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## CONVENIENT SYNTHESIS OF (E)-11-HEXADECENYL ACETATE; THE FEMALE SEX PHEROMONE OF THE BRINJAL MOTH *LEUCINODES ORBONALIS* GUENEE

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**Abstract:** (E)-11-Hexadecenyl acetate, the female sex pheromone of *Leucinodes orbonalis*, the shoot and pod borer of brinjal plant (egg plant, *Solanum melongena*), has been synthesized in 27% overall yield employing a short stereospecific convergent route. In this synthesis, readily available starting material, 1,10-decanediol was mono brominated, protected as the tetrahydropyranyloether and subsequently used to alkylate 1-hexyne, which was obtained from alkylation of acetylene with 1-bromobutane. The dialkyl acetylene of C-16 chain length with the potential double bond at 11<sup>th</sup> position, which resulted, was reduced stereospecifically with sodium-liquid ammonia to give the corresponding olefin exclusively in the (E) configuration. Finally, removal of the protecting group followed by acetylation gave the desired pheromone in 99.9% isomeric purity.

### Introduction

Sex pheromones<sup>1</sup> produced by insects are present usually in sub-milligram quantities. Suitable synthetic routes of these pheromones, therefore, are essential in view of field trials and subsequent field applications. For this reason, a large number of routes for the synthesis of unsaturated long chain (from C-10 upto C-16) alcohols, acetates or aldehydes which often are the sex pheromones of Lepidoptera have been developed<sup>2,3</sup> over the last two decades in parallel with their chemical identification.

We previously reported that (E)-11-hexadecenyl acetate (HDA) was the female sex pheromone of *Leucinodes orbonalis* Guenee, the shoot and pod borer of the brinjal plant (egg plant, *Solanum melongena* L.) in Sri Lanka.<sup>4,5</sup> Concurrently, Chinese researchers<sup>6</sup> also reported the identification of the same sex pheromone of *L. orbonalis*. In addition, (E)-11-HDA has been established as a sex pheromone or a component of multicomponent sex pheromones of other lepidopteran species.<sup>2</sup>

Several routes have been established for the synthesis of (E)-11-HDA. These approaches demonstrate the use of secondary cyclopropyl carbinols,<sup>7</sup> triple bond migration methods,<sup>8</sup> acy silane/yliid chemistry,<sup>9</sup> Schlosser-Wittig reaction,<sup>10</sup> Grignard reaction,<sup>11</sup> organo boranes,<sup>12</sup>  $\alpha$  - diketones<sup>13</sup> and alkylation of alkynes<sup>14</sup> etc.. The simplest and most practical approach based on the usual method of obtaining long chain unsaturated compounds, was that of Botar et al.,<sup>14</sup> which transformed acetylene into a suitable higher alkyne, which was alkylated subsequently to produce the desired

C-16 chain length with the potential double bond at 11<sup>th</sup> carbon. In this convergent synthesis, however, several steps employed were unnecessarily complicated and long (eg. the production of 1,10-decanediol and the chemical purification of the alkyne and its subsequent alkylation). Also, the overall yield and the stereospecificity of this approach were not revealed.

For the intended field trapping<sup>5</sup> of the brinjal moth, (*E*)-11-HDA has been synthesized by an improved method. Overall yield of this method was 27% and the isomeric purity exceeded 99.9%. The total synthesis and the alternative simpler approaches used to avoid complications reported by Botar et al.<sup>14</sup> are described herein.

### Materials and Methods

<sup>1</sup>H-Nuclear magnetic resonance (N.m.r.) spectra were recorded on a JNM-PMX 60 and JNM GX 400 FT spectrometer. All values refer to samples in deuterated chloroform with tetramethylsilane as the internal standard. <sup>13</sup>C-N.m.r. spectra were recorded on a JNM-GX FT spectrometer. Infrared (i.r) spectra were obtained on a Beckmann Acculab 8, for liquid films unless otherwise stated. Mass spectra (M.s.) were recorded on a Varian MAT CH -4B (EFO-4B-Qulle, direct injection 70 eV). Chemical analysis was carried out on a micro apparatus, model C,H,N, Rapid, Heraeus. Gas liquid chromatography (g.l.c.) was performed on SP 2340 capillary column (25 cm length x 0.25 mm inner diameter) with split (1:100), FID detector 260<sup>o</sup>C, injector 240<sup>o</sup>C, with nitrogen as carrier gas at a flow rate of 22 cm/s, temperature program 2 min at 60<sup>o</sup>C, 60 → 194<sup>o</sup>C, 8<sup>o</sup>C/min, hold. Analytical thin layer chromatography (t.l.c.) was performed on pre-coated silica gel plates (Merck, type 25, UV<sub>254</sub>) and using petroleum ether: ethyl acetate (9.5:0.5) as eluent. A 2% solution of potassium permanganate was used to visualize compounds. Kugelrohr distillation refers to short path distillation (bulb to bulb) and boiling points quoted are oven temperatures. All commercial solvents were distilled before use. Solvents for moisture sensitive reactions referred as dry conditions were obtained by following procedures; Tetrahydrofuran (THF) and diethyl ether (ether) by refluxing over powdered calcium hydride (CaH<sub>2</sub>) for 5 h followed by the addition of lithium aluminium hydride and refluxing for 1 h and distilling under nitrogen. Hexamethylphosphoramide (HMPA) and dimethylsulfoxide (DMSO) were stirred overnight with powdered CaH<sub>2</sub> and distilled from it under nitrogen. Drying reagents for organic solutions were potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>). Neutralizing reagents used were sodium hydrogen sulphate (NaHSO<sub>4</sub>) and ammonium chloride (NH<sub>4</sub>Cl). BuLi refers to 1.6 molar solution of n-butyllithium in hexane (Aldrich, USA). 1-bromobutane was purchased from Fluka Chemicals and 1,10-decanediol was from Aldrich Chemical Co. Low temperatures below 0<sup>o</sup>C were maintained by the use of liquid nitrogen/acetone baths. Homogeneity of chemical reactions were achieved by stirring with magnetic stirrers. Solvent evaporation refers

to the use of a Büchi rotary film evaporator operating at 15 mm Hg and a bath temperature of 25<sup>0</sup>C.

The route followed was based on scheme 1. In this convergent synthesis readily available 1,10-decanediol was mono brominated<sup>2</sup> with 48% HBr on Kutscher apparatus at 95-100<sup>0</sup>C and the monobromo alcohol (1C-N) which resulted was protected<sup>15</sup> as tetrahydropyranyl (THP) ether. On the left hand side 1-bromobutane was reacted with lithium acetylide<sup>16</sup> in liquid ammonia (NH<sub>3</sub> at -33<sup>0</sup>C to give 1-hexyne (1B-N). Lithiation<sup>17</sup> of this with Buli and subsequent alkylation with the bromodecanol-THP ether (1A-N) resulted in the desired carbon chain with the potential olefinic bond at 11<sup>th</sup> position. Reduction<sup>16</sup> of the triple bond with sodium/liquid ammonia at -40<sup>0</sup>C gave the desired olefinic configuration (E). Finally removal of protecting THP group of 3N by refluxing it with methanol/water (3:1)<sup>18</sup> and the alcohol (4N) which resulted, was acetylated to give the desired acetate (5N) in 27% overall yield starting from 1,10-decanediol and in > 99.99% isomeric purity.

The procedures employed to obtain (E)-11-HDA and all intermediates leading to it are as follows:

#### 10-Bromodecane-1-ol (1C-N)

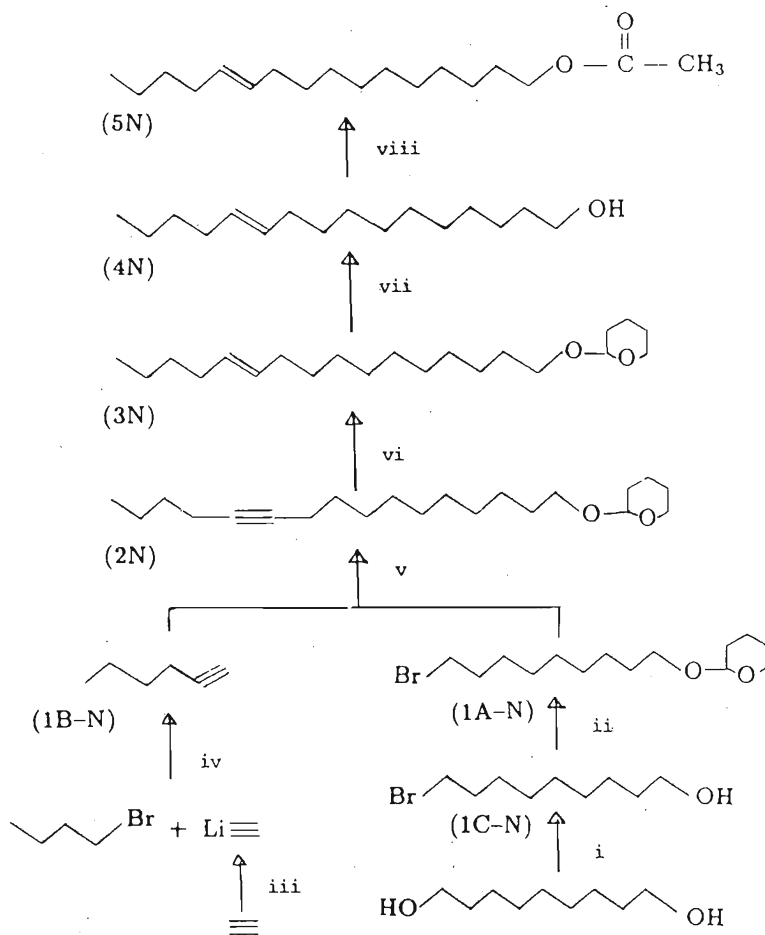
A mixture of 1,10-decanediol (17.4g, 100 mmol and 48% HBr 10g, 60 mmol) at 95-100<sup>0</sup>C was continuously extracted with toluene in a Kutscher extractor for 24 h. The organic layer which resulted was dried over K<sub>2</sub>CO<sub>3</sub> and distilled through a vigreux column to give 10.4g (60%), b.p. 134-140<sup>0</sup>C/0.5 mmHg, lit<sup>17</sup> 111-115<sup>0</sup>C/0.01 mmHg.

#### 10-Bromo-1-(tetrahydropyran-2-yloxy) decane (1A-N)

A solution of the above alcohol (3.80 g, 11.6 mmol) dihydropyran (1.69g, 20 mmol) and toluene-p-sulphonic acid (20 mg) in dry ether (190 ml) was stirred at 25<sup>0</sup>C for 24 h. Water was added and the organic layer was washed in turn with 2% aqueous NaHCO<sub>3</sub> (100 ml) and water (100 ml), dried over K<sub>2</sub>CO<sub>3</sub> and the solvent evaporated under reduced pressure to give a light yellow liquid. Small amounts of unreacted alcohol were distilled out and the desired product collected at 120<sup>0</sup>C/0.05 mmHg, to give 3.35g (86%).

#### 1-Hexyne (1B-N)

Acetylene gas was slowly passed into the dark blue solution of Li metal (0.063g, 16 mmol) in liquid NH<sub>3</sub> (40 ml) at - 33<sup>0</sup>C until the colour disappeared. This solution was treated with 1-bromobutane (1.37g, 10 mmol) followed by dry DMSO (2 ml). Stirring was continued for 1.5 h after which the temperature was increased to 25<sup>0</sup>C in a water bath and NH<sub>3</sub> was thus allowed to evaporate. Afterwards, NH<sub>4</sub>Cl was added to the reaction mixture and the product was isolated in ether (20ml x 3). The ether layer was



Scheme 1

- |   |  |
|---|--|
| i. 48%-HBr, toluene, 95-100 <sup>0</sup> C    | ii. DHP/H <sup>+</sup>                               |
| iii. NH <sub>3</sub> , -33 <sup>0</sup> C, Li | iv. DMSO, -33 <sup>0</sup> C, 1.5h                   |
| v. BuLi, 20 <sup>0</sup> C, HMPA              | vi. Na/NH <sub>3</sub> , -40 <sup>0</sup> C          |
| vii. PTSA, MeOH-H <sub>2</sub> O, heat        | viii. Ac <sub>2</sub> O/Pyridine, 80 <sup>0</sup> C. |

dried over  $\text{Na}_2\text{SO}_4$  and was subjected to atmospheric distillation through a vigreux column keeping the oil bath temperature at  $36^\circ\text{C}$ . Once the boiling point of this mixture reached  $40^\circ\text{C}$  the distillation was stopped. The ether, 1-hexyne (1:1) constant boiling mixture (1.8g) which resulted, was then dried by keeping overnight over  $\text{CaH}_2$  powder and used in the next reaction.

#### 10-(Tetrahydropyran-2-yloxy) hexadeca-5-yne (2N)

A solution of Buli (4.75ml, 7.6 mmol) was added to a stirred solution of 1-hexyne (0.59g, 7.2 mmol) in dry THF (10ml) keeping the temperature of the reaction mixture below  $20^\circ\text{C}$ .

Stirring was continued for further 10 min after which a solution of bromodecanol-THP ether (2.3g, 7.2 mmol) in HMPA (8 ml) was added keeping the temperature between  $20\text{-}25^\circ\text{C}$ . Stirring continued for an additional 1.5 h and then the reaction mixture was poured onto a large volume of ice and the product was extracted with ether (20ml x 3). The organic layer was washed with water (20 ml), dried over  $\text{Na}_2\text{SO}_4$  and ether was removed under reduced pressure. The liquid which resulted was distilled at  $115\text{-}120^\circ\text{C}/0.07$  mmHg (Kugelrohr) to give a colourless liquid, 1.87g (81%).

#### (E)-10-(Tetrahydropyran-2-yloxy) hexadeca-5-en (3N)

Small pieces of Na (0.45g, 19 mmol) was added to an efficiently stirred liquid ammonia (108 ml) at  $-40^\circ\text{C}$ , over a period of 15 min. The blue solution which resulted was then treated with the alkyne (2N; 1.35 g, 4.1 mmol) in absolute ether (12 ml). The above temperature was maintained for further 4 h after which it was allowed to rise to room temperature overnight. A saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (20 ml) was added to the reaction mixture and the products extracted into ether (20ml x 3). The ether layer was washed with water (20 ml), dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated under reduced pressure. The remaining liquid was distilled at  $110\text{-}117^\circ\text{C}/0.02$  mmHg 1.18g (89%).

#### (E)-Hexadeca-11-en-1-ol (4N)

(E)-11-Hexadecane-1-ol THP ether (3N; 1g, 3 mmol) was refluxed with a mixture of methanol and water (250ml, 3:1) and p-toluensulphonic acid (10 mg). Reaction was monitored by t.l.c. and after 3 h the reaction mixture was cooled, neutralized with a solution of 5%  $\text{NaHCO}_3$  and the solvent was removed under reduced pressure. The residue was extracted with ether (10 ml x 3), washed with water (10 ml x 2) and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent under reduced pressure and subsequent distillation,  $90\text{-}100^\circ\text{C}/0.015$  mmHg (Kugelrohr) gave the alcohol (4N) 0.64g (89%).

**(E)-Hexadeca-11-enyl acetate (5N)**

The alcohol (4N; 0.5g, 2 mmol), acetic anhydride (0.23g, 2 mmol) in dry pyridine (0.2 ml) was heated to 80°C for 4 h. Progress of the reaction was monitored by t.l.c. and at the end of 4 h the mixture was cooled, neutralized with diluted HCl acid (0.1 ml) and the products were extracted with ether (10 ml x 2). The ether layer was washed with a saturated aqueous solution of NaHCO<sub>3</sub> (5 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and solvent was removed under reduced pressure. The residual oil was distilled fractionally on Kugelrohr and the fraction boiled at 80-90°C/0.009 mmHg (lit<sup>14</sup> 108-110°C/0.05 mmHg) was characterized as the desired acetate, 0.49g (83%).

**Results**

The spectral characteristics of (E)-11-HDA and the intermediates leading to it are as follows,

**10-Bromodecane-1-ol (1C-N)**

<sup>1</sup>H-N.m.r.  $\delta$  : 1.33 (m, 16H), 3.16 (m, 1H), 3.63 (m, 4H) ppm.  
 i.r.  $\bar{\nu}$  : 3360 (b, s), 2940 (s), 2860 (s), 1450 (m), 1250 (m), 1050 (m) cm<sup>-1</sup>.  
 ms (m/z) : 221(1.1%, M<sup>+</sup> -18), 219(1%), 192(4.2%), 190(4.0%), 164(5.2%), 162(5.4%), 152(24%), 150(24%), 137(14%), 135(12%), 97(25%), 83(42%), 69(80%), 55(100%).

**10-Bromo-1-(tetrahydropyran-2-yloxy) decane (1A-N)**

<sup>1</sup>H-N.m.r.  $\delta$  : 1.06 (m, 22H), 3.26 (m, 6H), 4.36 (s, 1H) ppm.  
 i.r.  $\bar{\nu}$  : 2920(s), 2840(s), 1460(s), 1350(m), 1030(s)cm<sup>-1</sup>.  
 ms (m/z) : 321(1.25%, M<sup>+</sup>), 319(1.25%), 192(3.75%), 190(3.75%), 164(4.5%), 162(4.5%), 150(15%), 148(19%), 137(9.5%), 135(9.6%), 101 (2.75%), 85(100%), 69(64%), 55(80%).

**1-Hexyne (1B-N)**

<sup>1</sup>H-N.m.r.  $\delta$  : 0.92 (m, 3H), 1.92(m, 1H), 2.23(m, 2H), 1.4(m, 4H) ppm.  
 ms (m/z) : 82(0.1%), 81(8%), 67(55%), 57(95%), 43(35%), 41(100%).

**10-(Tetrahydropyran-2-yloxy) hexadeca-5-yne (2N)**

<sup>1</sup>H-N.m.r.  $\delta$  : 0.91(m, 3H), 1.39(m, 26H), 2.13(m, 4H), 3.62(m, 4H), 4.66(s, 1H) ppm.

i.r.  $\bar{\nu}$  : 2900(s), 2820(s), 2350(w), 1450(m), 10308(m)  $\text{cm}^{-1}$ .  
 ms (m/z) : 322 (2.0%,  $\text{M}^+$ ), 265(2.4%), 249(2.8%), 225(2.4%),  
 152(2.8%), 137(3.2%), 123(4.8%), 109(9.6%), 101(48%),  
 85(100%), 67(52%), 55(60%).

**(5E)-10-(Tetrahydropyran-2-yloxy) hexadeca-5-en (3N)**

$^1\text{H-N.m.r.}$   $\delta$  : 0.89(m, 3H), 1.33(bm, 30H), 3.66(m, 4H), 4.66(m, 1H),  
 5.49(m, 2H) ppm.  
 i.r.  $\bar{\nu}$  : 2910(s), 2880(s), 1450(m), 1030(m)  $\text{cm}^{-1}$ .  
 ms (m/z) : 324 (1.6%,  $\text{M}^+$ ), 251(4%), 238(2%), 222(2.1%), 152(4.1%),  
 123(6%), 109(12%), 101(40%), 85(100%), 69(50%), 55(90%).

**(11E)-Hexadeca-11-en-1-ol (4N)**

$^1\text{H-N.m.r.}$   $\delta$  : 0.89(m, 3H), 1.66(m, 20H), 2.13(m, 4H), 3.66(m, 2H),  
 5.45(m, 2H) ppm.  
 i.r.  $\bar{\nu}$  : 3300 (b,s), 3010(m), 2920(s), 2880(s), 1680(w), 1470(m),  
 1060(m)  $\text{cm}^{-1}$ .  
 ms (m/z) : 240(0.5%,  $\text{M}^+$ ), 222(6.5%), 196(3.8%), 168(3.8%), 152(4%),  
 123(7%), 110(25%), 96(75%), 82(78%), 69(72%), 55(100%).

**(11E)-Hexadeca-11-enylacetate (5N)**

$^1\text{H-N.m.r.}$   $\delta$  : 0.88 (t,  $J=6.6\text{H}_z$ , 3H,  $-\text{CH}_3$ ), 1.26 (m, 18H),  
 1.61 (m, 2H,  $\text{CH}_2-\text{CH}_2-\text{O}$ ), 1.96 (m, 4H,  $\text{CH}_2-\text{CH}=\text{C} \times 2$ ),  
 2.05 (s, 3H,  $\text{CH}_3-\text{C}=\text{O}$ ), 4.05 (t,  $J=6.24\text{H}_z$ , 2H,  $\text{CH}_2-\text{O}$ )  
 5.37 (m, 2H,  $-\text{HC}=\text{CH}-$ )ppm.  
 $^{13}\text{C-N.m.r.}$   $\delta$  : 170.7 (C=O), 130.3 (C=), 130.3 (=C), 64.7 (C-1), 28.6 (C-2),  
 25.8 (C-3), 29.7 (C-4), 29.5 (C-5), 29.5 (C-5), 29.3 (C-7),  
 29.1 (C-8), 28.6 (C-9), 31.9 (C-10), 130.3 (C-11), 130.3 (C-12),  
 32.6 (C-13), 32.4 (C-14), 22.1 (C-15), 13.9 (C-16) ppm.  
 i.r.  $\bar{\nu}$  : 3010(w), 2920(s), 2860(s), 1740(s), 1460(m), 1370((m),  
 1230(s), 1040(m), 970(m)  $\text{cm}^{-1}$ .  
 ms (m/z) : 282(1.0%,  $\text{M}^+$ ), 222(21.5%), 196(7.5%), 168(4.5%), 152(4.5%),  
 138(8%), 124(12%), 110(25%), 96(62%), 82(78%), 69(58%),  
 61(38%), 55(100%), 43(100%).

G.l.c. : Retention time 18.53 min (2 min, 60<sup>0</sup>C, 60-194<sup>0</sup>C, 8<sup>0</sup>C/min, SP 2340 capillary column)

Chemical analysis : C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> found C 75.65 H 11.3  
(282.28) calculated 76.5 12.13

### Discussion

In the approach described the total synthesis is achieved in 7 steps in 27% overall yield starting from readily available 1,10-decanediol. The use of corresponding diacid as the starting material as being used by Botar *et al.*<sup>14</sup> was unnecessary and was therefore avoided. In agreement with the findings of the above authors we also encountered considerable difficulties in isolating 1-hexyne because of its high volatility. After many attempts, however, this problem was overcome by the use of the following method.

The reaction products in ether were subjected first, to atmospheric distillation through a vigreux column keeping the oil bath temperature at 36<sup>0</sup>C. Most of the ether distilled out this way resulted in a constant boiling mixture which boiled at 40<sup>0</sup>C. Analysis of this by n.m.r. was found to contain 1:1 ether and 1-hexyne and was then dried by keeping over powdered CaH<sub>2</sub> for 12 h and used in the next reaction. The amount of BuLi used to generate the anion of 1-hexyne was calculated assuming 50% of alkyne in the mixture. This procedure was simpler than that of Botar *et al.* where 1-hexyne was chemically precipitated as dialkynyl-mercury compound (1) and released subsequently by the reaction of HCl or HCN.



Difficulties have also been reported in the alkylation of 1-hexyne with the C-10 bromo THP ether (1A-N) by Botar *et al.* in their synthesis. Usual problems in the coupling reactions in liquid ammonia are due to insolubility of bromo compounds when they exceed a certain chain length. This has been overcome lately by the use of BuLi as the metallation reagent and the addition of long chained bromo compounds in HMPA at relatively high temperatures measuring upto 25<sup>0</sup>C.<sup>17</sup> In our approach we employed this method and 87% alkylation was obtained. Reduction of the triple bond was achieved almost absolute isomeric purity (99.9%) by the method described in Bransma.<sup>16</sup> No trace of an isomer was seen by g.l.c. analysis on capillary column. The (E) configuration of the double bond which resulted was confirmed by observing signals of <sup>13</sup>C-N.m.r. for allylic carbons, C-10 and C-13 at 31.9 ppm and 32.6 ppm respectively. These values compared well with those published.<sup>14</sup> The corresponding values for above carbons in the (Z) olefin are in higher field at 27.2 ppm and 27.2 ppm.<sup>14</sup> The values reported for olefinic carbons in (E) configuration are 130.3 ppm for both carbons and our values fitted well with those of the (E) the configuration.



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