. Into the flask a solution of 4 g of benzoin in 30 ml of AR glacial acetic acid was introduced and treated with 6 g of benzylmercaptan. The reaction mixture was saturated with dry hydrogen chloride for 2 hours. About 10 g of pulverized anhydrous zinc chloride was introduced into the reaction flask and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The colourless crystals separated were filtered off and washed with cold ethanol followed by light petroleum ether (b.p. 40 - 60°), to yield 4 g (50%) of the product

melting at 178 - 180°C. Recrystallization from benzene gave fine colourless plates  
m.p. 180 - 181°C.

Anal. calcd. for  $C_{28}H_{24}S_2$  : C, 79.24; H, 5.66.

Found : C, 79.12; H, 5.81.

ν<sub>max</sub> 3783, 3733, 3696, 3635, 3485, 3179, 3139, 2891, 2849, 2727,  
2594, 2389, 2334, 2265, 2091, 1975, 1886, 1803, 1790, 1763, 1734,  
1672 (C = C), 1660, 1640, 1598, 1560, 1452, 1375, 1305, 1235, 1154, 1063,  
1027, 972, 864, 816, 772, 733, 705, 697, 638 m (S - aryl), 579 and 564  $cm^{-1}$ .

**b. Oxidation of (E)-1,2-bis(benzylthio)stilbene to (E)-1,2-bis(benzylsulphonyl)stilbene**

Into a 100 ml round-bottomed flask fitted with a reflux condenser 1 g of  
(E) - 1,2 - bis(benzylthio)stilbene and 30 ml of glacial acetic acid were introduced.  
The solid was dissolved by heating the flask on a mantle and 25 ml of 30%  
hydrogen peroxide was added. The mixture was refluxed for 1 hour and cooled to  
room temperature. The crystals separated were filtered to yield 825 mg (71.68%)  
of (E) - 1,2 - bis(benzylsulphonyl)stilbene. Recrystallization of the crude product  
from benzene gave a pure sample, m.p. 267 - 268°C

Anal. calcd. for  $C_{28}H_{24}S_2O_4$  : C, 68.85; H, 4.92.

Found : C, 68.62; H, 4.71.

ν<sub>max</sub> 3818, 3792, 3641, 3417, 3301, 3274, 3062, 2911, 2861, 2617, 2471,  
2441, 2279, 2140, 1982, 1940, 1903, 1882, 1812, 1796, 1767,  
1675 w (C = C), 1644 w, 1563, 1488, 1446 s, 1411, 1376, 1327 s (SO<sub>2</sub>), 1247,  
1139 s (SO<sub>2</sub>), 1124 s, 1077, 1029, 933, 844, 820, 793, 770, 722, 700,  
606 m (S - aryl), 561  $cm^{-1}$ ; MS, m/z (% int): 405 (8), 354 (2), 333 (2), 249 (15.2),  
178 (17), 105 (5), 92 (4.5), 91 (100), 78 (30), 69 (6), 57 (11) and 43 (6).

#### 4. Preparation of (E) - 1,2 - bis(*p*-tolylsulphonyl)stilbene

##### (a) Preparation of (E) - 1,2 - bis(*p*-tolylthio)stilbene

A solution of 3g of benzoin dissolved in 50ml of AR glacial acetic acid was taken in a 100ml two-necked round-bottomed flask, fitted with a gas inlet tube extending to the bottom of the flask, and a reflux condenser guarded with a calcium chloride drying tube. Then 5g of *p*-thiocresol was added and the solution was saturated with dry hydrogen chloride gas for 2 hours. About 7.5g of pulverized anhydrous zinc chloride was introduced in to the reaction flask, and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The crystalline (E) - 1,2 - bis(*p*-tolylthio)stilbene separated was filtered off, and washed with cold ethanol followed by petroleum ether (b.p. 40 - 60°C) to yield 3.2g (53.3%) of the product melting at 165 - 168°C. Recrystallization from benzene gave an analytical sample, m.p. 168 - 169°C.

Anal. calcd. for C<sub>28</sub> H<sub>24</sub> S<sub>2</sub>; C, 79.24; H, 5.66.

Found : C, 79.02; H, 5.42.

ν<sub>max</sub> 3723, 3553, 3355, 2911, 2815, 2729, 2482, 2067, 1896, 1666 m (C = C),  
 1595, 1461, 1376, 1269, 1183, 1072 m (S - aryl), 1036, 853, 807, 723,  
 696, 578, 542 cm<sup>-1</sup>; MS m/z (% int): 318 (3), 302 (5), 246 (39), 214 (65), 179 (6),  
 178 (11), 149 (6), 123 (32), 121 (6), 105 (100), 91 (9), 77 (46), 51 (9), 45 (9) and  
 43 (12).

**(b) Oxidation of (E)-1,2-bis(*p*-tolylthio)stilbene to (E)-1,2-bis-(*p*-tolylsulphonyl)stilbene**

Into a 100ml round-bottomed flask fitted with a reflux condenser 1g of (E) - 1,2 - bis(*p*-tolylthio)stilbene and 30ml of glacial acetic acid were introduced. The solid was dissolved by heating the flask on a mantle and 25ml of 30% hydrogen peroxide was added. The mixture was refluxed for 1 hour and cooled to room temperature. The crystals separated were filtered to yield 750mg (65.17%) of (E) - 1,2 - bis(*p* -tolylsulphonyl)stilbene. Recrystallization of the crude product from benzene gave a pure sample, m.p. 288 - 289°C.

Anal. calcd. for  $C_{28}H_{24}S_2O_4$  ; C, 68.85 ; H, 4.92.

Found : C, 68.64; H, 4.72.

$\nu_{\text{max}}$  nujal 3888, 3704, 3645, 3562, 3399, 3143, 3051, 2911, 2855, 2663, 2617, 2393, 1968, 1650 m (C = C), 1597, 1460, 1375, 1325 s (SO<sub>2</sub>), 1303, 1186, 1150 s (SO<sub>2</sub>), 1083 m (S - aryl), 1031, 814, 719, 703, 651, 618, 596, 568, 548 cm<sup>-1</sup>; MS m/z (% int): 333 (8), 270 (100), 180 (6), 178 (54), 155 (10), 139 (14), 123 (24), 105 (56), 91 (49), 77 (5), 71 (6), 60 (10), 57 (19), 45 (10) and 43 (21).

**5. Preparation of (E) - 1,2 - bis(*p*-chlorophenylsulphonyl)stilbene**

**(a) Preparation of (E) - 1,2 - bis(*p*-chlorophenylthio)stilbene**

A 100ml two-necked round - bottomed flask was fitted with a gas inlet tube extending to the bottom of the flask and a reflux condenser, guarded with a calcium chloride drying tube. In to the flask a solution of 3g of benzoin in 50ml of A.R. glacial acetic acid was introduced and treated with 3g of *p*-chlorothiophenol. The reaction mixture was saturated with dry hydrogen chloride for 2 hours. About 7.5 g of pulverized anhydrous zinc chloride was introduced in to the reaction flask,

and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The colourless crystals separated were filtered off and washed with cold ethanol followed by petroleum ether (b.p. 40 - 60°) to yield 3.4g (51.78%) of the product melting at 156 - 158°C. Recrystallization from benzene gave pure sample, m.p. 158 - 160°C.

Anal. calcd. for  $C_{26}H_{18}S_2Cl_2$ ; C, 67.24; H, 3.87.

Found : C, 67.44; H, 3.65.

ν<sub>max</sub> 3891, 3512, 3117, 2944, 2856, 2428, 2334, 2003, 1668 m (C = C), 1634, 1570, 1461, 1379, 1151, 1092 m (S - aryl), 1012, 815, 744, 722, 696, 648, 583, 520  $cm^{-1}$ ; MS m/z (% int): 432 (15), 431 (81), 429 (95), 323 (9), 321 (28), 288 (27), 286 (100), 285 (19), 284 (13), 235 (15), 233 (49), 210 (25), 179 (9), 178 (57), 176 (9), 165 (12), 152 (8), 143 (6), 105 (30) and 77 (9).

**(b) Oxidation of (E) -1,2 - bis(*p*-chlorophenylthio)stilbene to (E) -1,2-bis (*p* - chlorophenylsulphonyl)stilbene**

One gram of (E) - 1,2 - bis(*p*-chlorophenylthio)stilbene dissolved in 30ml of glacial acetic acid was taken in a 100ml round-bottomed flask fitted with a reflux condenser and 20ml of 30% hydrogen peroxide was added. The mixture was refluxed for one hour and cooled to room temperature. The crystals separated were filtered to yield 900 mg (79.1%) of (E) - 1,2 - bis (*p*-chlorophenylsulphonyl)-stilbene. Recrystallization of the crude product from benzene gave a pure sample, m.p. 279 - 280°C.

Anal. calcd. for  $C_{26}H_{18}S_2Cl_2O_4$ ; C, 59.09; H, 3.41.

Found : C, 59.32; H, 3.62.

ν<sub>max</sub> 3855, 3835, 3690, 3557, 3382, 3167, 2941, 2852, 2731, 2611, 2543, 2474, 2289, 1938, 1919, 1752, 1670 m (C = C), 1638, 1573, 1462, 1375, 1331 s (SO<sub>2</sub>), 1281, 1152 s (SO<sub>2</sub>), 1084 m (S - aryl), 1014, 823, 795, 756, 704, 630, 604 and 546  $cm^{-1}$ .

## 6. Preparation of (E)-1,2-bis( $\alpha$ -naphthylsulphonyl)stilbene

### (a) Preparation of (E)-1,2-bis( $\alpha$ -naphthylthio)stilbene

A solution of 3g of benzoin dissolved in 50ml of AR glacial acetic acid was taken in a 100ml two-necked round-bottomed flask, fitted with a gas inlet tube extending to the bottom of the flask, and a reflux condenser guarded with a calcium chloride drying tube. Then 5 g of  $\alpha$ -thionaphthol was added and the solution was saturated with dry hydrogen chloride for two hours. About 7.5 g of pulverized anhydrous zinc chloride was introduced in to the reaction flask, and hydrogen chloride was passed for an additional 30 minutes. The mixture was left in a refrigerator for two days. The crystalline (E)-1,2-bis( $\alpha$ -naphthylthio)stilbene separated was filtered off and washed with cold ethanol followed by petroleum-ether (b.p. 40 - 60°C) to yield 3.6g (51.29%) of the product melting at 112 - 113°C. Recrystallization from absolute alcohol gave an analytical sample m.p. 114 - 115°C.

Anal. calcd. for  $C_{34}H_{24}S_2$ ; C, 82.26; H, 4.83.

Found : C, 82.13; H, 4.62.

$\nu$  max 3804, 3407, 2901, 2724, 2591, 2288, 1753, 1737, 1696, 1666 m (C = C), 1589, 1509, 1460, 1375, 1269, 1208, 1167, 1151, 1069 (S - aryl), 863, 816, 758, 723, 702, 635, 587, 550, 512  $cm^{-1}$ ; MS m/z (% int): 450 (23), 354 (19), 338 (11), 318 (24), 250 (20), 249 (100), 171 (18), 159 (23), 121 (8), 115 (42), 107 (36), 105 (96), 79 (11), 77 (49), 57 (8) and 51 (6).

### (b) Oxidation of (E)-1,2-bis( $\alpha$ -naphthylthio)stilbene to (E)-1,2-bis( $\alpha$ -naphthylsulphonyl)stilbene

A solution of 1 g of (E)-1,2-bis( $\alpha$ -naphthylthio)stilbene dissolved in 30ml of glacial acetic acid was taken in a 100ml round-bottomed flask fitted with a reflux condenser and 20ml of 30% hydrogen peroxide was added. The mixture was

refluxed for one hour and cooled to room temperature. The crystals separated were filtered to yield 650mg (57.57%) of (E) - 1,2- bis( $\alpha$ -naphthylsulphonyl)-stilbene. Recrystallization of the crude product from absolute alcohol gave a pure sample, m.p. 318 - 319°C.

Anal. calcd. for  $C_{34}H_{24}S_2O_4$  ; C, 72.85; H, 4.28.

Found : C, 72.63; H, 4.44.

Nujal 3844, 3850, 3067, 2904, 2853, 2794, 2766, 2673, 2454, 2387, 1714,  
max 1682 w (C = C), 1459, 1376, 1306 s ( $SO_2$ ), 1150 m ( $SO_2$ ), 1073 (S - aryl),  
792, 754, 700, 650, 583 and 510  $cm^{-1}$ .

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